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**Deformation, Strengthening and
Fracture Mechanisms of Nanoscale
Al/SiC Multilayers**

TESIS DOCTORAL

LINGWEI YANG

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Basically, ...
Javier Llorca

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Resumen

Los nanolaminados de Al/SiC son materiales multicapa metal-cerámico con propiedades mecánicas singulares. Por ejemplo, se han reportado resistencias a temperatura ambiente extremadamente altas cuando el espesor de las capas individuales se reduce por debajo de 100 nm. Este comportamiento se ha atribuido a la elevada densidad de intercaras y al espesor nanométrico de las capas. Sin embargo, existen varios interrogantes fundamentales acerca de los mecanismos de deformación y fractura. Primero, no está claro cómo se pueden deformar las capas metálicas cuando su espesor se reduce a dimensiones nanométricas ni el papel que juegan las capas cerámicas en su deformación. Segundo, aunque su comportamiento es potencialmente muy anisótropo, estos materiales se fabrican en forma de películas delgadas y no ha sido posible caracterizar sus propiedades en distintas direcciones. Y, finalmente, aunque se ha propuesto que la alta densidad de intercaras debería hacer a estos materiales muy tolerantes al daño, no existen medidas fiables de su tenacidad a la fractura.

El trabajo llevado a cabo en esta tesis doctoral contribuye a aclarar algunas de estas cuestiones empleando una serie de técnicas de caracterización nanomecánica novedosas como la nanoindentación, la compresión de micropilares, los ensayos de microtensión o los ensayos de partición de pilares, para estudiar el comportamiento mecánico de nanolaminados de Al/SiC con espesores de capa entre 10 y 100 nm. Los ensayos mecánicos fueron complementados por un análisis detallado de los mecanismos de deformación mediante microscopía electrónica y simulaciones por elementos finitos. El objetivo último es entender la influencia de las propiedades de las capas individuales y de otras características microestructurales (la ondulación de las capas o las fronteras de grano columnares) en su respuesta tensión-deformación en diferentes direcciones.

Para ello, primero se determinó la resistencia de las capas de Al en función de su espesor y de la temperatura a partir de la dureza de los nanolaminados mediante una metodología inversa basada en simulaciones numéricas del proceso de nanoindentación por el método de los elementos finitos. El límite elástico de las capas de Al mostró un elevado efecto tamaño (“cuánto mas fina, más resistente”) a temperatura ambiente, que dependía no sólo del espesor de capa sino también del tamaño de grano. Esta conclusión se confirmó mediante la realización de ensayos mecánicos *in-situ* dentro de un microscopio electrónico de transmisión, que mostraron que las dislocaciones nucleaban en las intercaras Al-SiC, barrían los granos nanocristalinos de Al y eran absorbidas en las intercaras opuestas. Se observó una reducción dramática del límite elástico de Al con la temperatura, mayor para los espesores de capa más finos, que dio lugar a un efecto tamaño inverso a 100°C. Dicho comportamiento es compatible con mecanismos de deformación plástica controlados por difusión en las fronteras de grano y las intercaras que limitan la resistencia de las capas de Al nanométricas.

A continuación, la dureza medida por nanoindentación se comparó con la resistencia determinada por compresión de micropilares. Se encontró que la tasa de

endurecimiento por deformación y la resistencia máxima a compresión de los micropilares aumentaba mucho más rápido con la reducción del espesor de capa que la dureza. Simulaciones por elementos finitos revelaron que la coacción impuesta por las capas de SiC a la deformación plástica de las capas de Al era responsable de la alta tasa de endurecimiento. Además, se demostró que el efecto de la coacción dependía del cociente entre el espesor de capa y el radio del micropilar, debido al diferente peso de la contribución de las superficies libres del micropilar a su deformación. Este trabajo indica que considerar estos efectos es fundamental para entender el comportamiento mecánico de nanolaminados metal cerámicos bajo diferentes condiciones de ensayo.

También se estudió la respuesta anisótropa de los nanolaminados mediante la realización de ensayos de compresión de micropilares en direcciones perpendicular (90°), paralela (0°) y oblicua (45°) a la orientación de las capas. Los ensayos a 0° mostraron la mayor resistencia porque las capas de refuerzo de SiC estaban alineadas con la dirección de carga, mientras que los ensayos a 45° fueron los más blandos porque facilitaban la deformación de las capas de Al a cizalla. Se encontró que la resistencia para los ensayos a 90° estaba limitada por el agrietamiento de las capas de SiC en dirección perpendicular a las capas. Las resistencias máximas a 0° y 45° , sin embargo, estaban limitadas por el pandeo de las capas y la formación de bandas de cortadura alineadas con la fronteras de grano columnares. Mientras que la resistencia a 90° aumentaba sustancialmente con la reducción del espesor de capa, la resistencia a 0° y 45° resultó ser independiente del espesor de capa, y era controlada principalmente por el grado de ondulación de las capas, como cabría esperar para un fallo inducido por pandeo.

Finalmente, se determinó la tenacidad a la fractura de nanolaminados de Al/SiC, por primera vez, usando el método de partición de micropilares. Se encontró una tenacidad relativamente baja, del orden de $0.7\text{--}1.2 \text{ MPa}\sqrt{m}$, que aumentaba con la reducción del espesor de capa de 100 nm a 25 nm, para caer otra vez para un espesor de 10 nm. El análisis de las superficies de fractura mostró caminos de grieta relativamente tortuosos con signos claros de fractura dúctil de las capas de Al y deflexión de grietas en las intercaras de Al-SiC para espesores entre 25 y 100 nm, pero no para 10 nm. Estos resultados ponen de manifiesto el papel determinante de las intercaras y las fronteras columnares en la fractura de nanolaminados de Al-SiC. Este hecho se demostró mediante la realización de ensayos de microtracción en direcciones perpendicular y paralela a las capas. Bajo tensiones tractivas, los nanolaminados mostraron un comportamiento frágil, independiente del espesor de capa, y se encontró que la resistencia a la fractura estaba limitada por la resistencia de las intercaras en dirección perpendicular y por la resistencia de las fronteras de grano columnares en dirección paralela. Estos resultados indicaron que, aunque la reducción en el espesor de las capas cerámicas puede ser beneficioso para retrasar su fractura, la reducción del espesor de las capas de Al limita la energía disipada por deformación plástica. Como resultado, aunque los nanolaminados de Al/SiC muestran resistencias inusualmente altas, no pueden ser considerados como materiales tolerantes la daño.

Abstract

Nanoscale Al/SiC composite laminates are metal-ceramic multilayers with unique mechanical properties. In particular, extremely high strength has been reported at ambient temperature when the individual layer thicknesses are below 100 nm, and this behavior has been attributed to the large density of interfaces and to the nanoscale layer dimensions. Nevertheless, there are a number of fundamental questions about the deformation of metal-ceramic nanolaminates that remain unanswered. First, it is not clear how plasticity in the Al layers takes place when the length scale is reduced to the nanometer scale and what is the role of the ceramic layers on deformation. Second, although their behavior is potentially anisotropic, the fact that nanolaminates are often produced in the form of micrometer thick coatings has prevented the mechanical properties to be measured in different loading directions. And, finally, it has been proposed that the large density of interfaces can make these materials extremely damage tolerant but the fracture toughness has been rarely measured and the fracture mechanisms are unclear.

The work carried out in this thesis contributes to clarify these open issues by employing a set of novel nano-mechanical testing techniques like nanoindentation, micropillar compression, microtensile testing and micropillar splitting tests on Al/SiC nanolaminates with layer thicknesses in the range 10-100 nm. The mechanical tests were complemented with detailed transmission electron microscopy analysis of the deformed structures and finite element simulations to clarify the influence of the individual layer properties and other microstructural features (the layer waviness or columnar grains) on the overall stress-strain response of Al/SiC multilayers in different directions.

The strength of the Al layers as a function of layer thickness and temperature was obtained from the hardness of the nanolaminates by an inverse methodology based on the numerical simulation of the nanoindentation tests by means of the finite element method. The room temperature yield stress of the Al layers showed a large “the thinner, the stronger” effect, which depended not only on the layer thickness but also on grain size. This was confirmed by *in-situ* mechanical tests within the transmission electron microscope that showed that dislocations were nucleated at the Al/SiC interfaces, swept the nanocrystalline Al grains and were absorbed at the opposite interface. There was a dramatic reduction in the Al yield stress with temperature, which increased as the Al layer thickness decreased, and led to an inverse size effect at 100°C. This behavior was compatible with plastic deformation mechanisms controlled by grain boundary and interface diffusion at 100°C, which limit the strength of the ultra-thin Al layers.

Then, the hardness measured by nanoindentation was compared with the strength determined by micropillar compression. It was found that the strain hardening rate and the compressive strength of the micropillars increased much more rapidly with layer thickness reduction than the hardness. Finite element simulations revealed that the constraint imposed by the SiC layers on the plastic deformation of the

Al layers was responsible for the large strain hardening rate observed. Moreover, it was demonstrated that the degree of constraint depended on the ratio between layer thickness and micropillar radius due to the contribution of the free surface of the micropillars to deformation. This work shows that taking these effects into account is essential to understand the mechanical performance of metal-ceramic nanoscale multilayers measured under different testing conditions.

The anisotropic response of Al/SiC nanolaminates was also explored by performing micropillar compression tests in directions perpendicular (90°), parallel (0°) and oblique (45°) to the layer orientation. The 0° orientation showed the highest strength because the reinforcing SiC layers were aligned with the loading direction, while the 45° orientation showed the lowest strength because it promoted the deformation of the Al layers by shear. The strength for perpendicular loading was limited by the cracking of the SiC layers perpendicular to the layers as a result of the tensile stresses that developed in the SiC layers due to the constraint. The strength for parallel and oblique loading was, however, limited by buckling of the layers and the development of shear bands along the columnar boundaries. While the strength for perpendicular loading increased abruptly with layer thickness reduction, the strength for parallel loading was independent of layer thickness and controlled by the layer waviness, in agreement with buckling-induced failure.

Finally, the fracture toughness of the Al/SiC nanolaminates was determined, for the first time, by using the micropillar splitting method. The fracture toughness was relatively low, in the range $0.7\text{--}1.2 \text{ MPa}\sqrt{m}$. It increased as the layer thickness was reduced from 100 nm to 25 nm to decrease again for the smallest layer thickness of 10 nm. Analysis of the fracture surfaces revealed a tortuous crack path, with clear signs of ductile fracture of the Al layers and crack deflection at the Al-SiC interfaces for layer thicknesses between 25 and 100 nm but not for 10 nm. The results highlight the role of the Al-SiC interfaces and the columnar boundaries on the fracture of Al/SiC nanolaminates, as demonstrated by microtensile testing in directions perpendicular and parallel to the layers. Under tensile loading, the nanolaminates showed a very brittle behavior, independent of layer thickness. The tensile strength was found to be limited by the Al-SiC interface strength in the direction perpendicular to the layers and by the strength of the pre-existing columnar boundaries in the parallel direction. The results point out that, even though a reduction in the size of the ceramic layers has obvious benefits on delaying cracking of the SiC layers, the reduction in the thickness of the Al layers hinders energy dissipation by plasticity of the Al layers. As a result, Al/SiC nanolaminates are very strong, but cannot be deemed as damage tolerant materials.

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CHAPTER 1

Introduction

1.1 Nanolaminates as structural materials

“Smaller is stronger” is a well-established paradigm in Materials Science and Engineering, that has been one of the driving forces in recent years to develop new nanostructured metallic materials with improved mechanical properties. Nanotwinned (NT) metals, like NT-Cu, which have high density coherent twin boundaries (TBs) spaced on the nanometer scale in single grains, stand for a paradigmatic example Dao *et al.* (2006). While conventional nanocrystalline (NC) metals usually exhibit high strength but limited ductility and work hardening, NT-Cu combines very large strength with considerable ductility and work hardening Lu *et al.* (2009b), Lu *et al.* (2009a). The combination of high strength and high ductility in NT-Cu (as opposed to NC-Cu) can be found in the microstructural details that control the critical length scales. NC metals only have one characteristic length, scale, i.e., the nanoscale grain size. In contrast, NT metals have two critical length scales: grain size and twin thickness Zhu & Gao (2012). The randomly-oriented twin boundaries serve as effective barriers to dislocation motion in a manner analogous to the grain boundaries Shen *et al.* (2005b), Lu *et al.* (2012). Dislocations are confined within the twin lamellae and form dislocation pile-ups,

1.1 Nanolaminates as structural materials

giving rise to significant strengthening while retaining ample room for dislocation accumulation and plastic strain accommodation Yuan *et al.* (2016). Thus, it is clear that high strength/high ductility materials can be obtained by manipulating the microstructure at the nanoscale and this is a field of intense research. Different processing strategies have been used so far to manufacture nanostructured metallic materials with enhanced mechanical properties. Some of them are based on mechanical processes, such as severe plastic deformation Valiev (2011): equal-channel angular pressing Iwahashi *et al.* (1996), high pressure torsion Zhilyaev & Langdon (2008), accumulative roll-bonding Tsuji (2011), mechanical attrition Fecht (1995), mechanical machining Mann *et al.* (2011). Others include thermo-mechanical processes in the solid state (formation of ultrafine bainite or pearlite in carbon steels Caballero & Garca-Mateo (2011)) or rapid solidification from the vapor Dao *et al.* (2006) or liquid state Mahan (2000), Ross (1994).

Another class of nanostructured materials which have received a lot of attention in recent years are nano-laminated coatings (also referred to as nanolaminates). They are made up by the periodic stacking of two or more layers of dissimilar materials with individual layer thickness generally ≤ 100 nm and a total thickness of several micrometers. Nanolaminates can be produced via bottom-up processes (physical vapor deposition Mahan (2000) and electrodeposition Ross (1994), or via top-down processes (solid-state transformation Callister & Rethwisch (2013), accumulative roll bonding Carpenter *et al.* (2012), Tsuji *et al.* (2003), or solidification Callister & Rethwisch (2013), Shen *et al.* (2005a), Wang *et al.* (2011)). These materials have a huge areal density of interfaces between different materials which control up to a large extent their mechanical properties. Interfaces can act as sources of dislocations, sinks of dislocations via absorption and annihilation, barriers to dislocations and storage sites for dislocations Zhang *et al.* (2012b). A typical nanolaminate structure is shown in Fig. 1.1 where alternative Al and SiC layers are stacked periodically Lotfian *et al.* (2013).

Nanolaminates are often characterized by three main features. The first one is the type of the materials in each lamina, which leads to metal-metal Moncls *et al.* (2013), metal-ceramic Lotfian *et al.* (2013), ceramic-ceramic Hahn *et al.* (2016),

Figure 1.1: *Al/SiC nanolaminates with individual layer thickness of ≈ 100 nm.*

metal-metallic glass Knorr *et al.* (2013), etc. nanolaminates. The second one is the layer thickness and the third one is the type of interface (coherent, semi-coherent, incoherent, etc.). Depending on these features, nanolaminates with very different properties can be achieved but they generally possess better mechanical properties (strength, toughness, wear resistance, etc.) than their bulk counterparts, due to the high density of interfaces and to the nanoscale layer thickness Hultman (2006). As a result, they are currently used in many engineering applications, as summarized in Table 1.1.

Understanding the deformation and fracture mechanisms in these nanolaminate systems is very important to optimize the properties and also to take advantage of the large design space provided by the combination of layers of different materials and thicknesses with tailored interfaces. However, this task is very complex because the standard strengthening models available in the literature (e.g. Hall-Petch) are not always applicable to the characteristic length scales that control the mechani-

1.1 Nanolaminates as structural materials

Table 1.1: Nanolaminates used for different engineering applications

Type	Layer Thickness	Applications
Metal-metal	Cu/Nb,Cu/W	Radiation Resistant materials
	Co/Cu	Magnetic transducers-GMR
	Mo/Si	EUV lithographic system
	Nb/Ge	Superconductors
	Au/Cu	Integrated circuit interconnects
Metal-metallic glass	Cu/CuNb,Cu/CuTa	
	Cu/PdSi	Structural materials
	Cu/Cu-Zr	
Metal-ceramic	Ti/TiN	Aerospace protective coatings
	Cr/Nx	Wear resistant coatings
	Cr/Cr _x O _y	Solar absorber multilayers
	Cu/SiO ₂	Interconnects
	W/TiN	Super-hard coatings
Ceramic-ceramic	TiN/CrN	Thermal barrier coatings
	TiN/ZrAlN	Corrosion resistant coatings
	TiN/AlN	Super-hard coatings
	TiN/VN	

cal behavior of nanolaminates. In addition, nanoscale mechanical characterization techniques (including *in-situ* experiments within the scanning or transmission electron microscope) are necessary to resolve the deformation and fracture processes at the nanometer scale.

Most of the research work to ascertain the fundamental mechanisms of deformation and fracture in nanolaminates has been focused so far in metal-metal and ceramic-ceramic nanoscale multilayers. For instance, a coherent theory has been developed to explain the effect of layer thickness and interface character on the strength of metal-metal nanolaminates Misra *et al.* (2005), but it should be noticed that many important aspects (like the effect of temperature) are not well understood yet. Much less information is available for the case of metal-ceramic nanolaminates and this thesis is aimed at covering this gap.

1.2 Metal-ceramic nanolaminates

Metal-ceramic nanolaminates made up by the combination of a soft and ductile metal with a hard and stiff ceramic have shown a good combination of hardness, strength, toughness and wear resistance. For instance, Ti/TiN Bemporad *et al.* (2006), Cr/CrN Knotek *et al.* (1991), Cu/TiN Abadías *et al.* (2003) etc. have been used to protect structural components (like the compressor blades of aerospace engines) from wear degradation. Cr/Cr_xO_y and Ti/Ti_xO_y metal-ceramic nanolaminates Nunes *et al.* (2003) have been applied as solar absorbers in thermo-solar energy generation, while Cu/SiO₂ nanolaminates were used as interconnect materials in micro electro-mechanical systems Xu *et al.* (2001). Finally, the development of cellular phones has pushed the research in metal-ceramic nanolaminates towards base-metal electrode multilayer ceramic capacitors due to their high capacitance at large frequencies Kishi *et al.* (2003).

It is obvious that the full potential of the mechanical properties of metal-ceramic nanolaminates is not achieved in these applications but it is expected to design metal-ceramic nanolaminates that combine the ductility and toughness of metals with the hardness and high temperature strength of ceramics. Early studies in metal-ceramic composites showed that the elastic constraint imposed by the stiff ceramic reinforcement to the plastic deformation of metals introduced high hydrostatic stresses, which increased the strain hardening capacity of the metal and improved the strength Llorca *et al.* (1991). However, the presence of tensile triaxial stresses triggered early damage by void nucleation and growth in the metal and by tensile fracture in the ceramic Llorca *et al.* (1991), Singh & Lewandowski (1993), leading to low ductility and toughness, and the full potential of these materials could not be achieved. Nanolaminates, in which the mechanical properties of each layer can be controlled up to some extent by changing the layer thickness and the material, can potentially overcome these limitations.

1.3 Objectives and outline of the thesis

The objective of this thesis is to carry out an exhaustive analysis of the deformation and failure mechanisms in metal-ceramic nanolaminates. To this end, a model system made up by a soft metal (Al) and a hard ceramic (SiC) has been selected. Processing of the nanolaminates was performed by physical vapor deposition because this technique provides the flexibility to manufacture nanolaminates with different layer thicknesses (in the range from a few nm to 100 nm) and with different volume fractions of each material with very good reproducibility. A wide range of state-of-the-art nanomechanical characterization techniques (including instrumented nanoindentation, tension and compression tests on micron-sized specimens, *in-situ* mechanical tests within the transmission and scanning electron microscope) has been used to characterize the deformation and fracture mechanisms as a function of layer thickness, volume fraction of each material, orientation and temperature. This information, together with a detailed microstructural characterization of the materials, has provided a very detailed picture of the physical mechanisms responsible for the mechanical properties of this metal-ceramic nanolaminates. Based on this information, modeling and numerical simulations have been used to provide a quantitative link between the mechanisms and the macroscopic properties that will help in the design and optimization of the mechanical properties of these materials.

The thesis is divided into 7 chapters. Chapter 2 summarizes the current state-of-the-art on the mechanical properties of nanolaminates including the effect of layer thickness on the strength and on the deformation and fracture modes as well as on the influence of temperature on these properties. Chapter 3 describes the nanolaminate processing, the microstructural characterization techniques, and the nano-mechanical testing techniques employed in this work. The deformation mechanisms of Al/SiC nanolaminates as a function of the volume fraction of each material, layer thickness and temperature are studied in Chapter 4, while Chapter 5 focuses on the strain hardening mechanisms of Al/SiC nanolaminates, which are controlled by the interaction between the elastic deformation of the stiff ceramic

1.3 Objectives and outline of the thesis

layers and the plastic flow of the soft Al layers. In chapter 6, the anisotropic fracture mechanisms of the Al/SiC nanolaminate were analyzed as a function of layer thickness and orientation in compression. This is followed by chapter 7, in which the deformation and fracture of the Al/SiC nanolaminates in tension are explored for different layer orientations and the fracture toughness of the nanolaminates is assessed. The main conclusions and the suggestions for future work are finally summarized in chapter 8.

CHAPTER 2

State of the Art

Nanolaminates are periodical layered stacks of dissimilar materials with individual layer thicknesses in the range from hundreds of nanometers to a few nanometers. Their mechanical properties and their deformation and fracture mechanisms are strongly dependent on the individual layer thickness, the layer orientation and the interface structure. The mechanical properties of nanolaminates have been the focus of numerous studies in the past twenty years, especially at room temperature, while high temperature studies are still scarce. This chapter reviews the state-of-the-art in the mechanical properties of nanolaminates, including the effect of layer thickness on the strength and on the deformation and fracture mechanisms, as well as recent studies on their high temperature performance. Special attention is paid to the case of metal-ceramic nanolaminates, like the Al/SiC system, that is the object of this investigation. Finally, the objectives of the thesis are stated based on the current knowledge.

2.1 Effect of layer thickness on the nanolaminate strength

The strength of nanolaminates strongly depends on the individual layer thickness, either through the direct interaction of the deformation mechanisms, like dislocation glide and/or dislocation nucleation, with the interfaces, or because most microstructural features, like the grain size, the interface atomic structure or the presence of defects, are highly influenced by the individual layer thickness Pathak *et al.* (2015), Callisti & Polcar (2017). For instance, the grain size of the individual layers scales with layer thickness in most nanolaminates, as shown in Fig. 2.1 for Fe/Ag nanolaminates Li *et al.* (2016). Therefore, several size effects might compete simultaneously depending on whether the dislocation mean free path is controlled by the layer thickness or the grain size. For large layer thicknesses (several hundreds of nanometers), the grain size is usually smaller than the layer thickness, and the nanolaminate strength is mainly controlled by the dislocation-grain boundary interactions, as shown in Fig. 2.1 (b). However, the grain size is typically comparable to the layer thickness for small layer thickness (≤ 100 nm) and each layer can only accommodate one grain in the thickness direction. In this case, the strength is typically controlled by dislocation-interface interactions, as explained below.

Assuming the mean free path is controlled by the layer thickness (i.e., the layer thickness is smaller than the grain size), the actual deformation mechanisms and the variation of strength with the layer thickness strongly depend on the nature of the dissimilar materials that compose the nanolaminate. For instance, the individual layers co-deform via dislocation glide in most metallic nanolaminates, and the strength is controlled by the dislocation-interface interactions Monclús *et al.* (2013), Misra *et al.* (2005), Li *et al.* (2016), Chen *et al.* (2012). In contrast, the deformation mechanisms of some metallic nanolaminates which combine crystalline and amorphous layers differ in each layer and the interfaces must somehow accommodate the strain incompatibilities that develop across the crystalline-amorphous layers. Hence, the strength is typically controlled by the coupling of dislocation

2.1 Effect of layer thickness on the nanolaminate strength

Figure 2.1: (a) Grain size of the Fe and Ag layers as a function of the individual layer thickness in the Ag/Fe nanolaminates; (b) Hardness of the Ag/Fe, Cu/Fe and Ag/Ni nanolaminates as a function of layer thickness Li et al. (2016).

glide in the crystalline layers and shear band propagation in the amorphous ones Fan *et al.* (2016b), Guo *et al.* (2014b). Finally, metal-ceramic nanolaminates combine layers with a large mismatch in stiffness and strength, and it is not clear how deformation is accommodated in each layer under the applied stresses Pathak *et al.* (2015), Zhang *et al.* (2016), Lotfian *et al.* (2014). This section summarizes the most relevant observations describing how strength varies with layer thickness. For clarity, the discussion is divided into metallic nanolaminates with crystalline layers, metallic nanolaminates where one of the layers is amorphous and metal-ceramic nanolaminates.

2.1.1 Metallic nanolaminates

Metallic nanolaminates containing crystalline layers have been thoroughly studied in the past. One of the most important parameters that determines the strength of metallic nanolaminates is the interface structure. Depending on the registry

2.1 Effect of layer thickness on the nanolaminate strength

between the crystal structures of the two metals, the interfaces can be coherent or incoherent, with incoherent interfaces typically displaying the maximum strengthening. This is because the transfer of slip between the layers must involve dislocation multiplication, due to the discontinuity of slip planes and slip directions across the interfaces. Furthermore, the interfaces might have limited shear strength, due to amount of free volume, which leads to the attraction of glide dislocations and spreading of their core at the interface, requiring a large stress for de-pinning and transmission to the next layer. The most paradigmatic example of metallic nanolaminates with incoherent interfaces is the case of Cu/Nb, a system combining fcc and bcc metals Monclús *et al.* (2013), Misra *et al.* (2005), but other examples exist like Zr/Nb Callisti & Polcar (2017), Cu/Ru Zhou *et al.* (2016), Ag/Fe Li *et al.* (2016), Mg/Ti Lu *et al.* (2014), Cu/Fe Chen *et al.* (2012), etc. Fig. 2.2 shows schematically the typical variation of strength with layer thickness for metallic nanolaminates Misra & Hoagland (2007). When the individual layer thickness h is in the sub-micrometer to micrometer scale, the nanolaminate strength usually follows the traditional Hall-Petch (H-P) relationship:

$$\sigma_y = \sigma_0 + kd^{-0.5} \quad (2.1)$$

where σ_0 is the yield stress when the grain size is infinitely large (and it represents the overall resistance of the crystal lattice to dislocation motion) and the H-P slope, k , is a measure of the hardening contribution from the interfaces. At this length scale, dislocations pile-up at the interfaces, and the length of the pile-up scales with the layer thickness, hence giving rise to a nanolaminate strength that increases linearly with $h^{-0.5}$ Anderson & Li (1995).

The nanolaminate strength deviates from the prediction of the H-P model as the individual layer thickness is further reduced below several tens of nanometers because dislocation pile-ups are less likely at such small length scales. Instead, the confined layer slip (CLS) model derived from the Orowan bowing of single dislocations is considered a more realistic deformation mechanism Misra *et al.* (2005). At this length scale, dislocations are being bowed out in between the

Figure 2.2: Deformation mechanisms in metal-metal nanolaminates as a function of the layer thickness Misra & Hoagland (2007).

interfaces that act as strong barriers to dislocation transmission. In addition to the gliding mechanism of dislocation loops, dislocation segments must be deposited at the interfaces, which can interact with subsequent dislocation loops and cause some strain hardening. Based on this assumption, Misra *et al.* (2005) developed a model for the yield stress controlled by confined layer slip:

$$\sigma_y = M \frac{Gb}{8\pi} \left(\frac{4-\nu}{1-\nu} \right) \frac{1}{t} \ln \left(\frac{\alpha t}{b} \right) - \frac{f}{t} + \frac{Gb}{L(1-\nu)} \quad (2.2)$$

where M is the Taylor factor. G and ν the shear modulus and the Poisson's ratio of the layers, respectively, b the Burgers vector, t the layer thickness, and α the dislocation core cut-off parameter. The first term accounts for the Orowan stress, where low (high) values of α imply a wide (compact) dislocation core, while the second term considers the contribution of the interface stress f , that arises from the elastic deformation of the interfacial region, and is given as the gradient of the interface energy (γ) with respect to strain, as $f = \gamma + d\gamma/d\epsilon$ Cammarata *et al.* (2000). Finally, the third term accounts for strain hardening and L is the mean

2.1 Effect of layer thickness on the nanolaminate strength

spacing of glide loops in a parallel array within the layer, which is equal to b/ϵ , where ϵ is the applied plastic strain.

When the individual layer thickness reduces to a few nanometer (generally 1-5 nm), the strength typically reaches a constant plateau Misra *et al.* (2005) or decreases due to strain localization, determined by dislocation transmission across the interfaces. The interface barrier to slip transmission is characteristic of the interfacial structure. It is worth pointing out that for coherent interfaces (also referred to as transparent interfaces), softening often occurs when further reducing the layer thickness after reaching the strength plateau, due to the formation of fully coherent interfaces Li *et al.* (2016), Misra *et al.* (1998).

2.1.2 Metallic nanolaminates combining crystalline and amorphous layers

The case of metallic nanolaminates combining crystalline and amorphous layers constitutes maybe the most extreme example of a nanolaminate with incoherent interfaces. Interestingly, Cu/*a*-CuNb Fan *et al.* (2016b), Cu/*a*-CuTa Gu *et al.* (2016) and Cu/*a*-CuZr Zhang *et al.* (2015), Guo *et al.* (2014b) nanolaminates have shown a similar strengthening behavior as the individual Cu layer thickness is reduced, as that found in crystalline metallic nanolaminates, indicating that the behavior is controlled by the thickness of the softer crystalline layer. The indentation hardness of Cu/*a*-CuZr and Cu/Zr nanolaminate is compared in Fig. 2.3 Zhang *et al.* (2012c). They both follow a Hall-Petch type strengthening for large Cu layer thicknesses (≥ 50 nm), followed by a confined layer slip regime for layer thicknesses between 5 and 50 nm. The main differences were found for very small layer thicknesses (≤ 5 nm). While the fully crystalline nanolaminates led to softening with further layer thickness reduction, presumably due to dislocation transmission at interfaces, the crystalline-amorphous interfaces act as impenetrable barriers, as dislocations cannot exist in the amorphous layers. The differences in deformation mechanisms between both types of nanolaminates are schematically depicted in Figs. 2.4 (a, b, d, e). It was proposed that the amorphous layers can act as natural

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dislocation sinks and sources. When the layer thickness is smaller than the critical thickness for shear localization, the amorphous layers play the dominant role by absorbing incoming dislocations and emitting ready-to-slip dislocations in neighbor metallic layers and thus accommodate inelastic shear/slip transfer Zhang *et al.* (2012c), as shown in Fig. 2.4 (f). Thus, the single hairpin-shaped dislocation loops can only exist in isolated metallic layers instead of cutting across two (or more) layers, which renders the higher hardness/strength in the crystalline-amorphous nanolaminates.

Figure 2.3: Hardness of crystalline (Cu/Zr) and crystalline/amorphous (Cu/a-CuZr) nanolaminates as a function of individual layer thickness Zhang *et al.* (2012c).

2.1.3 Metal-ceramic nanolaminates

The previous examples are characterized by nanolaminates that combine layers with different crystal and/or atomic structure, but where the intrinsic strength of the individual layers is comparable. However, it is not clear how deformation is accommodated in each layer under the applied stresses when the mechanical mismatch between the layers is very large. This is the case, for instance, of metal-

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Figure 2.4: Schematics of the length-scale dependent deformation mechanisms of metal-metal and metal-metallic glass nanolaminates, including (a, d) the dislocation pile-ups against the interface at large thickness for metal-metal and metal-metallic glass nanolaminates, (b, e) the dislocation segments deposited at the interface due to glide of dislocation loops confined to crystalline layers at intermediate layer thickness for both nanolaminates, (c) large dislocation loop cutting across two layers of metallic layers at small layer thickness in the metal-metal nanolaminates, and (f) dislocations hit the opposite crystalline-amorphous interface, promoting the dislocation activity in the next crystalline layer for the metal-metallic glass nanolaminates Zhang *et al.* (2012c).

ceramic nanolaminates, that combine ductile and soft metals with stiff and brittle ceramics. Due to the large mechanical mismatch, the strength of metal-ceramic nanolaminates should be controlled by the plastic deformation of the softer metallic layers. This is the case, for instance, for Al/Si₃N₄ nanolaminates Wang *et al.* (2015), that display similar values of flow strength as a function of the layer thickness as those found in other metallic nanolaminates, as shown in Fig. 2.5. However, other metal-ceramic nanolaminates, such as Cu/TiN Misra *et al.* (1998), Ni/Ni₃Al Zhang *et al.* (2016), W/ZrN Abadias *et al.* (2008) or Cu/TiC He *et al.* (1998), have shown that, even though the strength is very dependent on the volume fraction

2.1 Effect of layer thickness on the nanolaminate strength

of the ceramic layers Lotfian *et al.* (2014), it is less sensitive to layer thickness variations, An example is plotted in Fig. 2.5 (b) where the hardness of Cu/TiN and Al/TiN nanolaminates versus layer thickness is compared Pathak *et al.* (2015). The strength increase with layer thickness reduction was large in Al/TiN, but the effect of layer thickness was negligible in Cu/TiN Bhattacharyya *et al.* (2008).

Figure 2.5: (a) Comparison of yield stress between the metal-metal and metal-ceramic nanolaminates with different layer thicknesses, Wang *et al.* (2015); (b) Hardness vs. bilayer thickness for Cu-TiN and Al-TiN. The bilayer thickness values are marked for each data point. The blue dotted line shows the best fit of the Hall-Petch equation for the Al-TiN nanolaminates. The orange dotted line shows the saturation in hardness values for Cu-TiN nanolaminates, Pathak *et al.* (2016).

In the case of Al/SiC nanolaminates that constitute the main focus of this work, previous studies have shown that the nanolaminate hardness is significantly enhanced when increasing the volume fraction of the ceramic layers Lotfian *et al.* (2014), which is expected due to the stronger nature of SiC. Fig. 2.6 shows the evolution of the Al/SiC nanoindentation hardness with the Al volume fraction. For a constant Al layer thickness (50 nm), the hardness increased linearly with the reduction of the Al volume fraction (black line in the figure). For a constant Al volume fraction, there was a marginal increase in hardness with Al layer thickness reduction (cf. Al₂₅SiC₅₀ with Al₅₀SiC₁₀₀). This result indicates a moderate size

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effect in the yield stress of the Al layers that has not been previously studied in detail. The work presented in chapter 4 will contribute to clarify this issue.

Figure 2.6: Nanoindentation hardness of Al/SiC nanolaminate as a function of Al volume fraction Lotfian et al. (2014).

There are several reasons for the discrepancies described above for metal/ceramic nanolaminates that are enumerated below:

1. The role of grain size

As described in the case of metallic multilayers, a competition can take place between grain size and layer thickness effects, depending on the length scale that determines the mean free path of dislocations during plastic deformation. As a matter of fact, the evolution in hardness with layer thickness in the case of Al/TiN and Cu/TiN nanolaminates, Fig. 2.5 (b), has been partially explained based on differences in the grain size of the individual layers. Both the Al and TiN layers in Al/TiN nanolaminates presented a columnar

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grain structure with in-plane grain sizes that were relatively larger than the individual layer thickness (i.e., an in-plane grain size of ≈ 100 nm for a layer thickness of 9 nm), while both the Cu and TiN layers were nanocrystalline with a grain size that was much smaller than the layer thickness in the case of Cu/TiN Pathak *et al.* (2015), which was attributed to their lower chemical affinity. For instance, transmission electron microscopy (TEM) images of the Cu/TiN nanolaminates with ≈ 63 nm and ≈ 7 nm layer thicknesses in Fig. 2.7 Pathak *et al.* (2015) show a smaller grain size of ≈ 25 nm in the former (Fig. 2.7a) and ≈ 5 nm in the latter (Fig. 2.7b). As a result, the hardness seemed controlled by dislocation/interface interactions in Al/TiN and by dislocation/grain boundary interactions in Cu/TiN, explaining partially the discrepancies.

Figure 2.7: Cross-sectional TEM of (a) Cu (50 nm)- TiN (50 nm) and (b) Cu (50 nm)- TiN (50 nm) nanolaminate, Pathak *et al.* (2015).

However, not all discrepancies can be attributed to grain size effects. In the case of Al/SiC nanolaminates discussed above, the SiC was amorphous and the Al layers had a columnar grain structure, similar to that found in Al/TiN nanolaminates, with grain sizes that were of the same order of magnitude than the layer thickness, as shown in Fig. 2.8 for Al/SiC nanolaminates with 50 nm thick layers Lotfian *et al.* (2013). Yet the hardness increase with

2.1 Effect of layer thickness on the nanolaminate strength

layer thickness reduction was modest (cf. Fig. 2.6), and so was for Al/Si₃N₄ nanolaminates with similar grain structures Wang *et al.* (2015). This is an area of active research that this work aims at clarifying.

Figure 2.8: Transmission electron microscopy image of an Al (50 nm)- SiC (50 nm) nanolaminate Lotfian et al. (2013).

2. The role of the ceramic layers

Due to their larger intrinsic strength, the ceramic layers are expected to undergo either elastic deformation or fracture during deformation. From the point of view of load support, the flexural stiffness of the ceramic layers should be reduced with layer thickness reduction, but further strengthening can also be expected from the layer thickness reduction from the fracture point of view, due to the Griffith effect that results from the reduction in the size of pre-existing flaws. So, it is not clear what can be expected from the layer thickness reduction in the ceramic layers. As a matter of fact, the stresses in the metallic layers might become so high and the fracture stress of the ceramic layers so large for very thin layers that it might be possible to activate plastic co-deformation of the metallic and ceramic layers, leading

2.1 Effect of layer thickness on the nanolaminate strength

to a transition from a brittle to a ductile behavior. This behavior was found in Al/TiN nanolaminates when the bilayer thickness was reduced to a few nanometers Mook *et al.* (2013), Li *et al.* (2014).

3. The role of constraint

The ceramic layers are expected to undergo elastic deformation when the metallic layers start to deform plastically. Thus, plasticity in the softer metallic layers takes place under highly constrained conditions. One intriguing observation, related to the constraint effects, is the conflicting trends observed on the strength evolution with layer thickness, depending on the mechanical testing technique. While the nanoindentation hardness determined for Cu/TiN showed a modest layer thickness dependence Pathak *et al.* (2015) (cf. Fig. 2.5(b)), the strength determined by micropillar compression in the same system displayed a much stronger variation with layer thickness reduction. This is shown in Fig. 2.9 that depicts the stress-strain curves for Cu/TiN nanolaminates as a function of layer thickness determined by micropillar compression Raghavan *et al.* (2015b). The maximum strength increased significantly as the layer thickness was reduced, from ≈ 1.5 GPa for Cu (700 nm) – TiN (1000 nm) to ≈ 3.0 GPa for Cu (2 nm) – TiN (10 nm). The reasons for these differences are not well understood, and understanding them is one of the objectives of this work, underlined in chapter 5.

2.2 Deformation and fracture modes versus layer thickness

Figure 2.9: Engineering stress-strain curves of Cu/TiN nanolaminates with different individual layer thickness obtained by micropillar compression Raghavan et al. (2015b).

2.2 Deformation and fracture modes versus layer thickness

The length scale dependent deformation mechanisms described in section 2.1 can lead to deformation and fracture behaviors that are also highly influenced by the layer thickness. Misra & Hoagland (2007) explored the deformation modes during rolling of Cu/Nb nanolaminates as a function of layer thickness, as summarized in Fig. 2.10. This study revealed that the layer thickness reduction of Cu and Nb was inhomogeneous for nanolaminates with initial layer thicknesses in the sub-micrometer to micrometer scale, and this behavior was associated with the formation of dislocation cell structures within the layers, as shown in Fig. 2.10 (b). This deformation heterogeneity was explained by the stochastic nature of the activation of dislocation sources that led to a non-uniform distribution of dislocation pile-ups. On the contrary, the Cu and Nb layers co-deformed uniformly in nanolaminates with initial layer thicknesses of a few tens of nanometers, as shown

2.2 Deformation and fracture modes versus layer thickness

in Fig. 2.10 (c), due to the activation of confined layer slip of dislocations loops that were distributed homogeneously across multiple layers. Finally, shear cracks were observed after the rolling process in nanolaminates with initial layer thicknesses of a few nanometers, as shown in Fig. 2.10 (d). This behavior was attributed to the activation of dislocation transmission across interfaces, which led to the development of shear localization as a result of the passage of several dislocations across the interface at the site of slip transmission.

Figure 2.10: Influence of the layer thickness on the deformation modes of Cu/Nb nanolaminates upon rolling parallel to the layer thickness: (a) Schematic of rolling deformation; (b) TEM observation of the Cu/Nb microstructure rolled to 50 % layer reduction with initial layer thickness of 600 nm; (c) TEM observation of the Cu/Nb nanolaminates with initial layer thickness of 75 nm to 30 nm; (d) Shear cracks after rolling of Cu/Nb nanolaminates with initial layer thickness of 15 nm Misra & Hoagland (2007).

2.2 Deformation and fracture modes versus layer thickness

The dependence of the deformation mechanisms with layer thickness yields the length scale dependent deformation and fracture behavior of nanolaminates, which have also been observed in other metallic, crystalline-amorphous and metal-ceramic nanolaminates Wu *et al.* (2014), Dayal *et al.* (2011). Micropillar compression (which is suitable for nanolaminates because they are often produced as a thin film) has been extensively employed to study the deformation and fracture modes because the deformation and fracture modes after the test can be directly studied from the morphology of the deformed micropillars. Images of the deformation of Al/Pd micropillars, as a function of layer thickness are depicted in Fig. 2.11 Dayal *et al.* (2011). For layer thicknesses in the sub-micrometer to micrometer scales (Fig. 2.11a), the micropillars often showed a uniform strain distribution along the length of the micropillar, with evidences of plastic barreling and extrusion of the softer layers at the free-surfaces. This has been mainly attributed to dislocation-dominated symmetric confined slip activity in the individual layers. In contrast, the micropillars showed strain localization by shear deformation for layer thicknesses of only a few nanometers (Fig. 2.11c) without significant barreling or extrusion. This behavior was attributed to mechanisms like grain boundary sliding, grain rotation and/or dislocation transmission across multiple interfaces. Finally, a combination of barreling and extrusion and shear localization has been typically observed in nanolaminates with intermediate layer thicknesses (Fig. 2.11b), which was a consequence of the coupling effect between dislocation-mediated plasticity and the asymmetric slip found for small layer thicknesses Zhang *et al.* (2012a).

Metallic crystalline-amorphous nanolaminates, such as Cu/*a*-CuZr Cui *et al.* (2016) and Cu/*a*-PdSi Knorr *et al.* (2013), have also been reported to show similar length scale dependent deformation modes under uniaxial compression, as shown in Fig. 2.11 (d, e, f). As discussed above, amorphous-crystalline interfaces can be regarded as impenetrable barriers for dislocation transmission, similar to incoherent interfaces in metal-metal nanolaminates. These studies suggest that plasticity initiates in the softer metallic layers, followed by a marked strain hardening, which was attributed to the dislocation multiplication that might take place within the crystalline layers. Co-deformation between the amorphous layers and the metal-

Figure 2.11: (a, b, c) Compressed Al/Pd nanolaminates with bilayer thickness of 80, 20 and 2 nm Dayal et al. (2011); (d, e, f) Compressed Cu/a-CuZr nanolaminates with 100 nm thick CuZr and 100 nm, 50 nm and 10 nm thick Cu layers Guo et al. (2016).

lic layers seemed to prevent or delay the formation of shear bands until the layer thickness was reduced to a few nanometers.

Similar observations have been done in metal-ceramic nanolaminates. However, co-deformation between the metallic and ceramic layers is not typically observed due to the large mismatch in strength between the layers. Micropillar deformation for layer thicknesses of a few tens of nanometers has been observed to proceed initially by the constrained plastic deformation of the metallic layers, while the ceramic layers are still elastically deforming, leading to barreling and extrusion of the metallic layers at the free surface of the pillar (see Fig. 2.12a,b) Lotfian *et al.* (2014), Raghavan *et al.* (2015b). This is usually accompanied by a large strain hardening rate in the stress-strain curve, as shown for Cu₅TiN₁₀, which has not been explained so far, and which will be the focus of the studies presented in chapter 5 of this thesis. At larger applied strains, fracture of the ceramic layers seems to control the maximum strength of the micropillars, especially for

2.2 Deformation and fracture modes versus layer thickness

the thicker layers. For instance, cracking of the TiN layers, preferentially at the columnar grain boundaries in Cu/TiN micropillars with 1000 nm thick TiN layers (see Fig. 2.12c,d), led to softening of the micropillar response, as shown in Fig. 2.9 Raghavan *et al.* (2015b). Similar trends were observed for smaller layer thicknesses down to 10 nm thick TiN layers, but at increasing fracture stresses (Fig. 2.9). This behavior was presumably due to the Griffith effect that results from the decrease in the size of pre-existing flaws with layer thickness reduction. Plastic co-deformation of the metallic and ceramic layers has only been observed to take place for extremely small ceramic layer thicknesses, like for Al/TiN with 5 nm thick layers, Li *et al.* (2014).

Figure 2.12: Deformation and fractures of (a, b) 5 nm Cu – 10 nm TiN and (c, d) 700 nm Cu – 1000 nm TiN micropillars after micropillar compression tests at room temperature Raghavan *et al.* (2015b).

Similar micropillar compression studies in Al/SiC nanolaminates are, however, limited. Micropillar compression studies in Al/SiC nanolaminates with 50 nm

2.2 Deformation and fracture modes versus layer thickness

thick layers also confirmed that deformation was initially accommodated by the constrained plastic deformation of the Al layers, without SiC cracking Lotfian *et al.* (2014), as shown in Fig. 2.13. No further studies have been performed to study the deformation and fracture mechanisms at larger applied strains as a function of layer thickness, and this will be the focus of the work presented in chapter 6.

Figure 2.13: (a) Deformed Al/SiC micropillar at small applied strain($\approx 8\%$); (b) Cross-sectional TEM image of the deformed Al/SiC micropillar, showing the constrained plasticity of the soft Al layers, without cracking of the SiC layers Lotfian *et al.* (2014).

Finally, mechanical characterization in most nanolaminates has been limited to study the mechanical response by nanoindentation or micropillar compression when the loading direction was perpendicular to the layers. It is expected that the nanolaminates will present a strongly anisotropic mechanical response with respect to the layer orientation but very little is known on this subject due to experimental difficulties. In addition, the mechanical response in tension is unknown. Thus, chapters 6 and 7 will contribute to increase our knowledge in this area by exploring the influence of layer orientation in the mechanical response in

2.3 Effect of temperature on deformation mechanisms

compression and tension by means of the novel nanomechanical characterization techniques presented in chapter 3.

2.3 Effect of temperature on deformation mechanisms

It is expected that temperature will also influence the layer thickness dependent strength of nanolaminates because it can trigger other deformation mechanisms (dislocation climb and cross-slip, grain boundary and interface diffusion) that can dramatically affect the size effects encountered at room temperature. So far, only a small number of nanolaminate systems have been studied at elevated temperature, such as Al/SiC Lotfian *et al.* (2014), Lotfian *et al.* (2012), Cu/Nb Monclús *et al.* (2013), Mara *et al.* (2008), Cu/TiN Raghavan *et al.* (2015b), Cu/Cr Raghavan *et al.* (2015a), Raghavan *et al.* (2015c) or Cu/W Monclús *et al.* (2014a), Wheeler *et al.* (2015b). And the few studies that exist have shown that the high temperature response can be quite different to that found at room temperature.

The first evidence that other deformation mechanisms could be activated at elevated temperature for the length scales involved in nanolaminates was found for Al/SiC nanolaminates. The compressive stress-strain curves of a 50 nm layer thick Al/SiC nanolaminate at 23°C and 100°C are plotted in Fig. 2.14. The micropillars tested at 23°C presented a very high strain hardening rate, reaching a stress of 3.1 GPa at 8% applied strain. The micropillars tested at 100°C displayed a much softer behavior, with the flow stress saturating at 1.6 GPa when the applied strain reached $\approx 8\%$. Detailed scanning electron microscopy (SEM) images of the deformed micropillars (inserts in the figure) revealed that Al extruded out of the edges of the micropillar at 100°C, contrary to the observations at room temperature (cf. also with Fig. 2.13). This behavior was indicative of a drastic softening of the Al layers at 100°C, which represents a homologous temperature of 0.4, and a complete loss of the constraint effect imposed by the SiC layers.

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Figure 2.14: Compression stress-strain curves of Al/SiC micropillars at 23°C and 100°C. The inserts are the morphologies of the deformed micropillars Lotfian *et al.* (2013).

The amount of Al extrusion at 100°C indicated that other mechanisms, like stress-assisted diffusion, could be activated at the length scales involved in nanolaminates. It is interesting to note that the drastic softening observed at 100°C could not be attributed to interface reactions, since the interfaces remained chemically sharp and free of reaction products at temperatures up to 150°C, as shown in Fig. 2.15. As a matter of fact, a separate study Lotfian *et al.* (2012) determined that interface reactions between Al and SiC only began at temperatures >200°C and were dominant at 300°C. Al and SiC reacted above 200°C to form Al_4C_3 and Al_4SiC_4 compounds (see the diffraction patterns in Fig. 2.16b) and free Si (see the elemental maps in Fig. 2.16c) as a reaction product, These chemical reactions were responsible for the large drop in hot hardness above 200°C and the increase in room temperature hardness after high temperature annealing, Fig. 2.16 (a).

Preliminary nanoindentation studies suggested that the layer thickness had a strong influence on the elevated temperature response even in the range between

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Figure 2.15: High magnification TEM image of the Al/SiC interface after micropillar compression at 100°C showing no reaction products Lotfian *et al.* (2013).

25°C and 150°C Lotfian *et al.* (2014) for which no chemical reactions took place. Based on the general creep equation:

$$\dot{\epsilon} = A\sigma_y^n \exp\left(-\frac{Q}{RT}\right) \quad (2.3)$$

where A is a pre-factor, R the gas constant (≈ 8.314 J/K mol), Q the activation energy and n the stress exponent, it is possible to establish an analogy between H and σ_y at a constant strain rate and to define an apparent activation energy for hardness $E_a = Q/n$, through the following Arrhenius type equation:

$$H = H_0 \exp\left(\frac{E_a}{RT}\right) \quad (2.4)$$

where H_0 is the extrapolated hardness at 0 K. The hardness versus $1/RT$ in logarithmic scale is plotted in Fig. 2.17 for nanolaminates with (a) 50 nm SiC layers and varying Al layer thickness and (b) 50 nm thick Al layers and varying SiC layer thickness Lotfian *et al.* (2014). These results suggest that the apparent activation energy E_a (in the range between 1-10 kJ/mol) was strongly dependent on Al layer thickness (Fig. 2.17a), but weakly dependent on SiC layer thickness (Fig. 2.17b).

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Figure 2.16: (a) Hardness as a function of test temperature in Al₅₀SiC₅₀ nanolaminates (solid symbols). The open symbols represent the hardness and modulus measured at ambient temperature after high temperature annealing; (b) Diffraction pattern, indicating the presence of reaction products between Al and SiC at 300°C; (c) The elemental maps obtained after testing at 300°C indicate that the dark layer pointed by the white arrow corresponds to a Si-rich area, presumably a reaction product between Al and SiC Lotfian et al. (2012).

This behavior supports the hypothesis that plasticity was mostly controlled by the metallic layers, and not by the ceramic ones, and that the layer thickness might have a strong influence on the elevated temperature response. Unfortunately more detailed analysis of the effect of layer thickness on the elevated temperature deformation mechanisms in Al/SiC were still missing at the beginning of this work, and this topic has been re-visited in chapter 4.

Similar results regarding the effect of temperature have been found in other nanolaminate systems very recently. For instance, elevated temperature studies in Cu/TiN nanolaminates, summarized in Fig. 2.18 (a), revealed that the strength decreased dramatically at 200°C and 400°C, and that the strength drop with temperature increased with layer thickness reduction, leading to an inverse size effect. A similar behavior was also found for accumulated roll bonding (ARB) and physical vapor deposition (PVD) processed Cu/Nb nanolaminates Monclús *et al.* (2013)

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Figure 2.17: Arrhenius plots of nanolaminate hardness versus temperature for (a) Al/SiC nanolaminates with 50 nm thick SiC layers and different Al layer thicknesses; (b) Al/SiC nanolaminates with 50 nm thick Al layers and different SiC layer thicknesses Lotfian et al. (2014) .

at 300°C, as summarized in Fig. 2.18 (b). In this case, a critical layer thickness L_{crit} was found, in between 5 and 18 nm for PVD and ARB processing, respectively, for which the hardness drop with temperature was minimum. This critical length was associated to a change in the main deformation mechanism: from confined layer slip above L_{crit} , to either dislocation transmission at interfaces and/or stress assisted diffusion below L_{crit} .

Additional evidence that soft metals like Al and Cu might deform by stress-assisted diffusion at a homologous temperature of ≈ 0.4 was found in Cu/Cr Raghavan *et al.* (2015c) and Cu/W nanolaminates Wheeler *et al.* (2015b). Cu/Cr and Cu/W micropillars compressed at 25-300°C are shown in Fig. 2.19 and Fig. 2.20, respectively. At room temperature, the plastic deformation of the softer Cu layers was constrained and failure took place in shear. They exhibited a much more uniform strain distribution at 300°C and showed the formation of nano- and ultra-fine grained crystals on the free surface of the micropillars, that can only be explained by a diffusional process.

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Figure 2.18: (a) Yield stress of Cu/TiN nanolaminates as a function of thickness of Cu interlayers at ambient and elevated temperatures and comparison with the theoretical trend expected from Hall-Petch (H-P) and confined layer slip (CLS) models Raghavan *et al.* (2015b); (b) Ratio of hardness at 300°C and 25°C in Cu/Nb nanolaminates as a function of layer thickness (normalized by L_{crit} , where $L_{crit} \approx 18$ nm for ARB and $L_{crit} \approx 5$ nm for PVD Cu/Nb multilayers) Monclús *et al.* (2013).

The contribution of diffusion to the deformation of the nanolaminates at elevated temperatures can be related to the nanoscale dimensions of the metallic grains and the large applied stresses. They can trigger a substantial contribution of grain boundary diffusion to deformation, even at the relatively large strain rates, $\approx 10^{-3}$ /s associated to micropillar compression tests. The activation energy for grain boundary diffusion for coarse-grain Cu is ≈ 104 kJ/mol and for lattice diffusion is ≈ 197 kJ/mol Frost & Ashby (1982), but it can drop substantially for Coble creep down to ≈ 62 kJ/mol Horvath *et al.* (1987). In the case of nanolaminates, the reported activation energies were 1-10 kJ/mol for Cu/Cr Raghavan *et al.* (2015c), Cu/W Wheeler *et al.* (2015b) and Al/SiC Lotfian *et al.* (2014) enforcing the view of an enhanced thermal activation.

Moreover, the diffusion distance x can be estimated using the solution of Fick's second law for non-steady state conditions expressed as Reed-Hill *et al.* (2004):

$$x = 2\sqrt{D_{gb}t} \quad (2.5)$$

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Figure 2.19: SEM images of Cu/Cr micropillars with Cu layer thickness of 20 nm and Cr thickness of 80 nm compressed at 25°C, 100°C, 200°C and 300°C, respectively Raghavan et al. (2015c).

where t is the time during which the specimen is held at temperature T . The mean diffusion distance for Cu, at ambient temperature is only ≈ 2 nm during a 2-minute compression cycle. However, it increases up to ≈ 234 nm at 200°C, which might be enough to trigger a change in the dominant deformation mechanism in nanolaminates. This offers an explanation for the difference in void-filling behavior of Cu/W nanolaminates observed at different temperatures Wheeler *et al.* (2015b), as shown in Fig. 2.20. In addition, it also explains why the deformation could not be fully accommodated by diffusion at these strain rates. If the pillar diameter had been less than the mean diffusion distance, then it might be expected to see behavior and activation energy values characteristic of pure diffusion, rather than the observed intermediate behavior.

Figure 2.20: HRSEM images of the FIB cross-sections of compressed Cu/W micropillars with individual layer thickness of 100 nm Wheeler et al. (2015b).

2.4 Summary and objectives of the thesis

Based on the above, several issues regarding the mechanical properties of metal-ceramic nanolaminates remain open:

1. The evidences presented show that the deformation of metal-ceramic nanolaminates is mainly accommodated by the soft metallic layers. However, the deformation mechanisms in ultra-thin metallic layers (100 nm) as a function of layer thickness and temperature are still unknown.
2. Layer thickness effects on the strength of metal-ceramic nanolaminates yield contradictory results depending on the testing technique: nanoindentation versus micropillar compression.
3. The deformation and fracture modes of nanolaminates have been mostly studied by nanoindentation and micropillar compression in the direction per-

2.4 Summary and objectives of the thesis

pendicular to the layers. Very little is known, however, about the mechanical behavior for other layer orientations and under tensile stresses.

This thesis aims at closing these gaps by exploring the deformation, strengthening and fracture mechanisms in a model metal-ceramic nanolaminate like Al/SiC. Emphasis is put on the effect of layer thickness, temperature and loading direction. Starting from conventional nanoindentation and micropillar compression tests, various novel nano-mechanical techniques have been employed to achieve these objectives, including tensile and fracture testing techniques at the microscale. In all cases, the deformation mechanisms were characterized with the aid of advanced electron microscopy observations, while the stress state was ascertained by means of micromechanical finite element simulations.

CHAPTER 3

Materials and Experimental Techniques

3.1 Processing of Al/SiC nanolaminates

The Al/SiC nanolaminates were deposited on thermally oxidized (111) oriented Si single-crystals by magnetron sputter deposition (a form of physical vapor deposition), which is one of the most versatile and widely used fabrication techniques for nanoscale multilayers. While accumulative roll bonding is also used to fabricate metal-metal nanolaminates Beyerlein *et al.* (2013), it is not suitable to fabricate metal/ceramic nanolaminates, due to the brittle nature of the ceramic layers. The advantages of magnetron sputtering include the ability to deposit a wide variety of conductive and non-conductive materials, including alloys and compounds, an accurate processing control (including layer thickness at the nanometer scale for the nanolaminates) and high deposition rates. The films were deposited in Los Alamos National Laboratory using a sputter unit made up of a high vacuum chamber with dual sputter guns, as shown in Fig. 3.1.

The base pressure of the sputtering unit was 10^{-7} Torr. All depositions were carried out in the sputter gas of Ar, with a working pressure of 3.0 mTorr (0.4

3.1 Processing of Al/SiC nanolaminates

Figure 3.1: (a) Schematic of sputter unit; (b) vacuum chamber with dual sputter guns.

Pa). The pure aluminum target (>99.99% purity, Kurt J. Lesker, Clairton, PA) was sputtered at a DC power of 95 W. SiC layers were deposited from a SiC target made by hot isostatic pressing (>99.5% purity, Kurt J. Lesker, Clairton, PA) using identical argon pressure and a RF sputter power of 215 W. The targets were pre-sputtered for about 10 minutes at 40 W for Al and 95 W for SiC to remove any oxides and contamination prior to film deposition. The sample holder was continuously rotated during sputtering to obtain a uniform layer thickness. The deposition rates were approximately 7.5 nm/min for Al and 3.9 nm/min for SiC. Alternating Al and SiC layers were deposited by means of a computer controlled shutter system to build up the multilayer structure. The total thickness of the nanolaminate was $>10\text{ }\mu\text{m}$ to reduce substrate effects during nano-mechanical testing.

Two nanolaminate series (named series I and II) were deposited up to a total thickness between 10 and 15 μm , as summarized in Table 3.1. In series I, the nominal SiC layer thickness was kept constant at 50 nm and the nominal Al layer thickness was varied between 10 and 100 nm. In series II, both the Al and SiC layers were grown to the same thickness and the nominal layer thickness was varied between 10 and 100 nm. Note that the label used to name each nanolaminate refers to the nominal thickness, in nm, of each layer, but that the real thickness might vary. For example, Al10SiC50 is the notation used to name the nanolaminate with

3.2 Microstructural characterization

a nominal Al and SiC layer thickness of 10 nm and 50 nm, respectively. The last column in Table 3.1 indicates the nominal volume fraction of Al, V_{Al} , in each case.

Table 3.1: Thickness, number of layers and layer nominal thicknesses in the series I and II nanolaminates.

Series	Samples	Thickness (μm)	Number of bilayers	t_{Al} (nm)	t_{SiC} (nm)	V_{Al}
I	Al10SiC50	≈ 15	250	10	50	0.17
	Al25SiC50	≈ 13.3	175	25	50	0.33
	Al50SiC50	≈ 15	150	50	50	0.5
	Al100SiC50	≈ 15	100	100	50	0.67
II	Al100SiC100	≈ 17	85	100	100	0.5
	Al25SiC25	≈ 14	280	25	25	0.5
	Al10SiC10	≈ 12	600	10	10	0.5

3.2 Microstructural characterization

The microstructure of the as-deposited or post-deformed Al/SiC nanolaminates were systematically characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). This section introduces details of each characterization technique, followed by a complete description of the microstructure of the nanolaminates under study.

3.2.1 Scanning electron microscopy

Scanning electron microscopy is a type of electron microscopy technique that produces images of a sample by scanning it with a focused beam of electrons. The specimen can be solid, bulk specimens of any size that fit within the microscope chamber. Fig. 3.2 schematically illustrates the main components of a SEM, including the electron gun, the magnetic condenser lens, the scanning coils, the specimen and the various signal detectors, all in a high vacuum environment. The imaging process begins with the generation of an energetic electron beam at the electron

3.2 Microstructural characterization

gun. The beam, typically having an energy ranging from 0.2 keV to 40 keV, is then focused to a spot size of about 0.4 nm to 5 nm in diameter by a series of magnetic condenser lens and rastered along the surface of the specimen with the aid of the scanning coils. The interaction of the electron beam with the sample surface produces various emission signals that contain information on the size, shape, texture and composition of the sample. In particular, secondary electrons (SE) are emitted very close to the specimen surface, providing mainly topographical information, while back scattered electrons (BSE) and X-rays, generated deeper below the surface, provide crystallographic, atomic and compositional information. Since the interaction volume of the SE is very small, and is located at the very top surface, SE imaging provides the highest resolution image, which has been very useful in this work to characterize the morphology of the layered structure and the deformation and fracture modes after mechanical testing. In particular, a FEI Helios 600i focused ion beam workstation has been employed, equipped with a field-emission electron gun (FEG), allowing resolutions better than 1 nm in SE imaging.

3.2.2 Transmission electron microscopy

Transmission electron microscopy is another powerful imaging technique that uses high-energy electrons to provide microstructural information down to atomic resolution. It is the technique of choice to characterize defects in crystalline materials, like dislocations, interfaces, grain boundaries, etc., owing to the small de Broglie wavelength of high-energy (100-400 keV) electrons. To this end, specimens for TEM characterization must be electron transparent (generally <100 nm), enabling the transmission of the incident electrons.

In the TEM, the incident electrons, also called primary electrons, emitted from the electron gun are accelerated towards the specimen at energies between 100 and 400 keV. A set of condenser lenses and apertures ensures parallel illumination of the specimen. Upon interaction with the specimen, the primary beam splits between the direct beam, formed by electrons that undergo inelastic scattering

Figure 3.2: Schematic of the main components of a scanning electron microscope.

without changing the incident direction, and diffracted beams that change their direction through elastic scattering by the lattice planes of the specimen that fulfill the Bragg condition. Depending on the operation of the objective and projection lenses and the set of objective apertures selected, different types of images can be generated. Diffraction patterns (DP) provide crystallographic information such as crystal orientation, lattice parameters, etc., while bright-field (BF) and dark-field (DF) imaging, generated by selecting either the direct or one of the diffracted beams, hold information about morphology, grain size and defect structure. Finally, phase contrast analysis by combining the direct and diffracted beams allows the generation of high-resolution electron microscopy (HREM) images that can be used to infer information about the crystalline lattice at atomic resolution.

3.2 Microstructural characterization

In this work, three different microscopes have been used: a FEI TecnaiTM F300, at the Center for Integrated Nanotechnologies (CINT) of Los Alamos National Lab for the *in-situ* TEM experiments, a JEOL JEMTM 2100, at the National Laboratory for Electron Microscopy (CNME) of the Complutense University of Madrid and a FEI TalosTM F200 at IMDEA Materials Institute, which is shown in Fig. 3.3.

Figure 3.3: Configuration of the FEI Talos F200 TEM system: (a) General view, (b) The vertical column setup, (c, d) The specimen holder.

The preparation of electron-transparent TEM specimens is challenging and complex, since it requires reducing the thickness down to below 100 nm without introducing damage. Nanomaterials, such as nanopowders or nanotubes, can be quickly prepared by the deposition of a dilute sample containing the specimen onto support grids or films, but bulk materials and coatings need to be subjected to

mechanical milling, chemical etching, ion milling, etc. Among the possible TEM sample preparation techniques, focused ion beam (FIB) milling is the only one that allows the precise site selection of the TEM specimen in the bulk sample, which is important for this work. Therefore, FIB milling was the technique used to fabricate electron transparent lamellae in the Al/SiC nanolaminates and its principles are introduced in detail in the next section.

3.2.3 Focused ion beam milling

Microstructural characterization and the nanomechanical testing methods (like micropillar compression, microtension, etc.) employed in this work rely on the accurate fabrication of small volume specimens with specific geometries, which can be implemented by FIB milling. The basic concept of the FIB microscope is similar to that of the scanning electron microscope, but uses ions like Gallium (Ga^+), Helium, etc., instead of electrons for imaging or removal of material. A fine tungsten pin covered with liquid Gallium (Ga) is used as ion source from which Ga atoms are extracted and ionized via high voltage. The use of Ga is advantageous for two reasons. Firstly, Ga has a low melting point and hence it exists in the liquid state near room temperature. Secondly, Ga can be focused to a very fine probe size, less than 10 nm in diameter. Such Ga^+ ions are then accelerated in the range of 0.5-50 keV and focused on the sample via electrostatic lenses. By controlling the strength of the electrostatic lenses and adjusting the effective aperture sizes, the probe current density (and therefore the beam diameter) may be varied from tens of pA to several nA corresponding to a beam diameter of ≈ 5 nm to ≈ 0.5 μm , respectively. Almost all materials can be structured by FIB, ranging from soft matter (polymers) to ultra-hard material (diamond) Wheeler *et al.* (2015c). However, when using FIB for surface structuring, it should be kept in mind that this method can lead to ion implantation, thermal stresses and defect formation Bei *et al.* (2007), Motz *et al.* (2005). Most FIB microscopes are equipped with an additional scanning electron column. Such SEM/FIB systems are extremely useful since they allow for *in-situ* observation with the electron beam during ion beam

3.2 Microstructural characterization

milling. Another advantage of the SEM/FIB systems is that they can also be used for ion-beam assisted deposition in selected locations. This is very useful when depositing metals (like Pt) to protect selected locations from further interaction with the ion beam. The FIB/SEM system employed in this work was a FEI Helios NanoLabTM DualBeamTM 600i FIB microscope, as shown in Fig. 3.4. The ion beam is aligned at 52° with respect to the electron beam, therefore the ion beam impinges at 90° with respect to the sample while electron imaging takes place at 52°, as shown in Fig. 3.5.

Figure 3.4: (a, b) View of the FEI Helios 600i focused ion beam system: (1) Electron beam, (2) Gallium ion beam, (3) EasyliftTM micromanipulation module, (4) Metal deposition module, (5) EBSD detector and (6) Chamber.

One of the wide application of FIB milling is to fabricate thin TEM specimen using the “lift-out” technique Mara *et al.* (2008). This technique requires little or no initial specimen preparation but the FIB system must be equipped with a micromanipulator or microprobe to transfer the membrane from the sample to a TEM grid. The total fabrication time for a site specific TEM specimen by this method is on the order of several hours, depending on the material composition, geometry of the bulk sample, etc. The final size of the electron transparent cross-

Figure 3.5: Schematic diagram of the configuration of the FIB/SEM dual beam apparatus. The sample is tilted to 52° , so ion milling occurs at 90° to the sample surface while electron imaging takes place at 52° .

section varies, but it can be as large as 150 square microns, and as small as 45 square microns.

Fig. 3.6 includes images of a typical “lift-out” process taken during fabrication of a thin TEM lamellae from one of the Al₅₀SiC₅₀ nanolaminates. The process begins with the location of the area of interest, over which a layer of FIB-deposited Pt strip is placed to protect the surfaces during FIB milling, as shown in Fig. 3.6 (a). This step is especially important when surface phenomena on bulk samples (like nanoindentation imprint, compressed micropillars) are to be analyzed Helmersson *et al.* (1987), Kishi *et al.* (2003). After that, two polygonal trenches are milled on either side of the Pt line, using a large beam current (like 9.3 nA, 21 nA) to achieve fast ion milling, leaving a wall of material in the center that is typically $\approx 2 \mu\text{m}$ thick and $\approx 10 \mu\text{m}$ long, as shown in Fig. 3.6 (b). The trenches themselves are approximately $\approx 10 \mu\text{m}$ wide, $\approx 10 \mu\text{m}$ long, and 5-10 μm deep. After that, a smaller beam current (0.79 nA) is employed to further thin the central membrane between the two trenches to a thickness of approximately $\approx 1 \mu\text{m}$, which is the recommended value for the next step in the specimen preparation. The next step

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consists on cutting away the left, bottom and bottom right sides of the membrane, by tilting the specimen at 52° with respect to the ion beam and using a medium ion current (2.5 nA, 0.79 nA), so that it remains attached to the bulk substrate only at the right upper corner of the membrane. When finished, the nearly suspended membrane shown in Fig. 3.6 (c) must be transferred to a Cu grid, using a tungsten needle that is attached to a micromanipulator that is capable of moving it through exceptionally fine motions with a great deal of control. This process is the most critical and difficult part in the whole “lift-out” procedure, as shown in Fig. 3.6 (d). The thin tungsten needle must be first glued to the left upper corner of the membrane by ion beam assisted Pt deposition, after which the membrane is completely detached from the bulk substrate by ion milling the remaining right upper corner. After that, the needle is lifted out from the bulk substrate and the membrane is transferred to the Cu grid, again using Pt deposition, as shown in Fig. 3.6 (e, f). The final milling step involves thinning the membrane down to a thickness <100 nm, using low ion beam currents from 0.24 nA, down to 80 pA or 40 pA, to ensure minimum ion beam damage. In order to minimize taper, the membrane is over-tilted by $1\text{-}2^\circ$ with respect to the ion beam during the last polishing steps.

3.2.4 Microstructure of the Al/SiC nanolaminates under study

Fig. 3.7 (a-h) shows BF-TEM and HREM images of the Al/SiC nanolaminates studied in this thesis. The layers were relatively uniform throughout the thickness of the laminate in all cases. The Al layers grew with a nanocrystalline structure, while the SiC layers were amorphous. Due to their amorphous nature, the SiC layers interrupted the crystalline growth of each Al layer, forcing the next Al layer to re-nucleate. As a result, the Al layers presented a nanocolumnar grain structure where the vertical, columnar grain size, d_v , was equal to the layer thickness, h_{Al} . Interestingly, the lateral grain size, d_l , scaled with the layer thickness but did not follow a constant relation with it, as shown in Table 3.2. The lateral grain size

Figure 3.6: Lift-out process to fabricate a TEM lamellae from a 50 nm layer thick Al/SiC nanolaminate sample.

was larger than the layer thickness for Al layer thicknesses below 25 nm, while it was smaller than the layer thickness for thicknesses above 50 nm. For instance, the 10 nm thick Al layers showed a lateral grain size of ≈ 30 nm, irrespective of the thickness of the SiC layers (compare Al₁₀SiC₅₀ and Al₁₀SiC₁₀). This result indicates that the Al grains nucleated on each consecutive SiC layer and grew quickly up to 30 nm in the in-plane orientation, and that the nucleation process on top of each consecutive amorphous SiC layer was independent of its thickness. As the Al layer thickness increased, columnar growth proceeded and the

3.2 Microstructural characterization

grains experienced some lateral grain growth at a rate smaller than the increase in thickness. As a result, the aspect ratio of the Al grains changed at 50 nm, with the vertical dimension becoming longer than the lateral grain size. The Al layers displayed a random texture in the thickness range studied. No formation of secondary phases or intermixing could be found at the Al-SiC interfaces, as shown in the HREM image of Fig. 3.7 (h). Finally, even though the Al and SiC layers were relatively uniform in thickness, the actual thicknesses measured in the BF-TEM micrographs were slightly different from the nominal ones, as reported in Table 3.2.

Table 3.2: Actual thickness of Al and SiC layers and Al grain sizes in series I and II nanolaminates, measured by transmission electron microscopy.

Series	Nanolaminate	Thickness μm	Layer thickness		Al grain size		V_{Al} (%)
			h_{Al} (nm)	h_{SiC} (nm)	vertical, d_v (nm)	lateral, d_l (nm)	
I	Al10SiC50	≈ 15	10 ± 1	46 ± 3	10 ± 1	29 ± 5	≈ 17.9
	Al25SiC50	≈ 13.3	21 ± 1	44 ± 2	21 ± 1	47 ± 12	≈ 32.3
	Al50SiC50	≈ 15	52 ± 2	44 ± 2	52 ± 2	48 ± 7	≈ 54.2
	Al100SiC50	≈ 15	90 ± 8	48 ± 3	90 ± 8	65 ± 12	≈ 64.3
II	Al10SiC10	≈ 12	8 ± 1	11 ± 2	8 ± 1	29 ± 6	≈ 42.1
	Al25SiC25	≈ 14	25 ± 4	25 ± 7	25 ± 4	47 ± 11	≈ 50
	Al100SiC100	≈ 17	100 ± 6	148 ± 5	100 ± 6	62 ± 12	≈ 40.8

Fig. 3.7 (a-g) also shows that the Al-SiC interfaces developed some roughness as a result of the competitive columnar grain growth process that takes place in each consecutive Al layer Lotfian *et al.* (2012). The interface roughness developed, combined with the shadowing effects that are inherent to the PVD process, led to the development of a columnar structure and layer waviness, as shown in Fig. 3.8 (a) and (b) for Al100SiC100. Within each columnar colony, the layers followed an arched shape, with the valleys situated at the columnar boundaries. Void formation at the columnar boundaries was detected by imaging under slightly underfocused conditions to enhance Fresnel contrast. They are presumably formed due to shadowing effects. The layers were continuous across several columnar colonies despite the development of a columnar structure and the associated waviness, except in

3.2 Microstructural characterization

the case of the thinnest layers of 10 nm, where some intermixing of the layers was observed, as suggested for Al10SiC10 in Fig. 3.8 (c) and (d).

Table 3.3 summarizes the width of the columnar boundaries, d_c and the degree of waviness, ω , of the series I and II nanolaminates as a function of layer thickness. Note that ω was quantitatively determined as the layer waviness amplitude, d_A (as measured in Fig. 3.8b), divided by the columnar width d_c . Interestingly, the width of the columnar boundaries d_c correlated with the layer thickness, increasing from 171 ± 27 nm for Al10SiC10 to 713 ± 221 nm for Al100SiC100. This trend in series II nanolaminate is in agreement with the assumption that columnar colonies develop as a consequence of interface roughness combined with the shadowing effects inherent to the PVD process, because the interface roughness period follows the lateral grain size of the Al layers, that also increases with layer thickness. The degree of waviness ω was, however, similar in all cases within experimental scatter.

Table 3.3: The columnar boundary width, d_c , and the waviness degree, ω (defined as the layer waviness amplitude, d_A , divided by the columnar width, d_c), in the series I and II nanolaminates.

Series	Nanolaminate	Columnar Width, d_c nm	Waviness degree ω
I	Al10SiC50	420 ± 8	0.13 ± 0.02
	Al25SiC50	439 ± 32	0.1 ± 0.01
	Al100SiC50	869 ± 168	0.12 ± 0.05
II	Al10SiC10	171 ± 27	0.11 ± 0.01
	Al25SiC25	305 ± 73	0.12 ± 0.02
	Al50SiC50	450 ± 105	0.13 ± 0.03
	Al100SiC100	713 ± 221	0.15 ± 0.02

It should be emphasized that a complete microstructural characterization is critical to achieve a full understanding of the mechanical response of metal/ceramic nanolaminates. The grain size and morphology of the Al layers will determine their size dependent yield stress, while columnar boundaries and layer waviness can determine the fracture and deformation modes, especially when the nanolaminates are loaded parallel to the layers, as will be explained in chapter 6.

3.2 Microstructural characterization

Figure 3.7: BF-TEM images of Series I samples: (a) $Al_{10}SiC_{50}$, (b) $Al_{25}SiC_{50}$, (c) $Al_{50}SiC_{50}$, (d) $Al_{100}SiC_{50}$. BF-TEM of Series II samples: (e) $Al_{10}SiC_{10}$, (f) $Al_{25}SiC_{25}$, (g) $Al_{100}SiC_{100}$; (h) HREM of $Al_{100}SiC_{100}$.

Figure 3.8: Columnar colony microstructures in the (a, b) Al₁₀₀SiC₁₀₀ and (c, d) Al₁₀SiC₁₀ nanolaminates. The red arrows indicate the discontinuity of the layers in the thinnest Al₁₀SiC₁₀ nanolaminate by intermixing of the SiC layers with Al grains.

3.3 Nanomechanical testing techniques

The Al/SiC nanolaminates studied in this work were produced in the form of relatively thin coatings and the characterization of their mechanical response for different loading modes (tension/compression as a function of layer orientation) required the use of a range of different micro- and nano-mechanical testing strategies. They include *ex-situ* nanoindentation, micropillar compression, micropillar splitting, as well as *in-situ* SEM microtensile testing and *in-situ* TEM nanopillar compression. This section gives a general introduction to the different nano-mechanical testing methods and the testing equipment employed in this work.

3.3.1 Description of the nano-mechanical testing instruments used in this work

Mechanical testing of the Al/SiC nanolaminates under different loading modes were carried out in a range of nanomechanical testing platforms, that are described below.

Stand-alone systems

Two stand-alone systems have been used in this work to carry out the nanoindentation and micropillar compression work presented in chapters 4 and 5, respectively: the TI 950 TriboIndenterTM from Hysitron and the NanoTestTM platform III from Micro Materials. Photographs of the systems are shown in Fig. 3.9.

The Hysitron TI950 TriboIndenterTM uses a vertical axial-loading system based on a piezoelectric force transducer and capacitance depth-sensing indenter head. The system is equipped with a (1) low-load transducer, (2) a high-load transducer, (3) an optical microscope and (4) a sample positioning stage, as shown in Fig. 3.10. The low-load transducer can reach a maximum force of 12 mN with force resolution <1 nN and displacement resolution <0.02 nm. This transducer is also capable of

Figure 3.9: (a) Hysitron Ti950 TriboindenterTM, (b) Micro Materials NanoTestTM.

measuring the stiffness continuously (nano dynamic mechanical module, nanoDMA mode) during testing. The high-load transducer reaches a maximum load of 1 N with force resolution $<1 \mu\text{N}$ and displacement resolution $<0.1 \text{ nm}$. Finally, all the hardware is embedded on an active vibration isolation system and located in a thermal and acoustic enclosure designed to minimize vibrations, thermal drift and acoustic noise during testing. Additionally, a high temperature stage (xSolTM) can be installed for high-temperature experiments.

The NanoTestTM, however, operates with a horizontal loading configuration and utilizes a pendulum based loading system, equipped with an induction coil for load actuation and a depth sensing three parallel plates capacitor. As shown in Fig. 3.11, the system is composed of (6) a pendulum, (7) a sample positioning stage 3 X, Y and Z axis controllers (1, 2 and 3), 2 optical microscopes (4) and (5) and (8) an oxygen detector. The chamber can be purged with inert gas (Ar) to prevent oxidation during elevated temperature testing. Fig. 3.12 shows in detail the configuration of the pendulum module. By passing a current through the in-

3.3 Nanomechanical testing techniques

Figure 3.10: Elements of the Hysitron TI950 TriboIndenterTM : (1) Low load transducer, (2) High load transducer, (3) Optical microscope and (4) X-Y positioning stage.

duction coil at the top, the pendulum rotates around a frictionless pivot towards the magnet, thus pushing the indenting tip into the sample. The displacement of the indenter into the sample surface is measured by a set of parallel plate capacitors, with one plate attached to the pendulum and the other to the main frame of the instrument. A set of damping plates located at the bottom provides air damping to minimize pendulum oscillation prior to measurements. The configuration allows a wide loading range from 10 μN to 500 mN.

The NanoTestTM system is very well suited for elevated temperature testing, because, firstly, the system uses a horizontal loading configuration so that electronics do not suffer from convection heating; secondly, because the system allows for independent heating of the indenter tip and the specimen, which helps controlling thermal drift; and finally, because the entire system is placed inside a chamber that can be purged with Ar down to oxygen contents $<0.1\%$, thus minimizing oxidation of the sample surface, tip degradation as well as contamination effects. Fig. 3.13 shows the schematic of the hot stage and heated tip set-up for the NanoTestTM system.

Figure 3.11: Configuration of the NanoTestTM nano-mechanical system: (1) Z stage controller, (2) X stage controller, (3) Y stage controller, (4) X-Z plane optical microscope, (5) Y-Z plane optical microscope, (6) Pendulum.

Maintaining thermal equilibrium between the tip and the sample during high temperature testing is very important, but challenging due to the difficulties in the precise temperature measurement of both the indenter tip and the indented sample surface. In the NanoTestTM hot-stage system (Fig. 3.13), there are three separate thermocouples located at the hot-stage, the indenter and the surface of a reference sample, respectively. The first thermal-couple in the sample stage measures the temperature that is close to the bottom of the sample. Since there are always thermal gradients in the thickness direction of the tested sample, the temperature at the sample surface is different from that at the bottom. Therefore, the thickness of the tested sample should be as thin as possible to minimize the temperature difference between the bottom and the top surfaces. The second thermal-couple is at the indenter. It measures the temperature of the indenter heater that is also several mm far away from the indenter tip. Finally, the third thermal-couple is on the reference sample that has the same thickness than the tested sample. It measures the temperature of the reference sample surface, which is expected to be the closest to that of the tested sample, and so the thermocouple should be located as close as possible to the tested region to minimize any discrepancy. Based on the

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Figure 3.12: Schematic representation of the loading and displacement sensing systems in the Micro Materials NanoTestTM pendulum structure Wheeler & Gunner (2013).

reference sample temperature, the stage and the indenter heater temperatures are then calibrated to minimize thermal drift before each high temperature tests. The procedure is as follows: the stage temperature is firstly adjusted by a proportional-integral-derivative (PID) controller to impose the temperature of the reference sample surface to the target temperature. After that, the indenter temperature is adjusted also by PID controller to minimize the thermal drift between the indenter and the tested sample by performing tests at each temperature and measuring the pre- and post- thermal drifts. Once the equilibrium indenter temperature is determined, the power of the PID controller is finally fixed to minimize temperature fluctuations of the indenter during the tests.

In this work, most of the elevated temperature nanoindentation and micropillar compression tests were conducted within the NanoTestTM system.

Figure 3.13: Schematic of the hot stage and heated tip set-up for the Micro Materials NanoTestTM system Wheeler et al. (2015a).

In-situ systems

Two *in-situ* nano-mechanical testing systems have been employed in this work. One is a Hysitron PI87HT *in-situ* PicoIndenterTM that operates inside the SEM and that it was used in this case to study the response of Al/SiC nanolaminates under tension. The other is a Hysitron PI95 PicoIndenterTM that operates inside a TEM and that was used to study the deformation mechanisms of Al/SiC in response to compressive loading.

Fig. 3.14 shows the configuration of the PI87HT PicoIndenterTM module. The sample stage contains 5-degrees of freedom, allowing for accurate positioning in the XYZ- direction and proper alignment of the sample through the tilt & rotation movements. Thanks to the positioning stage, as shown in Fig. 3.15, the specimen inside the SEM/FIB system can be positioned also for ion beam assisted preparation/modification as well as for advanced imaging, EDS and EBSD analysis. The system is equipped with either a low load or a high load transducer. The low-load transducer has a maximum force of 30 mN with a force resolution <1 nN and displacement resolution <0.02 nm, while the high-load transducer can

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reach a maximum force of 150 mN, with force resolution $<1 \mu\text{N}$ and displacement resolution $<0.1 \text{ nm}$. The system is also able to perform high temperature tests within the ultra-high vacuum of the microscope chamber, up to a temperature of 800°C , with independent sample and indenter tip heating to control thermal drift. Contrary to the stand-alone systems, on top of the direct observation of the deformation evolution, the PI87HT PicoindenterTM allows performing microtensile tests, because the SEM aids on the alignment process of the dog-bone shaped specimen with the special tensile hook-like grip, as shown in Fig. 3.21 . More details on the experimental procedure are supplied in chapter 7.

Figure 3.14: Schematic of the *in-situ* PI87HT PicoIndenterTM Hintsala et al. (2017).

Fig. 3.16 shows the configuration of the other *in-situ* testing module used in this work, a Hysitron PI95 PicoIndenterTM for *in-situ* testing in the TEM. The PI95 utilizes three levels of control for tip positioning and mechanical testing. In addition to a three-axis coarse positioner and a 3D piezoelectric actuator for fine positioning, the instrument is equipped with a transducer for electrostatic actuation and capacitive displacement sensing. With these newly developed transducers, quantitative force-displacement curves can be acquired *in-situ*. Unlike the stand alone systems that rely on open-loop, piezo-controlled, series-loading mechanisms for indentation, which introduce unavoidable artifacts into the load-displacement curves, the PI 95 transducer provides highly accurate depth-sensing capability.

Figure 3.15: Set-ups of the PI87 PicoIndenterTM module inside the FEI Helios 600i SEM/FIB system.

Furthermore, because of the electrostatic actuation aspect of the transducer, substantially large forces can be realized without suffering a force sensitivity penalty. For a miniature transducer, the maximum force is 1.5 mN, and the maximum displacement is 5 μm . Both resolutions are <200 nN and <1 nm, respectively.

Figure 3.16: The configuration of the PI-95 TEM PicoIndenter employed in this work.

The tested specimen should be thin enough to be electron transparent, so that the dislocation activity can be observed simultaneously during the *in-situ* test. To this end, focused ion beam should be used to fabricate and transfer the thin specimens from the bulks. In this work, the Hysitron PI95 PicoIndenterTM

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was used to study the deformation mechanisms of Al/SiC nanolaminates under compression inside a FEI TecnaiTM F300 microscope. These experiments were carried out in the Center for Integrated Nanotechnologies (CINT) of Los Alamos National Lab with the help of Dr. Nan Li and Dr. Nathan Mara. More details are provided in chapter 5.

3.3.2 Nano-Indentation probes

Generally, nano-mechanical testing involves loading a specimen of a given geometry with a specific hard indenter tip or probe. Up to now, different geometry indenters, made of single crystal diamond, sapphire, tungsten carbide, cubic boron nitride, etc. have been developed to meet the requirements for different nano-mechanical tests. For example, sharp three-sided pyramidal indenters (Berkovich, cube cornered,) and four-sided pyramidal indenters (Vickers) have been widely used for instrumented nanoindentation tests in bulk specimens Oliver & Pharr (1992). Spherical indenters are also widely used to study elasto-plastic transitions through nanoindentation tests Pathak & Kalidindi (2015). While flat-ended indenters can be also used for nanoindentation, they are widely employed for the compression tests on small volume micropillars Palomares-García *et al.* (2017), typically machined by FIB, as will be presented in chapter 4. Regarding fracture characterization, among all the possible geometries, sharp nanoindenters (Berkovich, cube-cornered) are advantageous to generate cracks on the sample surface due to the large stress concentrations induced near the indenter's corners. They are widely employed to estimate the fracture toughness of bulk materials and coatings Fan *et al.* (2016a). Recent progress in fracture toughness measurements at the micrometer scale involves the micropillar splitting method in which a sharp indenter is used to crack a micropillar Sebastiani *et al.* (2015a), as will be described in more detail in the context of Al/SiC nanolaminates in chapter 7. Fig. 3.17 shows the geometries of range of typical nano-indentation probes.

The exact geometry of the nano-indenter used is an important information for each nano-mechanical test. For instance, in the case of instrumented nanoinden-

3.3 Nanomechanical testing techniques

Figure 3.17: Geometries of various types of nano-indentation probes, including the Berkovich, cube-cornered, Vickers, spherical and flat-ended indenters.

tation, the Young's modulus and hardness of the tested sample are derived from the projected contact area that can only be calculated from the precise knowledge of the area function of the indentation probe. Therefore, in order to guarantee the reliability of nanoindentation measurements, the area function of each indenter should be regularly calibrated. Table 3.4 lists the area functions of typical nano-indentation probes. Note that the projected areas of the sharp indenters, like Berkovich, cube-cornered and Vickers, are equivalent to the projected area of conical indenters of a specific centerline-to-face angle (semi-angle, φ). For example, a Berkovich indenter, with $\varphi = 65.3^\circ$, yields a projected area that is equal to a conical indenter with $\varphi = 70.3^\circ$. This feature is important for finite element modeling of the nanoindentation process, because this analogy can be used to reduce considerably the size of the model, because conical nanoindentation can be modeled using a 2 dimensional, axisymmetric approach. This approximation will be employed in chapter 4 to implement an inverse methodology that allows to extract the strength of the Al layers based on the nanoindentation response of the Al/SiC nanolaminates.

Most nanoindentation probes are made of diamond, because diamond is the hardest material in earth, with a Young's modulus of ≈ 1.1 GPa. However, since diamond oxidizes at $\approx 400^\circ\text{C}$, diamond indenters might be problematic for high temperature tests. For this reason, the last years have seen the development of indentation probes made of other hard materials with the intention of extending

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Table 3.4: Geometric factors for commonly used indenter profiles. r represents the radius of the flat-ended indenter.

Indenter	Projected Area	Semi-angle, φ	Equivalent cone angle
Berkovich	$24.562h_c^2$	65.3°	70.32°
Cube-corner	$2.598h_c^2$	35.26°	42.28°
Vickers	$24.504h_c^2$	68°	70.3°
Sphere	$\pi(2Rh_c - h_c^2)$	-	-
Flat-end	πr^2	0°	-
Conical	$\pi(h_c \tan^2(\varphi))$	φ	φ

nanindentation to even higher temperatures. Table 3.5 lists the thermo-elastic properties of some of these indenter materials. One of the most important limitations when performing high temperature nanindentation is the reactivity of the indenter material with the tested sample. For instance, diamond indenters have been found to dissolve in carbide forming metals like Ti at indentation temperatures above 300°C Wheeler & Michler (2013), Wheeler *et al.* (2015a). Nowadays, the highest reported nanindentation temperature is $<900^\circ\text{C}$, due to the limitations found on the selection of proper indenter material. In any case, the elevated temperature nanindentation and micropillar compression experiments carried out in this work, and presented in chapters 4 and 5, were carried out at a maximum temperature of 150°C , and therefore did not suffer from this type of problems when using diamond indenters.

Table 3.5: Elastic properties of the commonly used nano-indenters fabricated with different hard materials Wheeler & Michler (2013).

Indenter Materials	Young's Modulus E (GPa)	Poisson's Ratio ν
Diamond	1139.2	0.07
c-BN	681.6	0.15
B ₄ C	461	0.21
SiC	515.7	0.17
WC	706.7	0.194
WC(-6%)Co	541.7	0.2
Al ₂ O ₃	463.7	0.24

3.3.3 Nano-mechanical testing methods

Nanoindentation

Nanoindentation is the most widely used nano-mechanical testing method because it is easy to implement and it can be applied to any type of materials. Properties like the Young's modulus, and hardness can be easily obtained from the load-displacement curve, and several methods have been also proposed to obtain other properties like strain rate sensitivity Lu *et al.* (2005), the stress-strain response Pathak & Kalidindi (2015) or fracture toughness Sebastiani *et al.* (2015a). The typical nanoindentation test involves indenting a mirror-like polished material with a hard nanoindentation probe (Fig. 3.10). The process is similar to conventional micro-hardness testing, but it does not require the direct measurement of the indentation imprint, because the contact area is directly estimated from the load-displacement curve using different methods, as that proposed by Oliver & Pharr (1992). The Oliver-Pharr method assumes that during indentation, the material undergoes elastoplastic deformation during loading and purely elastic recovery during unloading, as shown in Fig. 3.18, and relies on the determination of the initial unloading stiffness, S , that depends on the reduced modulus, E_r , and the contact area, A_c , through:

$$E_r = \frac{S\sqrt{\pi}}{2\beta\sqrt{A_c}} \quad (3.1)$$

where β is a dimensionless parameter that depends on the indenter geometry ($\beta=1.034$, for a Berkovich indenter) and E_r is given by:

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (3.2)$$

where E and ν stand for the elastic modulus and Poisson's ratio of the tested material, and E_i and ν_i , for the elastic modulus and Poisson's ratio of the indenter.

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Figure 3.18: Typical force-displacement curve from a nanoindentation test in an Al/SiC nanolaminate. The insert is an illustration of the surface profile on the loaded and unloaded conditions Oliver & Pharr (1992).

Oliver and Pharr relies on the following expression to obtain the contact depth h_c at maximum load P_{max} :

$$h_c = h_{max} - \epsilon \frac{P_{max}}{S} \quad (3.3)$$

where h_{max} is the maximum depth and ϵ is a geometrical constant that adopts a value of 1 for a flat punch, 0.75 for a paraboloid indenter, and 0.72 for a conical indenter. The value of ϵ that best describes the unloading behavior of a Berkovich indenter is 0.75.

The contact area, A_c , can then be easily estimated from the calibrated area function $f(h_c)$, from which the hardness H will be given by:

$$H = \frac{P_{max}}{A_c} \quad (3.4)$$

Since S , P_{max} and h_{max} are directly determined from the force-displacement curve of Fig. 3.18, the elastic modulus E and the hardness H can be easily obtained using

the Oliver-Pharr method through equations 3.1 to 3.4. This methodology has been implemented in chapter 4 to obtain the nanolaminate hardness and elastic modulus as a function of layer thickness in the temperature range between 25°C and 100°C.

Micropillar compression

One of the main disadvantages of instrumented nanoindentation tests is that the material is subjected to a complex multiaxial stress-state, and it is not straightforward to relate hardness with uniaxial strength, specially for anisotropic materials. Micropillar compression tests were developed to overcome this limitation. This method relies on the fabrication of micropillars, typically using FIB milling as described in section 3.2.3, and it is implemented by compressing the pillars with a flat-ended hard punch, so that the uniaxial compressive stress-strain response can be obtained in a small volume. Moreover, the deformation and fracture modes can be easily characterized from the deformation morphology of the micropillars after testing.

Accordingly, micropillar compression tests constitute a powerful tool to study the stress-strain behavior and the deformation and fracture mechanisms of the Al/SiC nanolaminates, as a function of loading direction. The technique has been used extensively in this work and is briefly described below.

The micropillar milling procedure is schematically illustrated in Fig. 3.19. The first step involved milling a relatively wide micropillar, $\approx 4 \mu\text{m}$ in diameter and $\approx 1 \mu\text{m}$ in height, using a concentric annular milling pattern at a relatively large ion current (9.3 nA) (Fig. 3.19a). The outside diameter of the trench must be selected to be larger than that of the compression punch, to prevent contact with the surrounding material during the test. After that, reduced ion currents, from 0.73 nA to 0.23 nA were employed to further refine the micropillar diameter and increase its height to the desired sizes, such as $2 \mu\text{m}$ in diameter and $4 \mu\text{m}$ in height, in the case of the example (Fig. 3.19b,c). A final polishing step was carried out with a very small ion current (40 pA) to remove the taper of the micropillar (Fig. 3.19d). The diameter and the height of the final micropillar were carefully

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measured in order to determine the stress and strain curves after the micropillar compression tests.

Figure 3.19: Milling process to fabricate a $2\mu\text{m} \times 4\mu\text{m}$ micropillar on Al50SiC50 nanolaminate.

The as-fabricated micropillars were then compressed using a flat punch. A schematic illustration of the micropillar compression test is shown in Fig. 3.20 for the case where the loading direction was perpendicular to the layers, although tests were also carried out for loading parallel and at 45° with respect to the layers. Several experimental artifacts may influence the outcome of the micropillar compression tests. The first is the FIB induced damage that might lead to Ga^+ implantation, the introduction of point and line defects, the precipitation of Ga^+ containing phases and/or the generation of a thin amorphous layer at the micropillar surface. However, the TEM studies of the micropillar edges did not revealed any of these effects, except for some Ga^+ implanatation, that in any case, is expected to have a negligible effect in the case of the Al/SiC nanolaminates, because the length scale that controls the mechanical strength, the layer thickness, is orders of magnitude smaller than the pillar diameter. The second is the misalignment

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between the surface of the flat punch and the top surface of the micropillar, which could lead to initial contact problems and changes in the slope of the initial loading segment in the stress-strain curves. These alignment problems are inherent to the micropillar compression tests, but they were minimized by using a double-tilt stage to correct the sample alignment prior to the compression test. The third one is the tapered geometry of the micropillar. A large taper could induce a non-uniform stress field with larger stresses at the upper part of the micropillar. In this work, all Al/SiC micropillars were subjected to a final polishing step, using small ion currents of 24 pA or 40 pA, and the final taper angle was below $<2^\circ$. The last artifact is related to the elastic deformation of the surface at the base of the micropillar, which might introduce an extra compliance on the measured displacement. This contribution was accounted for by applying the Sneddon's correction Sneddon (1965) to the measured displacement, which considers that the compliance $C_{sneddon}$ associated with the elastic deflection of the surface at the base of the pillar follows:

$$C_{Sneddon} = \frac{\sqrt{\pi}(1 - \nu^2)}{2E_{base}\sqrt{A_p}} \quad (3.5)$$

where E_{base} is the modulus of the base material, A_p is the cross-sectional area at the base of the pillar, and ν is the Poisson's ratio of base material. Once $C_{sneddon}$ is obtained, the contraction of the micropillar, u_{pillar} , was estimated from the measured total displacement, u_{total} , according to:

$$u_{pillar} = u_{total} - C_{Sneddon}P \quad (3.6)$$

where P is the measured load.

The engineering compressive stress σ_{eng} and strain ϵ_{eng} , were determined from the initial length L_0 and the initial top cross-sectional area A_0 of the pillar following:

$$\epsilon_{engineer} = \frac{u_{pillar}}{L_0} \quad (3.7)$$

$$\sigma_{engineer} = \frac{P}{A_0} \quad (3.8)$$

3.3 Nanomechanical testing techniques

Figure 3.20: Schematic illustration of micropillar compression test on a nanolaminate for layers oriented at 90° with respect to the loading direction.

This methodology was employed to study the initial stages of deformation for pillars with layers oriented at 90° with respect to the loading direction, as a function of layer thickness and temperature (chapter 5) and to analyze the deformation and fracture modes, as function of layer thickness and loading direction (chapter 6).

Finally, one should keep in mind that pillar size effects may influence the obtained stress-strain response during micropillar compression tests. It is now widely accepted that single crystal micropillars are prone to strong size effects and that their yield/flow strengths can increase significantly by decreasing the micropillar size Greer & De Hosson (2011). Pillar size effects have been traditionally rationalized by using a power-law equation for the yield stress, $\sigma_y \propto A\phi^{-a}$, where A is a constant, ϕ is the micropillar diameter and a is the power law exponent ($a = 0.5-0.97$ for FCC, $0.42-0.68$ for HCP and $0.22-0.48$ for BCC crystals Greer & De Hosson (2011), Fertig & Baker (2009)). Possible mechanisms controlling the size effect in single phase metals involve dislocation starvation Greer *et al.* (2008), the limited availability of dislocation sources Volkert & Lilleodden (2006) and FIB damage El-Awady *et al.* (2009), Bei *et al.* (2007), none of which is likely to control the nanolaminate micropillar behavior, because the characteristic length scale that

controls the mechanical properties of the nanolaminate (the layer thickness or the grain size) is much smaller than the micropillar diameter Lotfian *et al.* (2012), Singh *et al.* (2010b). However, some discrepancies exist when the micropillars are very small Zhang *et al.* (2014a), Zhang *et al.* (2012b) and pillars of different diameter were also studied, with diameters ranging between 1 and 2 μm , to explore size effects. These results are presented in chapter 6.

Microtensile testing

Both the nanoindentation and micropillar compression tests mentioned above are carried out in compression. The failure modes in uniaxial compression are mainly shearing and barreling, which are quite different from necking in uniaxial tension. However, no previous knowledge on the tensile behavior of metal-ceramic nanolaminates can be found in the literature due to experimental difficulties. Uniaxial tensile testing of micrometer scale specimens is difficult to implement, because of some major challenges: (1) the fabrication of a freestanding and stress-free specimen, (2) the development of a strategy to grip the specimen, (3) the alignment of the specimen in the loading direction (even a slight misalignment may result in significant unaccounted flexural stresses on the specimen, invalidating the test by premature failure of the specimen), and (4) the application of small forces (on the order of μN) Haque & Saif (2002). These difficulties have been overcome in this work by using focused ion beam milling to prepare a dog-bone shape microtensile specimen attached to the edge of a bulk specimen and to fabricate a micro-gripper out of a diamond indenter, as shown schematically in Fig. 3.21. The tests were carried out *in-situ* inside the SEM to ensure proper alignment of the specimen. Using this novel methodology, the tensile deformation and fracture of the sample can be monitored *in-situ*, while the stress-strain response is obtained simultaneously, which is useful to study the progressive deformation and crack propagation. This is the first time the fracture mechanisms of Al/SiC nanolaminates are studied in tension. The details of the method and the results are presented in chapter 7.

Figure 3.21: SEM micrograph showing the experimental set-up to carry out microtensile tests inside a SEM in the Al/SiC nanolaminate with the hook-like grip.

CHAPTER 4

Effect of Layer Thickness and Temperature on the Deformation Mechanisms

4.1 Introduction

As reviewed in chapter 2, the deformation of metal-ceramic nanolaminates is mainly controlled by the plastic deformation of the metallic layers. In the particular case of Al/SiC nanolaminates, it is expected that the hardness will be dependent on the layer thickness and temperature, as both factors will modify the strength of the soft Al layers. Nevertheless, quantitative information about the mechanical properties of metallic layers in metal/ceramic nanolaminates is very limited Fertig & Baker (2009) and the influence of temperature on the strength of these materials has not been explored and this is the main objective of this chapter. This information can be very useful to understand the dominant deformation mechanisms as a function of layer thickness as well as to explore the role played by grain boundary/interface diffusion during high temperature deformation.

4.2 Experimental procedure

Al/SiC nanolaminates are ideally suited for this investigation because previous work Lotfian *et al.* (2013), Lotfian *et al.* (2012), Singh *et al.* (2010b), Deng *et al.* (2005) has shown that the (amorphous) SiC nanolayers undergo elastic deformation and their mechanical properties are independent of temperature up to 300°C Lotfian *et al.* (2014), Mayer *et al.* (2015). Moreover, the yield stress of the SiC layers seems to be independent of layer thickness, at least for layers as thin as 25 nm Lotfian *et al.* (2014), in agreement with what has been observed for other amorphous ultra-thin layers like PdSi Knorr *et al.* (2013). Thus, changes in the strength of the Al/SiC nanolaminate as a function of the layer thickness and/or temperature have to be attributed to the Al layers. In order to obtain quantitative information on the mechanical properties of the Al layers, an inverse methodology, based on the finite element analysis of the nanoindentation of Al/SiC multilayers, has been developed. Using this inverse methodology, the yield stress of the Al nanolayers, with thicknesses in the range 10 to 100 nm, was obtained from 25°C to 100°C, from nanoindentation tests carried out in Series I nanolaminates, in which the SiC layer thickness was kept constant and equal to 50 nm. These values of the yield stress were then validated by comparing the numerical predictions of the nanoindentation hardness with the experimental results obtained in the other set of nanolaminates (series II), in which the thickness of Al and SiC layer was the same (between 10 and 100 nm). Finally, the quantitative values of the yield stress of the Al nanolayers as a function of temperature and layer thickness were used to ascertain the dominant deformation mechanisms in light of the current theories for plastic deformation of ultra-thin metallic films.

4.2 Experimental procedure

Nanoindentation tests were carried out using the NanoTestTM platform with a Berkovich diamond tip. Nanoindentation tests were performed at 25, 50 and 100°C. Samples were bonded to the heater plate using a high temperature adhesive and both the sample and indenter were independently heated to the target temperature, as explained in section 3.3.1. The temperature of the components

was carefully calibrated before the nanoindentation test at each temperature to minimize thermal drift that was measured during 5 minutes. Thermal drift before and after the thermal calibration at 100°C is shown in Fig. 4.1. The measured thermal drift was lower than 0.01 nm/s in all cases.

Figure 4.1: *Drift measurements of an Al/SiC nanolaminate before and after the thermal calibrations at 100°C*

The tests were carried out with a loading rate of 10 mN/s to a maximum load of 100 mN. The maximum load was held constant for a dwell period of 5 s prior to unloading at 20 mN/s. The total penetration depth was carefully controlled within 1 μm , less than 10% of the total nanolaminate thickness, to eliminate substrate effects. This penetration depth was also deep enough, as compared to the individual layer thickness, to obtain the effective nanolaminate response. At least 8 indentations were performed at each temperature in each nanolaminate. The load-penetration curves after nanoindentation were analyzed using the Oliver-Pharr method, Oliver & Pharr (1992) (section 3.3.3). Selected indents were

4.3 Experimental results and discussion

cross-sectioned with a FEI Helios Nanolab 600i dual-beam system to analyze the deformation patterns in the TEM.

4.3 Experimental results and discussion

4.3.1 Ambient and elevated temperature hardness

The hardness of Al/SiC is known to vary with the volume fraction of the constituents and the strength of each individual layer Lotfian *et al.* (2014). The hardness of the nanolaminates is plotted in Fig. 4.2 (a,b) as a function of Al volume fraction, V_{Al} , and of Al layer thickness, h_{Al} , respectively, in the temperature range 25-100°C. The hardness of the series I nanolaminates (constant SiC layer thickness) increased nonlinearly as the Al volume fraction decreased, Fig. 4.2 (a). In contrast, previous work on nanolaminates with constant Al thickness and varying SiC thickness Lotfian *et al.* (2014) showed a linear increase of hardness as Al volume fraction decreased. This difference implies that the strength of the Al layers depends on the layer thickness, because of their nanocrystalline microstructure, while the strength of the amorphous SiC layers is size independent Monclús *et al.* (2014b). The nanoindentation tests of the series II nanolaminates confirmed this hypothesis: the hardness increased as the layer thickness decreased at a constant Al volume fraction of 50%, reaching a peak for a layer thickness of 25 nm (Fig. 4.2b). This behavior is similar to that reported in other metal-ceramic nanolaminates like Ti/TiN, Hf/HfN or W/WN Shih & Dove (1992). It is worth noting that the Al100SiC100 and Al50SiC50 nanolaminates showed similar hardness, and this may be due to the fact that the critical dimension controlling the strength was the lateral grain size, which was also similar in both nanolaminates and smaller than the layer thickness, as was found in section 3.2.4 and summarized in Table 3.2. Interestingly, the trend was not maintained for the Al10SiC10 nanolaminate, suggesting that other deformation mechanisms and/or microstructural changes may be triggered when both layers are reduced to this extremely small scale. The reasons for this behavior will be discussed below in more detail.

4.3 Experimental results and discussion

Figure 4.2: (a) Hardness of series I nanolaminates as a function of Al volume fraction, V_{Al} , and temperature. (b) Hardness of series II nanolaminates as a function of Al layer thickness, h_{Al} , and temperature.

The nanolaminate hardness experienced a significant reduction with temperature, as shown in Fig. 4.2, which was more marked for the thinner nanolaminates. According to micropillar compression tests in Al50SiC50 Lotfian *et al.* (2013), the reduction in strength with temperature could be attributed to a reduction in the Al yield stress and to the development of interface sliding at the Al-SiC interface. The contribution of Al-SiC interface sliding to the high temperature deformation of micropillars Lotfian *et al.* (2013) was evidenced by extrusion of Al grains out of the free edges of the micropillar. However, the lack of free surfaces and the constraint imposed by the surrounding undeformed material renders unlikely that interface sliding might contribute to a large extent to the deformation in the case of nanoindentation. In addition, it is also unlikely that the mechanical properties of the SiC layers experience any softening at 100°C. Thus, it was assumed that the hardness drop with temperature of the Al/SiC nanolaminates was a direct consequence of the reduction in the yield stress of the Al layers. It should be noted that 100°C represents a homologous temperature of 0.4 for Al, high enough to activate dislocation climb and/or interface and grain boundary diffusion. These mechanisms can lead to a marked softening of the nanocrystalline Al layers, be-

4.3 Experimental results and discussion

yond to what it would be expected only by the reduction of shear modulus with temperature.

Electron-transparent lamellae across indents were prepared by focused ion beam milling after nanoindentation at different temperatures and examined by TEM. Representative TEM images of the indents carried out at room temperature for nanolaminate layer thicknesses of 100, 25 and 10 nm are shown in Fig. 4.3 (a) to (c). The layered structure was preserved in all cases, with no evidence of interface fracture or interface sliding. It is clear that the deformation of the Al layers was severely constrained by the hard SiC layers Sun *et al.* (2010), especially under the indentation imprints where the imposed strains are more severe, as evidenced by the large reduction in Al layer thickness. The reduction of the Al layer thickness was accompanied by a change in grain shape, which grew parallel to the layers, as shown by the white arrows. This indicates that plastic deformation processes took place not only at interfaces or grain boundaries, but also within the grains. However, not a single dislocation could be observed in the deformed layers, suggesting that the deformation is either not due to dislocation motion or that the small grain size precludes any storage of dislocations, that annihilate either at grain boundaries and/or interfaces after slipping across the grain. Thus, it should be emphasized that the dislocation density within the deformed layers remains extremely low and the large apparent strain hardening usually found in Al/SiC multilayers cannot be due to dislocation storage within the metallic layers but to the constraint imposed by the stiff ceramic layers on the plastic deformation of the metallic layers Lotfian *et al.* (2012). This statement might not hold true for other metal-ceramic nanolaminates, like Al-TiN Li *et al.* (2014), where high strain hardening rates have been associated with plastic co-deformability of the two layers when the ceramic layers become extremely thin. No evidence of such effects have been found, however, in the case of Al/SiC nanolaminates.

As opposed to the Al layers, the SiC layers did not undergo large thickness reductions but they deformed permanently to accommodate the indenter shape. Despite the brittle nature of SiC, some plastic deformation cannot be ruled out due to the large hydrostatic stresses imposed below the indenter. Some cracking of the

Figure 4.3: BF-TEM images of Series II nanolaminates after room temperature nanoindentation: (a) Al100SiC100, (b) Al25SiC25, (c,d) Al10SiC10.

SiC layers is evident, especially for the thicker layers in Al100SiC100, as pointed by the black arrows in Fig. 4.3 (a). Cracks are perpendicular to the layers as a result of the bending stresses and provide paths where the Al can plastically flow during deformation. The extent of cracking of the SiC layers was reduced for the thinner SiC layers (Al25SiC25 and Al10SiC10), as a result of their larger bending compliance and to their enhanced ductility (Fig. 4.3 b-d) Deng *et al.* (2005). In any case, cracking of the SiC layers was not the major mechanism accommodating the imprint imposed by the indenter. Thus, the mechanism was not considered in the inverse methodology to determine the yield strength of the Al layers.

4.4 Inverse methodology

The experimental results presented above indicate that the hardness of Al/SiC nanolaminates is mainly controlled by the composite response of the constituents.

4.4 Inverse methodology

It is reasonable to assume that the strength of the amorphous SiC layers was independent of the layer thickness and temperature, at least up to 100°C. Therefore, the experimental variation of the nanolaminate hardness with layer thickness and temperature has to be attributed to changes in the Al yield strength and/or to the Al/SiC interfaces. Under these hypotheses, it is possible to obtain the yield stress of the Al layers from the nanolaminate response using an inverse methodology based on the numerical simulation of the nanoindentation experiments with the finite element method. This phenomenological model attributes all hardness changes to changes in the flow stress of the Al layers with layer thickness and temperature, without making any assumptions on the operating deformation mechanisms. In order to validate the approach of the inverse methodology, the mechanical response provided by the numerical model (in terms of hardness) was first fitted with the experimental results for series I nanolaminates at 25, 50 and 100°C. And the accuracy of the quantitative data determined for the Al yield stress was then assessed by comparing the predictions of the numerical model with the experimental results of series II nanolaminates at different temperatures.

4.4.1 Finite element model

The numerical simulations of the nanoindentation experiments were performed using the finite element method with the commercial software Abaqus 6.13. The axisymmetric 2D model is depicted in Fig. 4.4 (a). It includes the Al/SiC nanolaminate with 10 μm in thickness (similar to the real nanolaminate thickness and with the top layer of SiC), the Si substrate and the rigid conical indenter. The lateral dimensions of the model were large enough to avoid any boundary effects. The indenter semi-angle was 70.3°, resulting in the same projected area as that of a Berkovich indenter Fischer-Cripps (2009). The actual average layer thickness measured by TEM (Table 3.2) was used in each case, leading to 7 different models to represent the nanolaminates in series I and II (Fig. 4.4b). The waviness of the layers was not explicitly included in the models because it does not influence

the hardness when the indentation is perpendicular to the layers Jamison & Shen (2014).

Figure 4.4: (a) Schematic of finite element models to simulate nanoindentation of the Al/SiC nanolaminates. (a) Series I nanolaminates (Al100SiC50, Al50SiC50, Al25SiC50, Al10SiC50). (b) Series II nanolaminates (Al100SiC100, Al25SiC25, Al10SiC10).

The model was discretized using two-dimensional four-node linear axisymmetric elements with reduced integration (CAX4R) and the mesh was refined around the upper-left corner. It was checked that the mesh used in the simulations was fine enough to provide results independent of the element size. The boundary conditions were consistent with the axial symmetry of the model: the horizontal displacement of the left boundary was impeded while the bottom boundary was fully constrained in both the horizontal and vertical directions. The remaining

4.4 Inverse methodology

surfaces were unconstrained. The indenter was represented by a rigid surface. The friction coefficient between the nanolaminate and the indenter was 0.1.

The Al and SiC were modeled as isotropic, elastoplastic solids, with no strain hardening, following the J2 theory of plasticity. This assumption was a compromise to limit the number of parameters to determine from the inverse analysis, but has been proven to yield reasonable results in previous micropillar compression studies in the same material Lotfian *et al.* (2013). Si was modeled as an isotropic, elastic solid. The elastic modulus and Poisson's ratio of all three materials were obtained from literature Lotfian *et al.* (2012) and are listed in Table 4.1. Even though SiC is a brittle material, it undergoes plastic deformation under the indent due to the high compressive hydrostatic stresses. The yield stress of SiC was 7 GPa, as estimated from the nanoindentation response of 1 μm thick monolithic SiC films. It was assumed constant and independent of SiC layer thickness and temperature. The Al yield stress was varied in the range 0.2 to 1.6 GPa because this was the range expected for the yield stress of the Al nanolayers in the temperature range under study.

Table 4.1: Elastic constants of Al, SiC and Si.

Materials	Young's Modulus, (GPa)	Poisson's Ratio
Al	70	0.34
SiC	300	0.14
Si	187	0.28

The maximum penetration of the indenter was set to 1 μm in all cases and the hardness was obtained from the simulated load-penetration curves from the Oliver-Pharr method Oliver & Pharr (1992), following the same procedure as in the experimental work. Simulations were carried out using Abaqus/Standard within the framework of the finite deformations theory with the initial unstressed state as reference.

4.4.2 Numerical results and determination of the Al yield stress

Representative load-penetration curves obtained from the numerical simulations of the Al50SiC50 nanolaminate are plotted in Fig. 4.5 for different values of the Al yield stress. They show that the nanolaminate deformation was very sensitive to the Al flow stress although the deformation mechanisms did not change. The contour plots of the accumulated plastic strain, $\bar{\epsilon}_p$, in the Al50SiC50 nanolaminate at the maximum indentation depth of 1 μm are shown in Fig. 4.6 (a, b) for Al yield stresses of 0.4 and 1.4 GPa, respectively. The plastic zone was confined below the contact area in both cases and it was localized in the Al layers. Plastic deformation of the SiC layers only occurred in a very small region encompassing two or three SiC layers under the indenter. Pile-up formation around the indenter was not observed, and this confirmed the validity of the Oliver and Pharr method to compute the hardness.

Figure 4.5: Load-penetration curves obtained from the numerical simulation of the Al50SiC50 nanolaminate as a function of Al yield stress.

Figure 4.6: Contour plot of the accumulated plastic strain, $\bar{\epsilon}_p$, in the Al50SiC50 nanolaminate at the maximum indentation depth of 1 μm : (a) Al yield stress of 0.4 GPa, (b) Al yield stress of 1.4 GPa

The hardness of the series I nanolaminates as a function of Al yield stress obtained from the numerical simulations is plotted in Fig. 4.7 (a). The hardness scaled linearly with the Al yield stress and the slope was independent of the Al volume fraction in the nanolaminate and around ≈ 2.7 , which is remarkably close to the Tabor factor between hardness and yield stress in metals Fischer-Cripps (2009).

The master curves in Fig. 4.7 (a) of the influence of the Al yield stress on the nanolaminate hardness in series I (nanolaminates with a constant SiC layer thickness) were the foundation of the inverse methodology to obtain the yield stress of Al as a function of the layer thickness and temperature from the experimental values of the hardness. These master curves are re-plotted in Fig. 4.7 (b) as solid lines. The solid symbols in Fig. 4.7 (b) stand for the experimental hardness at different temperatures, which are plotted on top of the master curves obtained from the numerical simulations. The corresponding abscissa in Fig. 4.7 (b) provides the quantitative value of the Al yield stress to attain the experimental hardness according to the numerical simulations. The estimations of the Al yield stress as a function of actual Al layer thickness (measured in the TEM images) and

Figure 4.7: (a) Master curves of the influence of Al yield stress on hardness of series I nanolaminates obtained from numerical simulations. (b) Determination of Al yield stress as a function of layer thickness and temperature from the master curves and the experimental values of the hardness of series I nanolaminates. See text for details.

temperature are depicted in Table 4.2. At room temperature, the yield stress of the Al layers was much higher for thinner layers, in agreement with “the thinner, the stronger” effect. This size effect on the yield stress disappears, however, at 100°C because the reduction in the yield stress with temperature was much more dramatic for the thinner Al layers.

Table 4.2: Al yield stress as a function of Al layer thickness and temperature.

h_{Al} (nm)	Yield stress (25°C) (MPa)	Yield stress (25°C) (MPa)	Yield stress (25°C) (MPa)
10	1477±39	1280±133	569±39
21	1243±206	877±79	100±38
52	877±64	714±64	190±79
90	891±140	803±140	415±98

4.5 Al deformation mechanisms as a function of layer thickness and temperature

4.4.3 Validation of the yield stress obtained by the inverse methodology

The estimations of the Al yield stress in Table 4.2 were validated against the experimental results of the hardness of the series II nanolaminates, in which the Al and SiC layer thicknesses were equal. To this end, the hardness was computed for the series II nanolaminates using the values of the Al yield stress determined from series I (Table 4.2). The experimental results and the numerical predictions are plotted in Fig. 4.8, and they show an excellent agreement when the nominal layer thickness was ≥ 25 nm at 25, 50 and 100°C, supporting the validity of the inverse methodology and the hypothesis made in this thickness range. Nevertheless, the numerical predictions overestimated the experimental hardness in the case of the thinnest nanolaminates (Al10SiC10) in the whole temperature range. The origin of this discrepancy is not obvious and several hypotheses can be advanced to explain this behavior. For instance, the layered structure of the Al10SiC10 could break down in some areas due to the small layer dimensions and the layer waviness, as discussed in section 3.2.4 in the light of Fig. 3.8 (c) and (d). It is also possible that the thickness of the SiC layers is not enough to constrain the deformation of the Al layers and/or that the assumption of a perfectly bonded interface does not hold anymore with such a large interface density.

4.5 Al deformation mechanisms as a function of layer thickness and temperature

4.5.1 Layer thickness

The values of the yield stress of the Al layers obtained from the inverse methodology are plotted as a function of the Al layer thickness at different temperatures in Fig. 4.9 (a). The results of the inverse methodology for layers with 10 nm in thickness were not included, as they could not be validated against the experimental

4.5 Al deformation mechanisms as a function of layer thickness and temperature

Figure 4.8: Validation of the inverse methodology by comparing the experimental results and the numerical predictions of the hardness for series II nanolaminates at 25, 50 and 100°C.

results of the series II nanolaminates. The experimental values of the yield stress of monolithic Al films of 1000 nm and 200 nm in thickness Deng *et al.* (2005), estimated from the room temperature nanoindentation hardness (assuming a Tabor factor of 2.7), were included in this figure for reference. The first interesting observation in this figure is the inversion of the size effect with temperature. While “the thinner, the stronger” holds at ambient temperature, the mechanical response at 100°C shows the opposite behavior with “the thicker, the stronger” and the size effect is not found at 50°C. The second observation is that the layer thickness was not the only controlling length scale as the 50 and 100 nm thick Al layers displayed identical yield stress, despite the difference in layer thickness. According to the microstructural characterization summarized in Table 3.2, the lateral grain size, d_l , became smaller than h_{Al} when the layer thickness reached 100 nm, and this feature should also play a role, as grain boundaries will also act as obstacles to dislocation glide. To account for this, the yield stress was plotted in Fig. 4.9 (b)

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as a function of the critical dimension, understood as the minimum between the layer thickness, h_{Al} , and the lateral grain size, d_l . This new representation of the data provides a clearer picture of the influence of the critical dimension (either layer thickness, h_{Al} , or lateral grain size, d_l) on the yield stress of the Al layers.

Figure 4.9: Evolution of Al yield stress at 25, 50 and 100°C as a function of (a) Al layer thickness, h_{Al} . (b) Minimum of Al layer thickness, h_{Al} , and lateral grain size, d_l

The room temperature results for the yield stress of Al layers with thickness in the range 25 to 100 nm showed the expected “the thinner, the stronger” size effect. In this size range, the Al yield stress is expected to be controlled either by the pile-up of dislocations at interfaces or grain boundaries Nix (1989), Thompson (1993), by the confined layer slip (CLS) of single dislocations Misra *et al.* (2005), Nix (1998) and/or by the activation of dislocation sources von Blanckenhagen *et al.* (2003). In the first scenario, the yield stress σ_y is expected to follow a Hall-Petch behavior according to:

$$\sigma_{Al} = \sigma_0 + kh^{-0.5} \quad (4.1)$$

Using the values in the literature for pure Al ($\sigma_0 = 10\text{-}20$ MPa and $k = 0.07$ MPa $\sqrt{m}$ Phillips *et al.* (2003)), the predictions of Equation 4.1 with $h=h_{Al}$ underestimated by a large extent the experimental values, Fig. 4.10 (a). If $h = \min\{h_{Al}, d_l\}$, the predictions of Equation 4.1 are closer to the experimental re-

4.5 Al deformation mechanisms as a function of layer thickness and temperature

sults but still underestimate the experimental data, Fig. 4.10 (b). These results are not surprising since it is well established that the mechanics of thin films is substantially different from that of polycrystalline metals.

Figure 4.10: Comparison between experiments and predictions of different model for the yield stress at room temperature when the critical distance controlling plastic deformation is: (a) the layer thickness, h_{Al} . and (b) the minimum between the layer thickness, h_{Al} , and the lateral grain size, d_l .

Nix (1989), for single-crystalline thin-films, and later Thompson (1993), for polycrystalline films, proposed different expressions accounting for the hardening due to the deposition of dislocation segments at the interfaces and grain boundaries in passivated thin-films. They can be combined in the following simplified equation:

$$\sigma_{Al} = M \frac{G_{Al} b_{Al}}{8\pi(1 - \nu_{Al})} \left[\frac{1}{h} \ln\left(\frac{h}{b_{Al}}\right) + \frac{4}{d} \ln\left(\frac{d}{b_{Al}}\right) \right] \quad (4.2)$$

where M is the Taylor factor, G_{Al} and ν_{Al} are the shear modulus and the Poisson's ratio, respectively, b_{Al} the Burgers vector, and d the grain size. The work of Nix (1989) and Thomson Thompson (1993) was the first to propose a $1/d$ dependency of the yield stress with grain size for thin-films, instead of the $1/d^{0.5}$ dependency coming from the classical Hall-Petch theory. If $M=3.1$ for an untextured film, and using the constants of Al ($G_{Al} = 24$ GPa, $\nu_{Al} = 0.3$, and $b_{Al} = 0.286$ nm), the predictions of Equation 4.2 are compared with the experimental results in Fig. 4.10

4.5 Al deformation mechanisms as a function of layer thickness and temperature

(a) assuming $h = d = h_{Al}$ and in Fig. 4.10 (b) assuming $h = h_{Al}$ and $d = d_l$. The variation in the curvature of the curve plotted in Fig. 4.10 (b) is due to changes in the aspect ratio of the grains around 50 nm, as indicated above. The qualitative agreement between the predictions of Equation 4.2 and the experimental data in Fig. 4.10 (b) is remarkable for sub-micrometer thick layers but the yield stress of the layers with thicknesses <100 nm was still underestimated.

Strengthening in ultra-thin films has also been explained by the confined layer slip of single dislocations constraint by the presence of impenetrable interfaces Misra *et al.* (2005), Nix (1998), Phillips *et al.* (2003). In this case, the stress required for dislocation glide inside one of the Al layers can be expressed as:

$$\sigma_{Al} = M \frac{G_{Al} b_{Al}}{8\pi} \left(\frac{4 - \nu_{Al}}{1 - \nu_{Al}} \right) \frac{1}{h} \ln \left(\frac{\alpha_{Al} h}{b_{Al}} \right) - \frac{f}{t} + \frac{G_{Al} b_{Al}}{L(1 - \nu_{Al})} \quad (4.3)$$

where a_{Al} is the dislocation core cut-off parameter, L_{Al} the mean spacing of glide loops in a parallel array within the layer, f the characteristic amorphous/crystalline interface stress and the remaining parameters in Equation 4.3 were well defined above. The predictions of Equation 4.3 using $a_{Al} = 1$, $L_{Al} = 30$ nm and $f = 1$ J/m² (which are sensible values for this nanocrystalline/amorphous multilayer) and the elastic properties of Al are plotted in Fig. 4.10 (a) and (b) and they are in very good agreement with the experimental data. Nevertheless, it should be noted that the predictions of Equation 4.3 do not depend explicitly on grain size. And, in addition, it is unlikely that confined layer slip is the mechanism controlling strength for layer thicknesses of 100 nm and above when the lateral grain size is smaller than the layer thickness.

Finally, the yield stress may be controlled by the activation of dislocation sources within the Al grains if dislocations are scarce von Blanckenhagen *et al.* (2003), Raghavan *et al.* (2015a), Dehm *et al.* (2001). The stress necessary to activate dislocation sources according to von Blanckenhagen *et al.* (2003) is given by

$$\sigma_{Al} = M \frac{G_{Al} b_{Al}}{s_{Al}/4} \quad (4.4)$$

4.5 Al deformation mechanisms as a function of layer thickness and temperature

where s_{Al} is the smallest between the grain size and the layer thickness, and $s_{Al}/4$ is an estimate of the most effective dislocation source length that might be contained within one grain. The predictions of Equation (4.4) are plotted in Fig. 4.10 (a) and (b) assuming $s_{Al} = h_{Al}$ and $s_{Al} = \min\{h_{Al}, d_l\}$, respectively. Both predictions overestimate the experimental values of the yield stress to a large extent, indicating that the plastic deformation of the nanolayered films is not controlled by the nucleation of new dislocations, and that the presence of pre-existing dislocations leads to yielding at lower stresses. Nucleation of partial dislocations at grain boundaries has also been suggested for Cu thin-films Gruber *et al.* (2008), but it is unlikely in the present case because of the high stacking fault energy of Al.

Summing up, these results indicate that the strength of sub-micrometer Al thin-films is controlled by grain boundary strengthening. A transition occurs, however, at 100 nm and plastic deformation becomes controlled by confined layer slip for thinner layers. This change is linked to the aspect ratio of the Al grains, which become wider than the layer thickness at this point. Note that previous works on other metal/ceramic nanolaminate systems, such as Al/Al₂O₃ Alpas *et al.* (1990), Al/TiN Bhattacharyya *et al.* (2008), Ti/TiN Daia *et al.* (2000), suggested the yield stress varied with the layer thickness following Hall-Petch model but no attempt was carried out in these investigations to determine the yield stress of the metallic layers from the nanolaminate strength. These results point out that it is important to consider other microstructural features, such as the grain size, to get a better understanding of the size effects.

4.5.2 Temperature

The experimental data presented above showed a dramatic effect of temperature on the mechanical properties of the nanolaminates and on the yield stress of the Al layers (Fig. 4.9). Moreover, the strength reduction increased as the layer thickness decreased, as shown in Fig. 4.11 (a) and, as a result, the size effect observed at 25°C was inverted at 100°C. The mechanisms controlling the yield stress

4.5 Al deformation mechanisms as a function of layer thickness and temperature

at room temperature (which were discussed above) only depend on temperature through the elastic constants, and it is obvious that other deformation mechanisms, such as dislocation climb, dislocation cross-slip and/or grain boundary and interface diffusion, have to be triggered at 100°C to explain the mechanical response. A temperature of 100°C represents a homologous temperature of ≈ 0.4 for Al, which is large enough to trigger diffusion-assisted mechanisms. Considering that the temperature sensitivity is much larger for the thinnest layers, it is instructive to analyze the results based on Coble creep due to grain boundary diffusion. In this case, the strain rate can be expressed as Coble (1963)

$$\dot{\epsilon}_{Al} = A \frac{\sigma_{Al}}{d^3} \exp\left(-\frac{Q_{Al}}{RT}\right) \quad (4.5)$$

where A is a constant that depends on the grain boundary diffusion, R the gas constant, d the grain size and Q_{Al} the activation energy for grain boundary diffusion. Re-arranging Equation 4.5, and considering that the grains have a lateral size, d_l and a height, d_v ($= h_{Al}$), the flow stress can be expressed as,

$$\sigma_{Al} = \frac{\dot{\epsilon}_{Al}}{A} \exp\left(\frac{Q_{Al}}{RT}\right) d_l^2 h_{Al} \quad (4.6)$$

and, therefore, should be proportional to the volume of the grains, $h_{Al} d_l^2$, for a given strain rate and temperature.

The dependence of the flow stress with $h_{Al} d_l^2$ is plotted in Fig. 4.11 (b) at 25, 50 and 100°C. Although this analysis can only be considered as indicative, the results at 100°C are in very good agreement with the behavior expected for Coble creep and support the hypothesis that interface and grain boundary diffusion might limit the potential strengthening obtained by reducing the thickness of the Al layer at temperatures as low as 100°C. These results contrast with those obtained in Cu/Nb nanolaminates, that show that strengthening due to size effects is still operative at temperatures as high as 300°C Monclús *et al.* (2013), which also represents an homologous temperature of ≈ 0.4 for Cu. So, either the behavior of the Cu/Nb interfaces at high temperature differs from that of the Al/SiC interfaces or the high temperature stability of ultra-thin Cu films is larger than that of Al.

4.5 Al deformation mechanisms as a function of layer thickness and temperature

Figure 4.11: (a) Reduction of the yield stress of the Al layers with temperature, $\sigma_y(T)/\sigma_y(25^\circ\text{C})$, as a function of the layer thickness, h_{Al} ; (b) Yield stress of the Al layers at 25, 50 and 100°C vs. $h_{Al}d_l^2$

CHAPTER 5

Strain Hardening Mechanism of Al/SiC Nanolaminates: Effect of Constraint and Temperature

5.1 Introduction

The last chapter unravels the role of Al plasticity, as a function of layer thickness and temperature, on the hardness of Al/SiC nanolaminates at temperatures up to 100°C. Even taking the strengthening effect of the Al layers into account, the enhancement in the hardness for the thinnest Al/SiC nanolaminates was not remarkable, and this behavior was surprising considering the general “the thinner, the stronger” effect for metal-metal nanolaminates. As reviewed in chapter 2, the dependence of hardness with layer thickness has been shown to vary from system to system in metal-ceramic nanolaminates. For instance, the hardness of Al/TiN nanolaminates showed a noticeable dependence with layer thickness, while it was rather weak in Cu/TiN nanolaminates. Some of these differences have been attributed to the characteristic length scale controlling plasticity in each case, which depends on the grain size of the individual layers. For instance, both Al and

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TiN layers in Al/TiN nanolaminates presented a columnar grain structure with in-plane grain sizes that were relatively larger than the individual layer thickness. Hence, the hardness was controlled by the interaction of dislocations with the metal-ceramic interfaces. In the case of Cu/TiN, both Cu and TiN layers were nanocrystalline with a grain size that was much smaller than the layer thickness (due to their low chemical affinity) and dislocation/grain boundary interactions seemed to control the plastic deformation.

All in all, the hardness of metal-ceramic nanolaminates has shown a relatively weak dependence on layer thickness (even when microstructural features, like the grain size in each layer, are considered) and this behavior was particularly obvious when the mismatch in mechanical properties between the soft metal and the hard ceramic layers was very large. The Al/SiC nanolaminates studied in this thesis are a paradigmatic example. The SiC layers are amorphous and, therefore, they do not introduce an internal length scale, like the grain size, that can compete with the layer thickness. As shown in the previous chapter, the hardness is strongly influenced by the volume fraction of the ceramic constituent, but the thickness of the Al layers has only a marginal effect on the hardness, even though their yield strength has been found to be strongly layer thickness dependent. This can be attributed to the large constraint imposed on the deformation of the metal-ceramic nanolaminates during the nanoindentation test. Under these circumstances, the plastic deformation of the metallic layers is not only confined by the ceramic layers, but there is an additional source of elastic constraint imposed by the undeformed material surrounding the hardness impression. These highly constraint conditions, in the case of nanoindentation, might conceal the actual role played by the active deformation mechanisms in the metallic layers. The motivation of this investigation was, therefore, to use an alternative nano-mechanical testing technique, like micropillar compression, to get a better understanding of the active deformation mechanisms and of the role of constraint in Al/SiC nanolaminates as a function of layer thickness and temperature.

To this end, micropillar compression tests were carried out in series II Al/SiC nanolaminates (with equal layer thickness, in the range 10 nm to 100 nm) at

ambient and elevated temperatures to study the layer thickness effect. The mechanical properties obtained by this technique were compared to those assessed by nanoindentation (presented in the previous chapter), in order to explore the effect of constraint for nanolaminates with different layer thicknesses. In addition, numerical simulations of the micropillar compression and nanoindentation tests were carried out by means of the finite element method in order to understand the experimental observations.

5.2 Experimental techniques

5.2.1 *Ex-situ* micropillar compression tests

Micropillars with 2 μm in diameter and 4 μm in height were fabricated following the annular milling procedure described in section 3.3.3. The milling was carried out in several steps by employing ion currents from 9.3 nA down to 80 pA in the final polishing step, to ensure minimum FIB induced damage. The final micropillars were slightly tapered, but the taper angle was generally $<2^\circ$. The micropillars were compressed in the NanoTestTM platform at 25 and 100°C using a 10 μm diamond flat punch. The thermal drift rates at both temperatures were carefully controlled within 0.1 nm/s. The compression tests were performed in displacement-control mode at a nominal strain rate of $1.25 \times 10^{-3} \text{ s}^{-1}$ up to a maximum engineering strain of 0.12. Engineering stresses were computed using the top cross-sectional area of the micropillars (Equation 3.7, 3.8).

5.2.2 Study of deformation mechanisms by *in-situ* micropillar compression tests in the TEM

In order to ascertain the deformation micromechanisms during micropillar compression, *in-situ* micropillar compression tests were also performed inside a transmission electron microscopy (Tecnai F20 FEI Co., Hillsboro, USA) in the Cen-

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ter of Integrated Nanotechnologies (CINT) of Los Alamos National Laboratory. Al100SiC100 and Al10SiC10 were chosen for this analysis. Note that the micropillars for the *in-situ* test should be thin enough (below 200 nm), in order to be electron transparent. The specimens were also fabricated by focused ion beam milling (see section 3.2.3). Unlike the micropillars for *ex-situ* tests, which were fabricated directly from the bulk nanolaminates, the fabrication procedure of the micropillars for the *in-situ* tests was rather complex, because the test specimen had to be transferred to a Cu TEM grid. The initial transfer process was similar to that used for regular TEM sample preparation, as described in section 3.2.3. Once the membrane, with dimensions $20 \times 5 \times 1 \mu\text{m}$, had been transferred to the TEM grid, several micropillars, ready for *in-situ* testing, were machined on the upper edge. The definition of the micropillar geometry required subsequent machining steps by mounting the membrane at 90° and 0° with respect to the ion beam, as seen in Fig. 5.1. The figure shows an Al100SiC100 membrane with up to 5 micropillars ready for testing. Secondly, final thinning down to electron transparency was achieved with the membrane oriented at 0° with respect to the ion beam. Several micropillar sizes were produced, but the results presented in this work correspond to the compression of micropillars having $\approx 1 \mu\text{m}$ in height, $\approx 500 \text{ nm}$ in width and $< 150 \text{ nm}$ in thickness. One of these micropillars is highlighted with a black rectangle in the general SEM view of the Al100SiC100 membrane of Fig. 5.1 (a). The micropillar profile and the final dimensions are detailed in the SEM view of Fig. 5.1 (b), while Fig. 5.1 (c) corresponds to a detailed edge-on view, showing a thickness of 145 nm. The micropillars were finally tested with a PI95 PicoIndenter (Hysitron Co.), as introduced in section 3.3.3, chapter 3. Although the compressive force and displacement were recorded continuously during the test, the main interest of these tests is to resolve the progressive dislocation activity, as well as the role of the ceramic layers upon deformation.

Figure 5.1: (a) SEM image of an Al100SiC100 membrane, mounted on the TEM grid, where up to 5 micropillars have been FIB machined and are ready for in-situ testing inside the TEM. The black rectangle points at one of the micropillars that was tested in this work, for which (b) shows the exact profile dimensions and (c) shows the edge-on view, where the final electron-transparent thickness (145 nm) can be computed.

5.3 Numerical model

The nanoindentation and micropillar compression tests were also simulated using the finite element method to ascertain the role of the constraint effect imposed by the SiC layers on the mechanical response as a function of the yield stress of the Al layers and the layer thickness. The geometrical model for the simulation of the nanoindentation test is the same as that employed in previous chapter and it is depicted in Fig. 5.2 (a) for the sake of completion. It includes all the layers of the Al/SiC nanolaminate with a total thickness of $10\text{ }\mu\text{m}$ (close to the actual nanolaminate thickness), the Si substrate and the rigid conical indenter with a semi-angle of 70.3° . Four models with equal Al and SiC nominal layer thicknesses

5.3 Numerical model

of 10, 25, 50 and 100 nm were built. The geometrical models were discretized using two-dimensional four-node linear axisymmetric elements (CAX4). The lateral dimensions of the models were large enough to avoid any boundary effect. The bottom of the model was fully constrained, while the top boundary deformed following the rigid indenter surface, with a friction coefficient of 0.1 between the nanolaminate and the indenter. The penetration depth was $1\text{ }\mu\text{m}$, within 10% of the total nanolaminate thickness, to avoid any substrate effect. The Oliver-Pharr method Oliver & Pharr (1992) was employed to extract the hardness from the simulated load-displacement curves.

Figure 5.2: Schematics of the finite element models: (a) Nanoindentation. (b) Micropillar compression.

The model geometry for the micropillar compression tests is shown in Fig. 5.2 (b). The micropillar radius was $1\text{ }\mu\text{m}$ and the length $4\text{ }\mu\text{m}$. Four models were built as a function of Al and SiC nominal layer thickness (10, 25, 50 and 100 nm). The base of the micropillar was modeled as a homogeneous, transversally-isotropic elastic medium with the properties of the Al/SiC nanolaminates in order to account for Sneddon effects (i.e. the elastic deflection of the bottom of the pillar Sneddon

(1965)) during the test. The models were also discretized using CAX4 elements. The bottom boundary of the model was fully constrained and a rigid flat punch was used to compress the pillars. The friction coefficient between the punch and the micropillar top surface was 0.1. As in the experiments, the engineering stress and strain were calculated using the initial diameter and length of the pillars from the computed load and displacement, based on Equation 3.7 and 3.8.

Al and SiC were modeled as isotropic, elastoplastic solids, following the J2 theory of plasticity with no strain hardening. This latter hypothesis was in agreement with the approach used in the previous chapter but was corroborated based on the *in-situ* TEM observations (see the next section) that demonstrated that the small layer thicknesses preclude any dislocation storage in the Al layers. The elastic moduli of Al and SiC were taken as 70 and 300 GPa, and the corresponding Poisson's ratios were 0.34 and 0.14, respectively. The properties of the homogeneous elastic solid at the base of the pillars were estimated from the average of the Voigt and Reuss limits for laminates of Al and SiC with equal layer thicknesses. Based on the results in last chapter, the yield stress of the SiC layers was fixed at 7 GPa and was considered independent of layer thickness and temperature. However, the Al yield stress can vary substantially due to changes in the layer thickness and temperature. Therefore, the Al yield stress was varied in the range 0.2 to 1.2 GPa to study the role of constraint as a function of layer thickness and yield stress of the Al layers. The Al-SiC interfaces were considered perfectly bonded in all cases.

5.4 Results

5.4.1 Deformation mechanisms by *in-situ* compression in TEM

Several interesting conclusions could be drawn from the videos acquired in the TEM during *in situ* compression of Al₁₀₀SiC₁₀₀ and Al₁₀SiC₁₀ micropillars. Under uniaxial stress conditions, there was no measurable evidence of plastic de-

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formation in the amorphous SiC layers, not even in the thinnest 10 nm thick layers, which seemed to deform only elastically, contrary to observations in other metal-ceramic nanolaminates like Al-TiN, where both layers co-deformed plastically when the ceramic layers were just a few nm thick Li *et al.* (2014). Therefore, the micropillars deformed by the plastic deformation of the Al layers, constrained by the stiff SiC layers, as was previously hypothesized. The diffraction conditions of individual grains changed continuously during deformation, making it difficult to ascertain the precise deformation mechanisms, but the observations suggest not only rotation of individual grains, which implies some strain accommodation mechanism at interfaces, possibly interface and/or grain boundary sliding, but also changes in the shape of the grains, as pointed by the arrow for the grain captured in the two snapshots, before and after compression (Fig. 5.3), similarly to what has been seen before in post mortem observations Sun *et al.* (2010). Based on the movement of the bent contours and on the fact that no dislocation multiplication and storage was observed upon deformation, it is possible that the grains deformed by the nucleation and annihilation of dislocations at grain boundaries and interfaces, that move across individual grains through a confined layer slip mechanism, as suggested in the previous chapter.

5.4.2 Mechanical properties by *ex-situ* micropillar compression

The engineering stress-strain curves obtained from the micropillar compression tests at 25°C and 100°C are plotted in Fig. 5.4 (a) and (b), respectively. In contrast to the hardness measured by nanoindentation (Fig. 4-2b), the stress-strain curves showed a marked influence of the Al layer thickness on the mechanical behavior at 25°C and 100°C. This influence was found in the strain hardening rate, the maximum compressive strength and the strain at which this maximum strength was attained, which increased as the layer thickness decreased. It should be noticed that the plateau in the stress-strain curves after the maximum compressive strength marked the onset of strain localization due to fracture of the SiC layers, which

Figure 5.3: BF-TEM images, of the Al100SiC100 micropillar (a) before the test and (b) after compression of ≈ 100 nm. The black arrows point to an individual grain, indicating a change of shape of the grain upon deformation.

occurred at higher applied stresses for smaller layer thicknesses. The fracture process will be analyzed in detail in the following chapter, while the focus of this part is the understanding of the large strain hardening rate observed in the compression experiments. As a matter of fact, the large strain hardening rates are surprising considering the lack of dislocation storage observed in the Al layers during the *in-situ* TEM tests.

It is a common practice for Berkovich indenters and homogeneous solids to relate the hardness H and the flow stress σ_f at a representative strain of $\approx 8\%$, with a Tabor constraint factor of ≈ 3 , so that $H = 3\sigma_f$ Tabor (2000). In this case, this relationship is only fulfilled for the Al100Si100 nanolaminate at 25 and 100°C, where σ_f was approximated by the compressive strength. On the contrary, the hardness to compressive strength ratio was ≈ 1.4 for the thinnest nanolaminates at both temperatures, probably due to the high strain hardening observed in the micropillar compression tests Gram *et al.* (2015).

The differences between the hardness and the micropillar compression tests are highlighted in the evolution of micropillar strength with Al layer thickness, which is plotted in Fig. 5.5 (a) at 25 and 100°C. While the hardness was relatively

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Figure 5.4: Engineering stress-strain curves obtained by micropillar compression at (a) 25°C and (b) 100°C.

insensitive to the Al layer thickness (Fig. 4.2b), the micropillar strength decreased rapidly as the layer thickness increased at 25 and 100°C. It should be noted that the drop in strength with layer thickness in the micropillar tests was controlled by the reduction in the strain hardening rate (Fig. 5.4a,b).

The effect of temperature on the hardness (measured by nanoindentation) and on the strength (measured by micropillar compression) is shown in Fig. 5.5 (b), in which the ratio of the hardness and of the strength between 100°C and 25°C is plotted as a function of the layer thickness. The reduction in hardness with temperature was always smaller than that in strength. Moreover, the hardness reduction with temperature increased as the layer thickness decreased and this behavior is consistent with a dominant deformation mechanism controlled by diffusive processes in the Al. They will be enhanced by the smaller Al grain size and the higher interface area associated with thinner layers Lotfian *et al.* (2014), as discussed in last chapter. However, the strength reduction with temperature measured in the micropillar tests was maximum for the intermediate layer thicknesses. In particular, the strength retention at 100°C of Al₁₀SiC₁₀ nanolaminate was very similar to the hardness retention measured by nanoindentation. Surprisingly, neither the high strain hardening rate nor the strength retention with temperature of

Figure 5.5: Evolution of the strength of the Al/SiC nanolaminates as a function of the Al layer thickness at 25°C and 100°C. (b) Reduction of the nanolaminate hardness and compressive strength from 25°C to 100°C as a function of the Al layer thickness.

the thinnest nanolaminates could be explained on the basis of the plastic flow of Al which was the dominant deformation mechanism according to the *in-situ* TEM tests (Fig. 5.3).

The reasons responsible for this discrepancy might be the different constraint effect imposed by the SiC layers on the plastic deformation of the Al layers, as a function of Al yield stress and layer thickness, as revealed by the morphology of the deformed pillars. Scanning electron micrographs of micropillars deformed up to a compressive strain of 0.12 are shown in Fig. 5.6. Most of the micropillars presented a mushroom shape. This shape was the result of the strain localization that took place after the maximum strength was reached because of the fracture and crushing of the SiC layers. However, micropillars deformed rather homogeneously and no SiC fracture was observed for stresses below the compressive strength. It should also be noticed that the lateral surface of the Al100SiC100 micropillars tested at 25°C and 100°C (Fig. 5.6a,b), respectively showed evidence of the plastic flow of Al, which was extruded from the lateral micropillar surface during compression. Obviously, the amount of extrusion was much more noticeable at high

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temperature due to the softening of the nanostructured Al layers. On the contrary, the lateral surfaces of the Al10SiC10 micropillars tested at 25°C and 100°C were smooth (Fig. 5.6e,f) and there was no evidence of extrusion of Al, even though the micropillars underwent a homogeneous deformation of $\approx 8-9\%$ before failure by crushing of the SiC layers in upper region of the micropillar. This result indicates that the plastic deformation of the Al was inhibited by the constraint of the stiff SiC layers and is in agreement with the high strain hardening rate observed in the micropillar compression tests. Finally, the Al50SiC50 micropillars showed a different behavior at 25°C (Fig. 5.6c) and 100°C (Fig. 5.6d). The extrusion of the Al during micropillar compression at room temperature was very limited while the extrusion of Al nanograins from the micropillar was dominant at 100°C. In fact, from a qualitative viewpoint, the extrusion of Al in the Al50SiC50 laminate tested at 100°C was more noticeable than that of the Al100SiC100 tested at the same temperature.

So, the results presented above seem to indicate that the different constraint imposed by the SiC layers to the plastic flow of Al was a critical factor responsible for the layer thickness effect observed in the micropillar compression tests and for the different effect of the temperature on strength and hardness as a function of the layer thickness. The numerical simulations presented in the next section were carried out to clarify this point.

5.4.3 Simulation results

The load-penetration curves obtained from the numerical simulations of nanoindentation in Al100SiC100 and Al10SiC10 nanolaminates are plotted in Fig. 5.7 (a) for two different values of the Al yield stress, 0.2 GPa and 1.2 GPa. The hardness obtained by the Oliver and Pharr method from the simulated indentation curves is plotted in Fig. 5.7 (b) for the Al100SiC100 and the Al10SiC10 nanolaminates as a function of the Al yield strength. The simulation results allow decoupling purely geometrical effects (due to layer thickness) from the expected size effect in the yield stress of the Al layers. The nanolaminate hardness was independent

Figure 5.6: Scanning electron micrographs of the micropillars after deformation up to 12% strain. (a) Al100SiC100 tested at 25°C. (b) Al100SiC100 tested at 100°C. (c) Al50SiC50 tested at 25°C. (d) Al50SiC50 tested at 100°C. (e) Al10SiC10 tested at 25°C. (f) Al10SiC10 tested at 100°C.

of the layer thickness (provided the volume fraction of each constituent is fixed) and increased linearly with the Al yield stress. Thus, the numerical simulations of the hardness test support the weak dependency of the hardness with the layer thickness reported in Fig. 4.2 (b) under the assumption that the strength of the SiC layers was independent of the layer thickness. The slight increase in hardness for the Al10SiC10 and Al25SiC25 nanolaminates at 25°C (Fig. 4.2b) comes about as a result of the higher strength of the Al layers because of the smaller grain size.

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Dislocation climb and/or interface and grain boundary diffusion at 100°C (which stands for 40% of the homologous temperature for Al) lead to a marked reduction in the Al yield stress, which is more pronounced in the nanolaminates with higher interface density and smaller grain size, as shown in the previous chapter. As a result, the reduction in hardness with temperature was more marked for the thinnest nanolaminates (Fig. 5.5b). Therefore, the simulations demonstrate that the hardness follows closely the evolution of the Al yield stress with temperature and layer thickness and this result has been the basis for the inverse methodology used in the previous chapter to determine the yield stress of the Al layers from the nanoindentation hardness of Al/SiC nanolaminates.

Figure 5.7: (a) Load-displacement curves obtained from the numerical simulation of the nanoindentation tests in Al100SiC100 and Al10SiC10 nanolaminates for two different values of the Al yield stress. (b) Numerical predictions of the hardness as function of the Al yield stress for the Al100SiC100 and Al10SiC10 nanolaminates.

The stress-strain curves obtained from the numerical simulation of the micropillar compression test are plotted in Fig. 5.8 (a) and (b) for the Al100SiC100 and Al10SiC10 nanolaminates, respectively. Three different simulations with different values of the Al yield stress (0.2 GPa, 0.8 GPa and 1.2 GPa) are shown in both cases to decouple the influence of the geometrical effect of layer thickness from the effect of the Al yield stress on the mechanical response. Contrary to the case

of nanoindentation, the micropillar results are not independent of layer thickness (even for a fixed volume fraction of each constituent of 50%). The stress-strain curves presented three different zones (with the exception of the Al100SiC100 nanolaminate with $\sigma_y = 0.2$ GPa). The initial elastic region, characterized by the elastic deformation of Al and SiC, was identical in all nanolaminates. The second region was triggered by the onset of Al plastic flow and the starting point only depended on the Al yield stress and not on the layer thickness. Moreover, large differences in the strain hardening rate were found in this second region as a function of the Al yield stress and layer thickness. The different deformation mechanisms responsible for this behavior can be understood with the help of the contour plots of the accumulated plastic strain for a far-field strain of 5% in Fig. 5.9 and Fig. 5.10. The deformation of the Al100SiC100 nanolaminate with a very low Al yield stress (0.2 GPa) took place by the plastic deformation of the Al layers between the SiC layers (Fig. 5.9a). The accumulated plastic strain in the Al layers was in the range 8-10% for an applied compressive strain of 5%, indicating that the applied strain was accommodated by the plastic deformation of the Al, which was extruded out from the micropillar surface. The strain hardening rate in this case was minimum because of the low constraint imposed by the SiC to the deformation of Al. However, this situation changed as the yield stress of the Al increased up to 0.8 GPa. The plastic deformation of the Al layers was impaired by the constraint imposed by the SiC, and the average plastic strain of the Al layers was in the range 4-6%, as shown in the contour plot of Fig. 5.9 (b). Larger plastic strains are only found near the micropillar free surface, where the constraint of the SiC vanishes. As a result, the applied strain has to be partially accommodated by the elastic deformation of the SiC layers, leading to a much higher strain hardening rate. Once this mechanism is activated, and the elastic deformation of SiC contributes significantly to the micropillar deformation in this region, the dependency of the strain hardening rate with the Al yield strength is very limited, as shown in the stress-strain curves for $\sigma_y = 0.8$ GPa and 1.2 GPa in Fig. 5.8 (a).

In the case of the Al10SiC10 nanolaminate, the constraint dominates the mechanical response in the second region of the stress-strain curves even when the Al

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Figure 5.8: Stress-strain curves obtained by the numerical simulation of the micropillar compression test. (a) Al100SiC100 nanolaminate with different values of the Al yield stress. (b) Idem for the Al10SiC10 nanolaminate.

Figure 5.9: Contour plot of the accumulated plastic strain, $\bar{\epsilon}_p$, in the Al100SiC100 nanolaminate at 5% applied strain. (a) Al yield stress, $\sigma_y = 0.2$ GPa. (b) Al yield stress, $\sigma_y = 0.8$ GPa.

yield stress is very low. The strain hardening rate is always very high and almost independent of the Al yield stress (Fig. 5.8b) because the constraint hinders the plastic deformation of the Al layers. Even in case of $\sigma_y = 0.2$ GPa, the plastic deformation of Al is limited to a small zone near the micropillar surface (Fig. 5.10a)

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and the applied strain has to be partially accommodated by the elastic deformation of SiC (Fig. 5.10).

Figure 5.10: Contour plot of the accumulated plastic strain, $\bar{\epsilon}_p$, in the Al10SiC10 nanolaminate at 5% applied strain. (a) Al yield strength, $\sigma_y = 0.2$ GPa. (b) Al yield strength, $\sigma_y = 0.8$ GPa.

The third region in the simulated stress-strain curves begins when the SiC layers start to yield (Fig. 5.8), leading to plastic deformation of both SiC and Al. The strain hardening rate in this region is much smaller and independent of the Al yield stress and of the layer thickness. From the experimental viewpoint, this region would never be attained because the SiC layers fracture before yielding (Fig. 5.6). So, a flow stress at a representative strain of 5% was chosen for comparison between experiments and simulations to account for strain hardening in strength but ensuring that the SiC layers were deforming elastically in all cases.

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The simulation results provide a rationale to understand the experimental increase in the strain hardening rate (and, thus, in strength) as the Al layer thickness decreased (Fig. 5.4a,b), which has to be attributed to the increased constraint

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imposed by the SiC on the plastic deformation of Al. While in the case of nanoindentation, the deformation under the indenter is always fully constrained by the surrounding material (and, thus, the hardness is independent of the layer thickness), the constraint under micropillar compression increases as the ratio between the Al layer thickness (t_{Al}) and the micropillar radius (R) decreases. If $t_{Al}/R > 0.05$, the plastic deformation of Al is largely unconstrained and Al is extruded from the micropillar surface, as shown in Fig. 5.6 (a) and (c) for the Al100SiC100 and Al50SiC50 nanolaminates, respectively. Obviously, the extrusion of Al is enhanced at high temperature because of the softening of the Al (Fig. 5.6b,d). However, the plastic deformation of Al is fully constrained in the Al10SiC10 micropillar ($t_{Al}/R = 0.01$) and there are no traces of extrusion of Al on the micropillar surface (Fig. 5.6e,f). Moreover, the ratio between the simulated hardness and strength, $H/\sigma_{5\%}$, is close to 3 for the Al100SiC100 nanolaminate (in agreement with the experimental results). This value is typical of elastoplastic materials and the micropillar deformation is controlled in this case by the plastic deformation of the Al layers. The $H/\sigma_{5\%}$ ratio in the simulations decreases down up to ≈ 1.5 as the layer thickness decreased (again in agreement with the experimental results) because constraint (rather than the plastic deformation of Al) was the main factor controlling the deformation of the micropillar.

The simulation results are also useful to understand the effect of temperature on the strength of the micropillars, as a result of the softening of the Al layers. The nanolaminate strength at 5% applied strain obtained from the numerical simulations is plotted as a function of the Al yield strength in Fig. 5.11 (a) for different layer thicknesses, showing the role of the geometrical constraint. In the case of the Al10SiC10 nanolaminate (which corresponds to $t_{Al}/R = 0.01$), the flow stress of Al has limited influence on the nanolaminate strength because the strain hardening rate is controlled by the constraint of the SiC layers. The strength of thicker nanolaminates is more sensible to the Al yield stress, as shown in the Al25SiC25 ($t_{Al}/R = 0.02$) and Al50SiC50 ($t_{Al}/R = 0.05$) nanolaminates. Finally, the thickest nanolaminate (Al100SiC100) is the most sensible to the reduction in the Al flow stress.

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Figure 5.11: (a) Numerical predictions of the compressive strength of the micropillars as a function of the Al yield stress for different values of t_{Al}/R . (b) Predictions of the reduction of the nanolaminate hardness and compressive strength (for a micropillar diameter of $2\ \mu\text{m}$) from 25°C to 100°C , as a function of the Al yield stress estimated for each layer thickness.

From the viewpoint of the Al, diffusive mechanisms are expected to be enhanced as the Al layer thickness is reduced because of the smaller grain size and the higher density of interfaces. Thus, the strength and hardness reduction with temperature, expressed by $H(100^\circ\text{C})/H(25^\circ\text{C})$ or $\sigma_{5\%}(100^\circ\text{C})/\sigma_{5\%}(25^\circ\text{C})$ should be maximum for the Al10SiC10 nanolaminate. This was the case for the hardness, but the maximum reduction in the compressive strength was found for the Al25SiC25 and Al50SiC50 nanolaminates (Fig. 5.5b). This apparent contradiction can be explained by the role played by the constraint on the micropillar compression of Al/SiC nanolaminates, as explained by the numerical simulations. The reduction in the yield stress of the Al layers $\sigma_{5\%}(100^\circ\text{C})/\sigma_{5\%}(25^\circ\text{C})$ is plotted in Fig. 5.11 (b) from the experimentally determined hardness drop with temperature, $H(100^\circ\text{C})/H(25^\circ\text{C})$. This result confirms the expected larger softening for the thinnest Al layers. In contrast, the predicted micropillar strength reduction with temperature, $\sigma_{5\%}(100^\circ\text{C})/\sigma_{5\%}(25^\circ\text{C})$, is larger for intermediate layer thicknesses of 50 nm, in good qualitative agreement with the experimental observations

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(Fig. 5.5b). This trend arises from the different constraint levels of the Al layers, as a function of layer thickness. The micropillar strength retention at high temperature was higher for the thinnest nanolaminates because the large constraint ($t_{Al}/R = 0.01$) limits the influence of Al yield stress on the strength (see Fig. 5.11a). The thickest nanolaminates display also a higher strength retention at high temperature because, despite the smaller constraint ($t_{Al}/R = 0.1$), the strength of the Al layers is less sensitive to the temperature due to their larger grain size and smaller interface density. Thus, the higher strength reduction occurs for intermediate layer thickness (25-50 nm). It should be emphasized that the qualitative agreement between experiments and simulations is remarkable considering that the simulations do not account for interface sliding effects, which are known to operate in Al/SiC at 100°C Lotfian *et al.* (2013). This is possibly the reason why the simulations predict the highest strength reduction for a layer thickness of 50 nm, while this is experimentally observed for 25 nm.

These results indicate that the mechanical response obtained from micropillar compression tests of nanolaminates should be analyzed with caution when the difference in elastoplastic properties between layers is very high. Substantial pillar size effects are expected to appear because of the changes in constraint as a function of the ratio between the thickness of the soft layer and the pillar radius. The Al/SiC system analyzed in an investigation is an excellent example.

Taking this into account, the temperature effects observed in Al/SiC nanolaminates agree well with the results obtained in other nanolaminates, such as Cu/Nb, manufactured by accumulated roll bonding, in which the optimum mechanical properties at high temperature (400°C) were found for layer thicknesses around 15-20 nm Monclús *et al.* (2013). Below this layer thickness, the main deformation mechanism changed from confined layer slip to stress assisted diffusional flow, and this transition led to a faster reduction in the mechanical properties at high temperature for the thinnest layers.

CHAPTER 6

Anisotropic Fracture Mechanisms of Al/SiC Nanolaminates by Micropillar Compression

6.1 Introduction

The effects of layer thickness and of the constraint on the deformation mechanisms of Al/SiC nanolaminates were analyzed in the previous chapters. This chapter focuses on the fracture modes of these nanolaminates as a function of layer thickness and layer orientation with respect to the loading axis. The motivation is two-fold. Firstly, as previously shown, fracture and crushing controlled the compressive strength of the Al/SiC nanolaminates loaded perpendicular to the layers (90° loading) by micropillar compression, as shown in Fig. 5.6. The compressive strength was also dependent on the layer thickness, as shown in Fig.

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5.4, and the finest layer thicknesses led to the higher compressive strengths. However, the role of the SiC layer thickness on the fracture response was not studied in detail. And secondly, the nanolaminates should present a highly anisotropic response due to the layered structure. However, nearly all previous experimental studies have been focused on techniques that apply the load perpendicular to the layers. So, there is a need to characterize the properties of these composites in other orientations to determine if the classical laminate theory is still applicable at the nanometer length scale.

The first evidence of the anisotropic response of Al/SiC nanolaminates was obtained by nanoindentation studies in Al₅₀SiC₅₀ that were carried in different directions with respect to the layers: perpendicular, at 45° and parallel Mayer *et al.* (2016). This preliminary work, carried out in collaboration with Mr. Carl Mayer, doctoral student from Arizona State University, showed that the indentation hardness and elastic modulus increased when the indentation was at 45° and parallel to the layers with respect to the results obtained by indentation perpendicular to the layers, as shown in Table 6.1 and Fig. 6.1. This is expected due to the more efficient load transfer from the Al matrix to the SiC layers as the angle between the layers and the loading axis decreases. According to the laminate theory Agarwal *et al.* (2006), the elastic modulus, E , under uniaxial loading, should follow:

$$E = E_L[\cos^4\theta + \frac{E_L}{E_T}\sin^2\theta + \frac{1}{4}(\frac{E_L}{G_{LT}} - 2\nu_{LT})\sin^2 2\theta] \quad (6.1)$$

where θ is the loading angle, E_L is the longitudinal (isostrain) modulus, E_T the transverse (isostress) modulus, G_{LT} the in-plane shear modulus obtained from the inverse rule of mixtures of the constituent layers and ν_{LT} the in-plane Poisson's ratio computed from the rule of mixtures of the constituents. Based on the elastic properties of Al and SiC (Table 4.1), the elastic moduli for the three loading orientations (perpendicular, at 45° and parallel to the layers) are also included in Table 6.1 and Fig. 6.1. The experimental variation of the elastic modulus with orientation obtained from indentation was much smaller than the theoretical predictions. This is not surprising because indentation is characterized by a complex

multiaxial stress field under the indenter, and the corresponding elastic modulus will be an “average” of the different orientations.

Table 6.1: Hardness and modulus of Al50SiC50 determined using nanoindentation for different orientations as well as the calculated modulus obtained from classical laminate theory Agarwal *et al.* (2006).

	Perpendicular	45°	Parallel
H_{ind} (GPa)	4.8 ± 0.4	6.1 ± 0.2	6.9 ± 0.3
E_{ind} (GPa)	111 ± 8	114 ± 3	126 ± 4
E (GPa) (Equation 6.1)	97	100	168

Figure 6.1: Effect of loading angle on the elastic modulus. The dashed line is the predictions of laminate theory for uniaxial loading. The half full symbols stand for the results of the finite element simulations of indentation for planar and wavy layers. The full symbols correspond to the experimental results Mayer *et al.* (2016).

These preliminary results were very useful to identify other microstructural features that could potentially affect the influence of orientation on the mechanical behavior, like layer waviness. As summarized in section 3.2.4, the as-deposited nanolaminates had an inherent layer waviness which resulted from the competitive columnar growth that takes place in the Al layers during sputtering Singh *et al.*

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(2010a) (Fig. 6.2a). It was concluded that layer waviness did not influence the indentation response perpendicular to the layers, but it had a crucial effect on the deformation behavior under parallel and inclined orientations. This is because layer waviness triggered buckling of the layers at much lower stresses than those required for perfectly straight layers. As a matter of fact, buckling of the layers was clearly evident in the FIB cross-sections of the parallel (Fig. 6.2b) and inclined (Fig. 6.2d) indentations, in contrast to indentations in the perpendicular direction (Fig. 6.2c).

Figure 6.2: (a) SEM image of the undeformed nanolaminate microstructure as well as the deformed regions underneath indentations in the (b) parallel, (c) perpendicular, and (d) inclined directions Mayer et al. (2016).

The different role of layer waviness was actually confirmed by finite element simulations of the indentation response as a function of loading direction for flat and wavy layers. As shown in Fig. 6.3, the initial layer waviness (right images in the figure) triggered more buckling in all indentation directions, except for 90° loading. This behavior can be qualitatively understood because the SiC layers behave as curved beams whose axial stiffness sharply decreases with curvature González & LLorca (2005). It was demonstrated that buckling had a large effect

on the indentation modulus as a function of layer orientation, as shown in Fig. 6.1, in which the modulus obtained from the simulation of flat and wavy layers is plotted together with the experimental results and the predictions from laminate theory. The largest effect of waviness was predicted for loading at 20° with respect to the layers, presumably because the indenter face forms 90° with the layers at one side for this orientation, Fig. 6.3 (b). All in all, the differences in the predicted indentation modulus could be up to 20%, and this emphasizes that even small changes in the microstructural features can have a significant impact on the mechanical response.

These preliminary results motivated the need of using a more appropriate experimental technique to study the anisotropy of the nanolaminates, like micropillar compression, that, contrary to nanoindentation, imposes a uniaxial stress field. Therefore, this method was used to study the anisotropic fracture properties of Al/SiC nanolaminates in this work. For this, micropillars of different sizes were tested for perpendicular (90°), inclined (45°) and parallel (0°) loading, as a function of layer thickness. The results were analyzed by finite element modeling to quantify the effect of layer waviness on the micropillar strength.

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Figure 6.3: Von Mises effective stress contours for indentations of flat (left) and wavy (right) nanolaminates loaded at (a) 0° , (b) 10° , (c) 20° , (d) 45° and (e) 90° . Waviness triggers buckling of the layers except for 90° loading Mayer et al. (2016).

6.2 Experimental techniques

Micropillars with either square or circular cross-sections were fabricated following the FIB procedures described in section 3.3.3. Micropillars fabricated on Al100SiC100, Al50SiC50, Al25SiC25 and Al10SiC10 with the layers oriented at 90° and 0° with respect to the loading axis are shown in Fig. 6.4. The lateral dimension (i.e., the side length or the diameter, for the square and circular cross-sections, respectively) was varied between $1\ \mu\text{m}$ and $2\ \mu\text{m}$ to study the effect of pillar size and geometry on the fracture response. The diameter/side length to height aspect ratio was 1:2 in all cases. Additionally, some Al50SiC50 pillars with layers oriented at 45° were milled to study the effect of inclined loading directions. Careful final milling was conducted in all cases to ensure that the pillar taper was always $<2^\circ$. Hereinbelow, a label defined as diameter/side length times height was employed to refer different sized micropillars. For example, a $2\mu\text{m}\times 4\mu\text{m}$ micropillar represents the micropillar having a diameter/side length of $2\ \mu\text{m}$ and a height of $4\ \mu\text{m}$.

The micropillars were compressed using either the stand-alone Hysitron TriboindenterTM or the Micromaterials NanotestTM, described in section 3.3.1, with a $10\ \mu\text{m}$ diamond flat punch. There is an important distinction between the two stand-alone instruments that should be addressed here. The results were identical with both systems, except for the stress evolution after the maximum compressive strength was reached. The Micromaterials NanotestTM gave rise to a stress plateau after the peak strength, as shown in Fig. 5-4 (a), while the peak strength was followed by stress softening in the Hysitron TriboindenterTM. This is because the latter possesses a better PID control than the former. This is crucial because both platforms are load-controlled instruments that use a feedback loop to perform displacement control tests like the ones shown here. While the PID control of the Hysitron TriboindenterTM is capable of reacting fast enough to capture the softening after micropillar collapse, the Micromaterials NanotestTM is not, giving rise to the plateau in stress. To avoid any instrumental artifacts, the stress-strain curves were

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Figure 6.4: Micropillars for perpendicular (90°) and parallel (0°) loading, fabricated in Al10SiC10, Al25SiC25, Al50SiC50 and Al100SiC100 nanolaminates.

interrupted at the peak strength, using an arrow to indicate the strain-to-failure of the pillars.

The micropillars were compressed in displacement control at a constant strain rate of $\approx 10^{-3}$ /s, up to a maximum strain of ≈ 0.15 . Prior to each test, thermal

drift was carefully monitored during 5-minute initial contact with a small load of $2\ \mu\text{N}$. The engineering stress and strain were calculated following section 3.3.3, and Sneddon effects were ignored. The deformed micropillars were characterized by SEM (FEI Helios 600i system) and TEM (Talos F200X, FEI).

6.3 Finite element model

Finite element simulations were carried out to unravel the role of the layer waviness on the fracture strength of the Al/SiC micropillars. Since all the layers in series II had a similar degree of waviness, (Table 3.3), the simulations were performed using the Al₅₀SiC₅₀ as a model system. The model included a rigid flat punch, a micropillar of dimensions $2\mu\text{m}\times 4\mu\text{m}$ with layers oriented at 0° , 45° and 90° with respect to the micropillar axis and the base material. A 2° taper was also considered to mimic the experimental conditions. The effect of layer waviness was accounted for by comparing the simulation results of micropillars with flat and wavy layers. Waviness was introduced by imposing a standard sinusoidal waveform with a wavelength of $0.5\ \mu\text{m}$ and amplitudes of 15 and 45 nm. The 45 nm amplitude is close to the amplitude observed experimentally (see Table 3.3).

Simulations were performed in 2-dimensional (2D) plane strain conditions. All the models were meshed with 4-node bilinear plane strain quadrilateral elements (CPE4). The total number of elements was more than 29425 elements, and it was checked that the discretization was fine enough. The displacements at the bottom of the base material were restricted, while the rest of the surfaces were stress free.

Al and SiC layers were modeled as elastic perfectly plastic materials without strain hardening, as in the simulations presented in previous chapters. The elastic modulus of Al and SiC were 70 GPa and 300 GPa, respectively, and the corresponding Poisson's ratios were 0.34 and 0.14, as summarized in Table 4.1. The yield stress of Al was 935 MPa, based on the results in chapter 4. The apparent yield stress of SiC was chosen 7 GPa, as estimated from nanoindentation results of $1\ \mu\text{m}$ thick monolithic SiC films. The base material was assumed to the elastic

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and isotropic and the elastic modulus and the Poisson's ratio were estimated from the average value of the isostrain and isostress composite moduli. The Al-SiC interfaces were perfectly bonded in all cases.

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6.4.1 Effect of layer orientation on deformation morphology

Engineering stress-strain curves from the pillar compression tests in Al₅₀SiC₅₀ with different layer orientations are shown in Fig. 6.5 (a) and (b). Each plot, corresponds to a different pillar geometry, i.e., $1\mu\text{m}\times 2\mu\text{m}$ and $2\mu\text{m}\times 4\mu\text{m}$, respectively. The arrows indicate the maximum compressive strength, and represent the strain to-failure of the pillars. The results in Fig. 6.5 show the same trends from the viewpoint of the effect of layer orientation on the mechanical response. There is also an effect of pillar size, that will be discussed later. The micropillars with the layers in the 0° orientation (parallel to the loading direction) are the strongest, those at 45° are the weakest, and the micropillars with layers in the 90° orientation (perpendicular to the load) have an intermediate strength. SEM images of the pillars after deformation are shown in Fig. 6.6. The strain is localized at the top of the pillar in the 0° orientation, Fig. 6.6 (a), and this behavior was caused by buckling of the SiC layers, as shown in Fig. 6.6 (b), that leads to the formation of shear bands and to the collapse of the pillars. The formation of shear bands in this orientation is not surprising and has also been observed in bulk Cu/Nb nanolaminates Nizolek *et al.* (2015). In the Cu/Nb case, cracks were not observed in the metallic multilayers, neither a pronounced load drop as the shear bands developed. This is in contrast to the present study where discontinuities in the SiC layers can be seen at the boundary of the shear band (Fig. 6.6b). Interestingly, bending of the layers tended to localize along pre-existing columnar boundaries

(i.e. the troughs in the waviness where the radius of curvature is small) within the nanolaminate microstructure.

Figure 6.5: Engineering stress-strain curves of micropillar compression tests in Al50SiC50 nanolaminates with different layer orientation. (a) Micropillar dimension $1\mu\text{m}\times 2\mu\text{m}$. (b) Micropillar dimension $2\mu\text{m}\times 4\mu\text{m}$.

Fracture occurred in a more brittle fashion in the 90° orientation, leading to the formation of a mushroom, as shown in Fig. 6.6 (c). This deformation pattern is triggered by the formation of vertical cracks on the SiC layers, Fig. 6.6 (d), as a result of the radial tensile stresses that develop in the SiC layers with the plastic deformation of the Al layers. The plastic deformation of the Al layers, constrained by the SiC layers, is evident by the small extrusions at the free surface. They can be observed in the lower, less strained part of the pillar (Fig. 6.6c). At the top of the pillar where the strains are larger, the SiC layers crack and the Al layers flow plastically within the cracks, leading to the formation of the mushroom morphology. The deformation behavior of the pillars loaded at 45° was also dominated by the buckling of the SiC layers, Fig. 6.6 (e). As seen in the cross-section (Fig. 6.6f), shear predominantly occurred in the direction normal to the layers, and it was preferentially localized along the weaker columnar boundaries, as indicated by the white arrows, instead of along the Al/SiC interfaces. The lack of delamination at the Al/SiC interface indicates that the interface shear strength

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Figure 6.6: SEM images of $1\mu\text{m}\times 2\mu\text{m}$ pillars and cross sections after compression.

is higher than the Al flow stress. The large shear strength of this interface has been demonstrated elsewhere Mayer *et al.* (2015). The layers tended to rotate to become perpendicular to the applied stress as a result of the shear localization along the pre-existing columnar boundaries and of the plastic deformation along the Al

layers. Thus, the layers at the top of the pillar formed an angle of approximately 60° with respect to the loading axis at the end of the test, which is different from the initial angle of 45° that can be measured on the undeformed section of the pillar. Micropillars oriented at 45° can accommodate large strains without failure, as opposed to the 0° and 90° orientations, which fail at strains of around 0.05-0.07.

6.4.2 Effect of layer thickness as a function of orientation

$2\mu\text{m} \times 4\mu\text{m}$ pillars oriented at 0° and 90° of Al₁₀SiC₁₀, Al₂₅SiC₂₅ and Al₁₀₀SiC₁₀₀ were tested to study the effect of layer thickness on the mechanical properties in different orientations. The engineering stress-strain curves for micropillars loaded at 90° and 0° , respectively, are plotted as a function of layer thickness in Fig. 6.7 (a) and (b). For 90° loading, the flow stress follows the “the thinner, the stronger” behavior, as explained in the previous chapter.

Figure 6.7: Engineering stress-strain curves as a function of layer thickness for Al/SiC nanolaminates loaded in different orientations. (a) Perpendicular to the layers (90°) and (b) Parallel to the layers (0°).

The SEM and TEM cross-sectional images of the pillars deformed at 90° , shown in Fig. 6.8, reveal the same type of deformation described in Fig. 6.6 (b,d) for layer thicknesses in the range 25-100 nm. Barreling (at the top of the micropillar) was

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induced by the cracking of the SiC layers (red arrows in the figure), followed by plastic flow of Al within the cracks, leading to the development of multiple shear bands and the formation of a mushroom morphology. The failure mechanisms in the micropillar with the thinnest layers (Al10SiC10), Fig. 6.8 (d), were somehow different. A single shear band was formed that led to the bending of the layers and to the opening of large cracks at the pre-existing columnar boundaries. The origin of this phenomenon is not clear and will be addressed later.

The effect of layer thickness was much weaker in pillars loaded at 0° , Fig. 6.7 (b). The strength seemed to increase with layer thickness, except for the Al10SiC10 nanolaminate that was the strongest. If these results are compared with those obtained under perpendicular loading, the strength of Al100SiC100 and Al50SiC50 pillars loaded at 0° is higher than that of those loaded at 90° , in agreement with a more efficient load transfer to the SiC layers in the former. However, the opposite behavior is seen for Al25SiC25 and Al10SiC10 nanolaminates and it can be explained by the early buckling of the SiC layers in the pillars loaded at 0° . As described before, the hard SiC layers buckle in compression, and trigger the formation of shear bands along the pre-existing columnar boundaries, leading to the complete collapse of the pillars, as shown in Fig. 6.9

6.4.3 Pillar size effects

The results plotted in Fig. 6.5 and Fig. 6.6 demonstrate that the maximum compressive strength depended on the pillar size. The compressive strength as a function of layer thickness for micropillars of $1\mu\text{m}\times 2\mu\text{m}$ and $2\mu\text{m}\times 4\mu\text{m}$ oriented at 90° is plotted in Fig. 6.10. The compressive strength was always larger for the smallest pillars ($1\mu\text{m}\times 2\mu\text{m}$) regardless of the orientation. Considering that the maximum compressive strength is limited by fracture of the SiC layers, it is possible that this size effect is related to the fracture of the SiC layers, and this hypothesis will be analyzed in more detail below.

Figure 6.8: SEM images and TEM cross-sections of the Al/SiC micropillars compressed at 90° : (a) Al100SiC100, (b) Al50SiC50, (c) Al25SiC25 and (d) Al10SiC10. Different fracture mechanisms are highlighted: the formation of shear bands (indicated by white lines), the cracking of columnar boundaries (CB, indicated by orange lines) and the cracking of SiC layers (indicated by red arrows)

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Figure 6.9: SEM images and TEM cross-sections of the Al/SiC micropillars compressed at 0° : (a) Al100SiC100, (b) Al50SiC50, (c) Al25SiC25 and (d) Al10SiC10. Different fracture mechanisms are highlighted: the formation of shear bands (indicated by white lines), the cracking of columnar boundary (CB, indicated by orange lines) and the cracking of SiC layers (indicated by red arrows).

Figure 6.10: Compressive strength of micropillars of $1\ \mu\text{m} \times 2\ \mu\text{m}$ and $2\ \mu\text{m} \times 4\ \mu\text{m}$ as a function of individual layer thickness. Data for micropillars oriented at 0° , 45° and 90° are included. Black symbols stand for $1\ \mu\text{m} \times 2\ \mu\text{m}$ pillars and red symbols for $2\ \mu\text{m} \times 4\ \mu\text{m}$ pillars.

6.5 Discussion

6.5.1 Effect of layer thickness on maximum compressive strength

A summary of the maximum compressive strength of $2\mu\text{m} \times 4\mu\text{m}$ pillars is shown in Fig. 6.11 as a function of layer thickness for pillars loaded at 0° and 90° . The maximum compressive strength at 90° increases abruptly as the layer thickness decreases, but this effect is not found at 0° . As discussed in Fig. 6.6 (d), the maximum compressive strength at 90° seems to be controlled by the formation of vertical cracks in the SiC layers, triggered by the radial tensile stresses that develop as a result of the plastic deformation of the Al layers. Once the SiC layers crack, the Al layers plastically flow within the cracks, leading to the formation of the mushroom morphology.

Due to its brittle nature, the fracture strength of the SiC layers is expected to be limited by the size of the pre-existing flaws. The analysis of the SEM and TEM images in Fig. 6.6 reveals that cracking of the SiC preferentially occurs along pre-existing columnar boundaries that have been shown to contain some voids (see the TEM-cross sections of the as-deposited laminates in Fig. 3.7 and 3.8). These voids arise due to shadowing effects during sputter deposition of the layers. If this is the case, the fracture stress of the SiC layers, σ_f , should be proportional to, according to the Griffith equation,

$$\sigma_f \propto \frac{K_{IC}}{\sqrt{\pi h}} \quad (6.2)$$

where K_{IC} is the fracture toughness of the SiC layers and the characteristic size of the pre-existing defects is assumed to scale with the layer thickness, h . The dashed line in Fig. 6.11 plots the expected variation in maximum compressive strength according to Equation 6.2, assuming that the radial tensile stresses that develop in the SiC layers scale with the compressive normal stress (which is reasonable for Al/SiC with equal layer thicknesses). This very simple analysis seems to agree

Figure 6.11: The maximum compressive strength of Al/SiC micropillars compressed at 90° (perpendicular) and 0° (parallel) as a function of individual layer thickness. The dashed blue line indicates the prediction of the Griffith model and the dashed orange line stands for the buckling load of a SiC plate in compression.

well with the observed compressive strength increase with layer thickness reduction down to 25 nm, but the experimental results for Al10SiC10 do not follow the trend. The deformation in this case was somewhat different, with the formation of a single shear band that led to bending of the layers and large crack openings at the pre-existing columnar boundaries, as shown in Fig. 6.8 (d). One could argue that, for Al10SiC10, the stresses get so high that plastic co-deformation of Al and SiC layers might be possible, as suggested in other metal-ceramic systems like Al/TiN Li *et al.* (2014). Nevertheless, the *in-situ* TEM studies presented in section 5.4.1 confirmed that the 10 nm thick SiC layers did not deform plastically. On the contrary, it should be reminded that, in the case of Al10SiC10, there were disruptions on the layered structure during growth, as shown in Fig. 3.8 (c, d). This may be the reason for weaker behavior of the thinnest multilayers in this case.

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In the case of pillars tested at 0° , an inverse size effect was found for the nanolaminates with layer thickness of 100, 50 and 25 nm, Fig. 6.11. Based on the TEM observations (Fig. 6.9), the compressive strength in this orientation should be limited by the buckling of the layers. Buckling was seen to occur within each columnar colony. By considering only the SiC layers, the critical buckling load, P_{cr} , of a SiC plate of thickness h , width equal to the columnar width, d_c , and constraint length, d_c , equal to the columnar width, is given by

$$P_{cr} = \frac{\pi^2 EI}{(Kd_c)^2} \quad (6.3)$$

where E is the elastic modulus of the SiC layer and K the effective length factor of the column (equal to 0.5 for constrained ends). The second moment of inertia I of the plate can be expressed as

$$I = \frac{d_c h_{SiC}^3}{12} \quad (6.4)$$

The critical buckling load of a SiC plate, with $E = 300$ GPa for SiC and the values of d_c and h_{SiC} listed in tables 3.2 and 3.3, is plotted as an orange dashed line in Fig. 6.11. It is not possible to relate directly the critical buckling load of a single plate of SiC with the failure of the nanolaminate under parallel loading, but it is interesting to notice that the higher compressive strength of the thicker multilayers may be actually related to the higher resistance to buckling of the layers. Again, the Al10SiC10 nanolaminate escapes the general trend but, this behavior may be due to the disrupted layered structure when the layers are so thin, as indicated above.

6.5.2 Effect of layer waviness

The results presented above show that fracture of the SiC layers, especially along pre-existing columnar boundaries, was the main mechanism responsible for the final failure. Moreover, the failure pattern was very sensitive to the loading direction. The micropillars oriented at 0° and 45° mainly collapsed by the buckling

of the SiC layers, while the micropillars oriented at 90° failed by their transverse cracking. It is well known that buckling is very sensitive to vertical alignment, so it was expected that layer waviness should have a strong influence on the failure strain.

In order to assess the effect of layer waviness on deformation morphology, the results of the finite element simulations of micropillars with undulated and flat layers are compared in Fig. 6.12 for the different orientations in the Al₅₀SiC₅₀ nanolaminate. The figures on the left contain the von Mises stress contours of micropillars with flat layers, while the figures on the right are of undulated layers for a waviness amplitude of 45 nm. The simulated stress-strain curves for flat and undulated layers are compared in Fig. 6.13, and the experimental results of $2\mu\text{m}\times 4\mu\text{m}$ pillars are also plotted for reference. In the case of the pillars at 0° , it is evident that the layer buckling at the top of the pillar found experimentally was only reproduced by the simulations considering undulated layers in Fig. 6.12 (b). Moreover, the stress-strain curve of the simulation with undulated layers predicted a maximum in the stress (denoted by arrows in Fig. 6.13a), as a consequence of the buckling of the layers, in agreement with the experiments. Analogously, the simulations of pillars loaded at 45° also showed a very different behavior for flat and undulated layers, Fig. 6.13 (c). Shear predominantly occurred parallel to the layers in the case of flat layers, along the Al layers with very little contribution from the SiC layers. This is in contrast with the wavy structure where the undulation of the layers interrupts the shear plane. This leads to the formation of shear bands perpendicular to the layers and to the development of domains where the layers are substantially rotated towards the applied stress. Moreover, the stress-strain curve for undulated layers displayed an increase in strain hardening while the stress-strain curve for flat layers of Fig. 6.13 (c) showed very little strain hardening and led to the development of strain localization along some of the Al layers, as shown in Fig. 6.12 (e). Finally, the simulations with flat (Fig. 6.12c) and undulated (Fig. 6.12d) layers at 90° were very similar, as well as the predicted stress-strain curves (Fig. 6.13b). This indicates that the effect of layer waviness is negligible in this orientation.

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Although the simulated stress-strain curves for the three orientations (Fig. 6.13) show a qualitative good agreement with the experimental ones, there are some quantitative discrepancies. There are a number of modeling assumptions which affect the simulation results, such as the consideration of plane strain and the use of sinusoidal waviness. However, the most significant of these is that the models did not account for fracture of the SiC layers, which occurs profusely at the last stages of deformation. It is interesting to note that, for instance, the simulations reproduced the large initial strain hardening rate observed experimentally for loading at 90° , even though the Al was assumed perfectly plastic. As discussed in the previous chapter, this was a consequence of the constraint imposed by the SiC layers on the plastic deformation of the Al layers, which led to a buildup of hydrostatic stresses and to an increase in the uniaxial applied stress required for yielding. However, this behavior was experimentally limited by cracking of the SiC layers, leading to a maximum stress prior to failure that was not reproduced by the simulations.

6.5.3 Effect of pillar size

The results discussed above point out that the fracture strength of the micropillars at 0° , 45° and 90° is determined not only by the layer thickness but also by the layer waviness. Since the experimental results summarized in Fig. 6.10 also shows that the maximum compressive strength was a function of pillar size, this section discusses the possible origins of this size effect.

Generally, size effects have been observed in micropillar testing of other materials, especially when testing single crystals of pure metals Greer & De Hosson (2011), Guo *et al.* (2014a), Zhang *et al.* (2014b). Dislocation starvation and the lack of dislocation sources have been proposed as the cause of this strength increase in other works Greer *et al.* (2008), Volkert & Lilleodden (2006). This mechanism is not likely the cause of the strengthening in the case of nanolaminates. While dislocation slip is more or less unimpeded in the case of single-crystal micropillars, the interfaces in the nanolaminate micropillars represent strong barriers for dislo-

Figure 6.12: Contour plot of the Von Mises stress at 6% strain of Al₅₀SiC₅₀ micropillars with planar and wavy interfaces: (a, b) 0° orientation, (c, d) 90° orientation. (e, f) 45° orientation.

cation transmission Tschopp & McDowell (2008), and dislocations have to glide confined within single layers Misra *et al.* (2005). As shown by previous studies by

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Figure 6.13: Engineering stress-strain curves of a $2\mu\text{m} \times 4\mu\text{m}$ pillar in $\text{Al}_{50}\text{SiC}_{50}$. Experimental results and finite element simulations (also of $2\mu\text{m} \times 4\mu\text{m}$) of nanolaminates with waviness amplitude of 0 nm, 15 nm and 45 nm at (a) 0° orientation, (b) 90° orientation, and (c) 45° orientation. The vertical arrows indicate the onset of failure.

Sun *et al.* (2010), this type of deformation results in very little residual dislocation density. Considering that the layer thickness is significantly smaller than the pillar diameter, it is unlikely that plasticity in the Al layers is affected by the pillar size.

In addition to dislocation starvation, size effects could also arise from artifacts of the FIB fabrication process. FIB is known to induce amorphization, defect de-

bris, dislocation loops, and ion implantation in some materials between 10 and 100 nm below the surface Bei *et al.* (2007), El-Awady *et al.* (2009), Shim *et al.* (2009). As these changes only affect a finite damage depth, this may generate a perceived size effect because a larger percentage of a small pillar will be damaged compared to a large pillar. Although this may be an issue in some material systems, Al-SiC nanolaminates have not shown significant FIB damage layers. TEM observations on Al-SiC pillars do not show any increase in dislocation density at the pillar surface and the surface amorphous layer which is only ≈ 4 nm thick. Since the pillar diameters in this study were on the order of micrometers, an amorphous layer of a few nm should have a negligible effect on the overall mechanical response.

Another origin of the size effect, that has not been proposed before, would be linked to the cracking of the SiC layers and it is related to the initial distribution of flaws within each micropillar. This type of size effect has been studied extensively in the ceramics literature using Weibull statistics Danzer *et al.* (2007), where the fracture strength decreases in larger samples because there is a higher probability for the sample to contain a strength-limiting flaw. Although this approach is most often used in tensile or bending tests, the same type of analysis has been successfully applied in compression Huang *et al.* (2014), Wong *et al.* (2006). One caveat to this analysis is that cracks could be propagated through mode I cracking in the case of wing cracks or mode II cracks due to the resolved shear stress at 45° . As our study is only concerned with determining if the apparent size effect can be attributed to a distribution of flaws, the cracking mode should not affect the dependence on the pillar size as long as the type of crack propagation is consistent in all pillars used in the analysis. There are several indications which support this failure mechanism in these pillars leading to a size effect. Firstly, small amounts of porosity are observed in the Al/SiC microstructures, especially when the layer thickness is small, and they are often in the troughs of the layer waviness where the uneven surface can cause shadowing during the deposition. Secondly, the largest size effect is observed at 90° , where the fracture behavior appears the most brittle (Fig. 6.5c), while the effect is greatly reduced at 45° , which deform predominantly by plastic shear of the Al layers. Finally, a smaller pillar size effect was observed

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in Al100SiC100, and this multilayer seemed to have a smaller population of pre-existing defects, as evidenced in Fig. 6.14 where cross-sections of $2\mu\text{m} \times 4\mu\text{m}$ pillars for Al100SiC100 and Al50Si50 are shown.

Figure 6.14: Micropillar cross-sections of (a) Al100SiC100 and (b) Al50SiC50 with dimension of $2\mu\text{m} \times 4\mu\text{m}$ and deformed at 90° orientation just before the peak strength.

In order to test this hypothesis, more than 10 additional micropillars with dimensions $1\mu\text{m} \times 2\mu\text{m}$ and $2\mu\text{m} \times 4\mu\text{m}$ were milled and compressed at 90° for each layer thickness in order to have an acceptable population statistics. Each pillar was strained to failure and the fracture stress was recorded (for consistency across all tests, the fracture stress was taken to be the first instance where the strain hardening rate becomes negative). The fracture stresses were assigned a probability of survival based on the proportion of pillars which failed at a lower stress. The two parameter Weibull distribution function can relate this probability of survival, P_s , to the fracture stress, σ , and the sample volume, V , according to the following equation:

$$P_s = \exp\left[-\frac{V}{V_0}\left(\frac{\sigma}{\sigma_0}\right)^m\right] \quad (6.5)$$

where m is the Weibull modulus and the constants V_0 and σ_0 are the characteristic volume and the characteristic strength, respectively Sun *et al.* (2010). Algebraic

manipulation of this equation yields the linear form:

$$\ln(\ln(\frac{1}{P_s})) - \ln V = m \ln \sigma + \ln(\frac{1}{V_0}(\frac{1}{\sigma_0})^m) \quad (6.6)$$

The corresponding Weibull plot of the fracture strengths of all series II nanolaminates yields Fig. 6.15. This plot clearly shows that except for that for the 100 nm layer thick sample, both the $1\mu\text{m} \times 2\mu\text{m}$ and $2\mu\text{m} \times 4\mu\text{m}$ data of the Al/SiC micropillars fall on a single line. Therefore, the fact that the mean strength of the $1\mu\text{m} \times 2\mu\text{m}$ micropillars is higher than that of the $2\mu\text{m} \times 4\mu\text{m}$ micropillars can be completely accounted for using the volume term in the Weibull equation. This indicates that probability of the micropillar containing a strength limiting flaw is proportional to the micropillar volume and leads to the observed size effect. The small amount of nonlinearity in the $2\mu\text{m} \times 4\mu\text{m}$ micropillar data is characteristic of a bimodal flaw distribution as seen in other works Danzer *et al.* (2007).

Figure 6.15: Weibull plot of the fracture strength of the $1\mu\text{m} \times 2\mu\text{m}$ and $2\mu\text{m} \times 4\mu\text{m}$ Al/SiC micropillars with different individual layer thickness.

CHAPTER 7

Fracture Mechanisms of Al/SiC Nanolaminates under Tensile Loading

7.1 Introduction

Fracture toughness is a key property of structural materials. It has been argued that the fracture toughness of metal-ceramics nanolaminates can be higher than that of conventional metal-ceramic composites due to several reasons. Firstly, cracking of the brittle ceramic layers can be delayed due their nanoscale dimensions, which limit the size of the pre-existing defects that initiate fracture. Secondly, the energy dissipated by the plastic deformation of the metallic layers can arrest cracks at the metal-ceramic interfaces. And finally, the large number of interfaces

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associated with the nanoscale dimensions of the layers can introduce substantial energy dissipation through crack deflection mechanisms Kumar *et al.* (2010).

However, our understanding of the fracture properties of nanolaminates is still very limited because most of them are fabricated in the form of thin-films or coatings, and appropriate techniques to measure the fracture toughness of coatings are still lacking. Several techniques have been proposed to measure fracture toughness at the microscale, most of them based on bending of cantilevers of different geometries, such as Chevron notch cantilevers Žagar *et al.* (2016), Mueller *et al.* (2015), clamped beams Jaya & Jayaram (2014) or double cantilever beams Liu *et al.* (2013). The main limitation of these techniques is that their results are very dependent on the geometry and quality of pre-notches that have to be introduced. Moreover, since the pre-notches are typically machined by FIB, ion induced damage at the root of the pre-notch may introduce some additional artifacts. These problems can be avoided by means of the micropillar splitting method, that has been used in this work to determine the fracture toughness of Al/SiC nanolaminates. Micropillar splitting is a novel technique Sebastiani *et al.* (2015b), Sebastiani *et al.* (2015a) that does not require the introduction of pre-notches. Instead, the cracks are introduced directly by a sharp pyramidal indenter and propagate in mode I.

As will be shown in this chapter, the fracture toughness results indicate that the fracture behavior depends not only on the Al-SiC interfaces, but also on other microstructural features like the columnar boundaries. The micropillar compression experiments presented in the previous chapter, especially those carried out parallel and oblique to the layers, already highlighted that the columnar boundaries and the layer waviness play an important role on the deformation behavior. However, their influence on fracture was somehow concealed by the fact that these tests were carried out in compression. To overcome this limitation and analyze the tension/compression asymmetry of nanolaminates, microtensile tests were performed parallel and perpendicular to the layers, and the results are also presented in this chapter. This is the first time that the tensile properties of metal-ceramic nanolaminates are determined.

7.2 Experimental techniques

7.2.1 Micropillar splitting tests

The fracture toughness was measured by the micropillar splitting method Sebastiani *et al.* (2015b), Sebastiani *et al.* (2015a). The experimental set-up is schematically shown in Fig. 7.1. This method employs a sharp cube-cornered indenter to load a notch-free micropillar up to a load that induces the fracture by splitting of the micropillar. The FIB milling procedure was similar to that described in section 3.3.3, but the dimensions of the micropillars were slightly different. In this case, the micropillars were milled with the layers oriented at 90° with respect to the loading direction. The micropillar diameter and length were $\approx 3 \mu\text{m}$, so that the aspect ratio was ≈ 1 . Micropillars were fabricated in Al100SiC100, Al50SiC50, Al25SiC25 and Al10SiC10 to study the effect of layer thickness on the fracture toughness (Fig. 7.2).

Figure 7.1: Schematic of the micropillar splitting test on a nanolaminate micropillar with diameter d and height h . Note that the dh in this test.

Cracks are initiated in a micropillar splitting test at the indentation corners and propagate in mode I until they reach the micropillar surface and induce splitting.

Figure 7.2: *Al/SiC micropillars with aspect ratio of 1 for the micro-splitting tests: (a) Al100SiC100, (b) Al50SiC50, (c) Al25SiC25 and (d) Al10SiC10.*

The cube-cornered indenter is a three-sided pyramidal indenter (see section 3.3.2) and three cracks develop, one at each corner. Therefore, cracks propagate in a symmetric mode in Mode I under tensile stresses parallel to the layers in the case of a micropillar with the layers oriented at 90° with respect to the loading axis. The symmetry of the problem is important to develop a numerical model to derive the fracture toughness from the measured force and displacement data. Note that it is not possible to apply the micropillar splitting method for other layer orientations as the induced cracks would not propagate symmetrically with respect to the layered structure.

The tests were carried out on the stand-alone Hysitron TriboindenterTM system described in section 3.3.1. This was the preferred platform as it allows positioning of the tip at the center of the micropillar top surface with a precision better than

10 nm, which is important to preserve the symmetry. This precision was possible using the scanning probe microscopy (SPM) imaging mode. The surface of the sample is scanned by the indentation probe with a small contact load of 2 μN to render a topographic image where the center of the micropillar can be precisely identified.

The splitting load P_c was unambiguously determined from a load drop in the load-displacement curve, and the fracture toughness, K_{IC} , could be derived from:

$$K_{IC} = \gamma \frac{P_c}{R^{3/2}} \quad (7.1)$$

where R is the micropillar radius and γ a parameter that depends on the elasto-plastic properties and the indenter geometry. This parameter was determined in this work with the aid of finite element simulations, as described in section 7.3.

7.2.2 *In-situ* microtensile tests

Dog-bone shape specimens were fabricated from the Al/SiC nanolaminates by FIB milling for the microtensile tests. Specimens with the layers oriented parallel and perpendicular to the loading axis were prepared and labeled 0° and 90° specimens, respectively. General views of both types of samples, one containing two microtensile specimens at 90°, and another containing three microtensile specimens at 0°, are shown in Fig. 7.3. The microtensile specimens are thus attached to a bulk sample in one end, which serves as support, and are free-standing at the other end, where the tensile load is applied. The shape of the head of the dog-bone specimens on the free standing end was carefully milled according to the shape of the diamond grip that was specifically designed and fabricated by FIB for microtensile testing, as shown in Fig. 3.21.

The fabrication of the microtensile specimens was a much more complex and time-consuming process than the fabrication of micropillars. The procedure requires the following steps:

Figure 7.3: Microtensile specimens fabricated from the Al/SiC nanolaminates with layers oriented at (a) 90° and (b) 0° .

1. The cross-section of a nanolaminate deposited on top of the Si substrate was carefully polished using standard metallographic preparation procedures. It is necessary to get a sharp edge where several microtensile specimens can be prepared.
2. A thin membrane was prepared by milling away material at the bottom, left and right. The membrane was prepared either parallel to the surface (for 0° loading) or parallel to the cross-section (for 90° loading), as shown in Fig. 7.4 (a). Enough material had to be milled away around the membrane to leave space for the tensile grip without touching any corners or edges of the bulk sample. Note that the milling procedure at this step requires that the ion beam etches the sample from two mutually perpendicular directions: one perpendicular to the surface and the other perpendicular to the cross-section. Thus, the sample was mounted on a 52° pre-tilted holder, so that

a stage rotation of 180° brings either the surface or the cross-section to a plane perpendicular to the ion beam. Ion currents in the range 2.5-47 nA were used at this stage and the final membranes were typically $\approx 14 \mu\text{m}$ in length, $\approx 20 \mu\text{m}$ in width and $\approx 2 \mu\text{m}$ in thickness.

Figure 7.4: SEM images taken at different steps of the microtensile specimen preparation process for 90° loading: (a) Preparation of a thin membrane, (b) definition of the gauge length and shape of the specimen head and (d) final polishing

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3. Once the suspended membrane was ready, ion milling was performed perpendicular to the membrane surface to obtain the final shape of the dog-bone specimen, as shown in Fig. 7.4 (b). A medium ion current (0.79 nA to 0.23 nA) was employed in this step to produce edges as smooth as possible, avoiding the formation of sharp corners. The main objective at this stage was to adjust the dimensions of the gauge section and to define the head of the microtensile specimen according to the shape of the diamond grip used to apply the tensile load, as shown in Fig. 3.21.
4. The final milling was carried out with the lowest current (80 pA to 40 pA) to minimize damage on the sidewalls of the gauge length, as shown in Fig. 7.4 (c). The time required to mill each microtensile specimens was >6 hours.

A minimum gauge length to width ratio of ≈ 5 was targeted in all cases. Due to the small nanolaminate thickness (15-20 μm), the gauge length of the microtensile specimens at 90° loading was limited to $\approx 5 \mu\text{m}$, so the width and thickness of the gauge section were fixed at $\approx 1 \mu\text{m}$. In the case of the microtensile specimens at 0° loading, the gauge length was parallel to the nanolaminate surface and therefore its dimension was not limited. In this case, the width and thickness of the gauge section were fixed at $\approx 1 \mu\text{m}$ and the gauge length at $\approx 10 \mu\text{m}$ in length, so that the aspect ratio was ≈ 10 .

Microtensile specimens prepared for nanolaminates Al100SiC100, Al50SiC50 and Al10SiC10 are shown in Fig. 7.5. The images on the left correspond to the specimens prepared for loading at 90° while those for 0° loading are on the right. More than 3 microtensile specimens were fabricated in each case to check the reproducibility of the tests.

The microtensile tests were performed in the *in-situ* Hysitron PicoIndenter 87 system inside the FEI Helios 600i SEM/FIB system. Details of the *in-situ* device were introduced in section 3.3.1. SEM images taken at different steps during the test are shown in Fig. 7.6. Alignment between the specimen and the diamond grip was carefully performed prior to testing. To this end, the tilt and rotation of the picoindenter's sample stage were adjusted to ensure that the loading direction was

Figure 7.5: Representative microtensile specimens fabricated on (a) Al100SiC100 oriented at 90° , (b) Al100SiC100 oriented at 0° , (c) Al50SiC50 oriented at 90° , (d) Al50SiC50 oriented at 0° , (e) Al10SiC10 oriented at 90° and (f) Al10SiC10 oriented at 0° .

strictly parallel to the gauge length and that the load was uniformly transferred from the diamond grip to the specimen head (Fig. 7.6a). Once aligned, the specimen was placed at a height below the diamond grip and gently approached to it by using the picoindenter's stage until the head was exactly positioned below the diamond grip, as seen in the SEM image of Fig. 7.6 (b). The microtensile specimen was then brought upwards to the same height than the diamond grip until the head was inserted within it (Fig. 7.6c). At this stage, contact was established by moving the sample to the left, ensuring that the contact load was $<100 \mu\text{N}$.

7.2 Experimental techniques

The test was performed in displacement-control mode until failure (Fig. 7.6d) at a displacement rate of 5 nm/s. The test was recorded continuously in the SEM.

Figure 7.6: SEM images of the microtensile test: (a) Initial position, (b) alignment stage, (c) motion of the specimen until the head is inserted inside the diamond grip and (d) after testing up to final failure.

Comparison of the elongation measured during the test from the recorded SEM images with the measured displacement indicated that the compliance of the *in-situ* test was very large. Possible sources of this compliance are thermal drift, an initially uneven contact between the specimen and the diamond grip and the deformation of the micropillar head. Attempts were made to measure the strain in the gauge length by applying digital image correlation (DIC) to the acquired SEM images. However, the maximum strain derived by DIC in the gauge length of the microtensile specimen was always very small (<0.02), and below the resolution of the SEM images. This suggests that the microtensile specimens showed a very brittle behavior, and that an accurate measurement of the strain was not possible. Therefore, no attempt to compute the strain from the acquired displacement was

made. Instead, the acquired load was converted into engineering stress based on the initial cross-sectional area of the gauge section.

7.3 Fracture toughness of Al/SiC nanolaminates

7.3.1 Micropillar splitting tests

The fracture toughness of Al/SiC nanolaminates was determined by the application of the novel micropillar splitting method Sebastiani *et al.* (2015b), Sebastiani *et al.* (2015a) described above. The force-displacement curves are plotted in Fig. 7.7 for Al/SiC micropillars with layer thicknesses of 100, 50, 25 and 10 nm. Up to 5 tests were carried out for each layer thickness and the results show good reproducibility. They are characterized by a monotonous increase of the load up to a critical load (P_c) that indicates the micropillar splitting. It is clear from the force-displacement curves that the critical load increases considerably as the layer thickness decreases from 100 nm to 25 nm, and drops again for a layer thickness of 10 nm. One interesting observation is the more compliant behavior of the Al10SiC10 nanolaminate, compared to the rest of the multilayers. It is speculated, based on the observation of the crack paths that will be presented below, that this extra compliance could come from the columnar boundaries. As reported in section 3.2.4, Al10SiC10 contained a higher density of columnar boundaries (the average columnar width was only 171 ± 27 nm, see Table 3.3). Interestingly, the micropillars with layer thickness of 100 nm and 50 nm were able to sustain some load after the onset of splitting, which indicates that the splitting process was gradual. The micropillars from Al25SiC25 and Al10SiC10 failed in a more brittle fashion, as indicated by the arrows.

The results in Fig. 7.7 suggest that the fracture behavior of Al/SiC nanolaminates depends on the layer thickness. SEM images of the micropillars after the splitting test are shown in Fig. 7.8. As expected, the cracks that lead to splitting initiate at the corners of the three-sided pyramidal indentation imprint and prop-

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Figure 7.7: Force-displacement curves from the micropillar splitting tests.

agate perpendicular to the layers until the free edges of the micropillars. Detailed observations of the sides of the micropillars provide some information on the crack propagation mechanisms. For instance, the high magnification image of Fig. 7.8 (b) shows a tortuous crack path, with evidence of crack deflection at the Al-SiC interfaces (see white arrow), as well as ligaments joining the two faces of the cracks (black arrow), which presumably indicate some plasticity of the Al layers. These observations suggest the operation of several energy dissipation mechanisms during crack growth for layer thicknesses of 100 nm and 50 nm. Moreover, it should be noticed that the crack propagation was parallel to the pre-existing columnar boundaries and it could be argued that the crack path seems to preferentially follow the pre-existing columnar boundaries from the observation of the crack path at the top surface of the micropillar (pointed by the red arrows).

Complete splitting of the micropillars took place after the critical load for layer thicknesses of 10 nm and 25 nm, as shown in Fig. 7.8 (f) and (h), in agreement with the load-displacement curves of Fig. 7.7, indicating a more brittle behavior. The fracture surface of the thinnest nanolaminate (Al₁₀SiC₁₀) looked, however, different to the rest, as seen in Fig. 7.8 (h). In this case, the crack propagated

Figure 7.8: SEM images of the micropillars after the splitting tests for (a,b) $Al_{100}SiC_{100}$, (c,d) $Al_{50}SiC_{50}$, (e,f) $Al_{25}SiC_{25}$ and finally (g,h) $Al_{10}SiC_{10}$.

leaving behind smooth terraces that do not show any traces of the energy dissipation mechanisms found for the thicker layers (crack deflection at the interfaces

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or plasticity of the Al layers). Moreover, the morphology of the terraces indicates that the crack propagation took place along the pre-existing columnar boundaries.

7.3.2 Determination of the fracture toughness

The determination of the fracture toughness from the critical splitting load relied on the finite element simulation of the micropillar splitting test to determine the γ constant in Equation 7.1. Neither the layered structure nor the columnar boundaries were considered explicitly in the model, i.e., the nanolaminates were modeled as homogeneous materials with the elastic and plastic properties of the corresponding nanolaminate. Fig. 7.9 shows the geometry of the finite element model. Only 1/3 of the micropillar and of the rigid cube-cornered indenter were modeled because of the symmetry. Symmetric boundary conditions were imposed on the left and right surfaces of the micropillar. The crack plane, aligned with the corner of the indenter and indicated in red in Fig. 7.9, was modeled with cohesive surfaces. A total number of $\approx 20,000$ 8-node linear brick (C3D8) elements were used to mesh the micropillar, with mesh sizes that were refined in the area of initial contact with the indenter.

The elastoplastic properties of the homogeneous materials representing each nanolaminate were chosen based on the nanoindentation results, assuming a Tabor factor of ≈ 3 , and they are depicted in Table 7.1.

Table 7.1: Elastoplastic properties of the homogeneous materials representing each nanolaminate in the finite element simulation of the micropillar splitting tests.

Micropillars	E GPa	Poisson's Ratio	H GPa	Yield stress GPa
Al100SiC100	140	0.2	5.7	2.11
Al50SiC50	141	0.2	5.7	2.11
Al25SiC25	141	0.2	6.8	2.52
Al10SiC10	140	0.2	6.5	2.41

Figure 7.9: *Finite element model of a micropillar splitting test.*

The maximum normal stress criterion was used to model the cohesive fracture, using the traction-separation law plotted in Fig. 7.10. The initial stiffness and cohesive strength of the crack were set to 10^5 GPa and 500 MPa, respectively in all simulations. The initial stiffness is much greater than the elastic modulus to minimize artificial compliances introduced by the cohesive elements. Moreover, an artificial viscosity of 10^{-6} s^{-1} was used to aid convergence during softening/debonding by forcing a positive tangent stiffness matrix over a short period of time. These values were necessary to satisfy both convergence and the criteria for brittle behavior. Two different values of the critical energy release rate (fracture energy), G_c , determined from the area beneath the traction-separation curve, were used in the simulations (1 J/cm^2 , 0.5 J/cm^2) to ascertain load start to drop, indicating the fracture of the cohesive surface. Fig. 7.11 shows the non-dimensional load, defined as $P_c/K_c R^{3/2}$, as a function of the non-dimensional displacement into surface, h/R , for the Al/SiC micropillars. The normalized load-displacement behavior resembles the elastoplastic indentation behavior of bulk materials until a sharp load drop

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occurs at a critical point. This behavior is consistent with the experimental observations (Fig. 7.7, 7.8). Note that the curves in Fig. 7.11 shows that the load drop occurs consistently at an approximately constant value for a given material, independent of the fracture energy, G_c .

Figure 7.10: Constitutive traction-separation relation for the cohesive interface crack, where K is the initial stiffness, and σ_{max} the cohesive strength. The area under the traction-separation curve determines the fracture energy G_c .

Initial contact of the cube-cornered indenter with the pillar resulted in elasto-plastic deformation and the size of plastic zone near the contact scaled with the applied displacement, in agreement with the experimental data. Median/radial cracks propagated stably both from the surface and subsurface as the displacement increased. Unstable crack propagation occurred at the maximum load, P_{cFEM} , leading to the micropillar splitting, as shown in Fig. 7.12.

The simulation results were then used to calibrate γ in Equation 7.1, which only depends on the material properties (E/H) and indenter geometry Sebastiani *et al.* (2015a). G_c is related to the fracture toughness, K_{IC} , through linear elastic fracture mechanics by:

$$K_{IC} = \sqrt{\frac{EG_c}{1-\nu^2}} \quad (7.2)$$

Figure 7.11: Non-dimensional load, defined as $P_c/K_{IC}R^{3/2}$, as a function of the non-dimensional displacement into surface, h/R , for the series II Al/SiC micropillars. The load drop occurs consistently at an approximately constant value for a given material, independent of the fracture toughness, G_c .

where E is the elastic modulus and ν the Poisson's ratio. So, once K_{IC} was estimated from the simulations, γ is given as:

$$\gamma = \frac{K_{IC}R^{3/2}}{P_{c_FEM}} \quad (7.3)$$

The constants γ , determined for each nanolaminate from the numerical simulations, are listed in Table 7.2. They were very similar in all cases and in the range 0.46-0.47. With this information, it was possible to estimate the fracture toughness using Equation (7.1) from the experimental critical loads, P_c . They can be found in Table 7.2.

Figure 7.12: Unstable crack propagation at: (a) one step before and (b) one step after the P_{c_FEM} was reached.

Table 7.2: P_c , γ and K_{IC} of the series II nanolaminates.

Micropillars	P_c mN	γ	K_{IC} $\text{MPa}\sqrt{m}$
Al100SiC100	2.74 ± 0.12	0.46	0.69 ± 0.04
Al50SiC50	3.87 ± 0.06	0.46	0.97 ± 0.02
Al25SiC25	4.63 ± 0.18	0.47	1.18 ± 0.05
Al10SiC10	3.74 ± 0.05	0.47	0.96 ± 0.01

7.3.3 Effect of layer thickness on the fracture toughness

The fracture toughness is plotted in Fig. 7.13 as a function of layer thickness. It is low in all cases, of the order of $0.7\text{--}1.2 \text{ MPa}\sqrt{m}$, probably due to the limited plasticity of the Al layers at this length scales and the brittleness of the ceramic SiC layers. Interestingly, the fracture toughness seems to increase from 100 nm to 25 nm, and decreases again for the smallest layer thickness of 10 nm. It is expected that, in the case of metal-ceramic laminates with cracks propagating perpendicular to the layers, the stresses at the crack tip might be relaxed by mechanism such

7.3 Fracture toughness of Al/SiC nanolaminates

as the plastic deformation of the metallic layers as well as crack arrest and crack deflection at the metal-ceramic interfaces Kumar *et al.* (2010). In this case, some ligaments could be seen in the fracture surfaces of Fig. 7.8 (black arrows), which presumably indicate that the Al layers may experience ductile fracture. However, it is unlikely that plasticity in the Al layers is responsible for the increase in fracture toughness with layer thickness reduction because the yield stress of the Al layers increases with layer thickness reduction from 100 nm to 25 nm (from 900 to 1200 MPa, see Table 4.2) and the size of the plastic zone ahead of the crack tip may be hampered by the presence of the interfaces. As a matter of fact, the fracture toughness of thin Al films with thickness of 100-125 nm (grain size ≈ 50 nm) has been reported to be rather small, 0.7-1.1 MPa $\sqrt{m}$ Kumar *et al.* (2009), which is one order of magnitude lower than that for pure bulk Al.

Figure 7.13: Fracture toughness versus layer thickness for Al/SiC nanolaminates.

The fracture surfaces in Fig. 7.8 showed that the cracks seemed to propagate close to the pre-existing columnar boundaries for layer thicknesses between 25 and

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100 nm, but they followed a tortuous path with clear signs of crack deflection (black arrows) at the Al-SiC interfaces. A schematic illustration of the interaction of the cracks with interfaces and columnar boundaries in this case is shown in Fig. 7.14 (a). Considering that the interface density increases with $1/h$, it is reasonable to assume that the increase in fracture toughness with layer thickness reduction may be a consequence of the higher energy dissipation by crack arrest/crack deflection at interfaces. Additionally, if cracks are arrested at the Al-SiC interfaces, higher fracture stresses are expected for the thinner SiC layers, based on Griffith (Equation 6.1).

Figure 7.14: Schematics showing the crack propagation mechanisms for layer thicknesses (a) 25-100 nm and (b) 10 nm.

For the thinnest Al₁₀SiC₁₀ nanolaminates, however, the fracture toughness dropped to $\approx 0.96 \text{ MPa}\sqrt{\text{m}}$. The fracture surfaces of Fig. 7.8 (g) and (h) suggest that crack propagation was smooth along pre-existing columnar boundaries, without evidence of Al plasticity and/or crack deflection at interfaces. A schematic illustration of the interaction of the cracks with interfaces and columnar boundaries in this case is shown in Fig. 7.14 (b). It is possible that plasticity in the Al layers is hampered for such thin layers, preventing the cracks to be arrested at interfaces. However, it should be reminded that, TEM revealed extremely narrow columnar grains in Al₁₀SiC₁₀ (see Table 3.3), and that there were doubts about

the continuity of the layers across the columnar boundaries, as shown in Fig. 3.8 (d,e). This may lead to the propagation of the cracks along the weaker columnar boundaries, and to the drop observed in the fracture toughness. In fact, there are other observations that suggest that Al₁₀SiC₁₀ might be more influenced by the columnar boundaries than the rest of the nanolaminates, such as the drop in hardness seen in Fig. 4.2 (b), the more compliant behavior of the load-displacement curves in the micropillar splitting tests (Fig. 7.7) or the cracks generated along columnar boundaries in the micropillar compression experiments of Fig. 6.8 (d).

7.4 Mechanical behavior of Al/SiC nanolaminates under tension

The fracture toughness experiments above revealed that interfaces and columnar boundaries had an important effect on the fracture toughness of Al/SiC nanolaminates. It is therefore expected that the tensile behavior might also be influenced by these microstructural features, yielding a large tension-compression anisotropy in Al/SiC nanolaminates. The experiments below were directed at answering this question.

7.4.1 Tensile stress-displacement curves

The engineering stress-displacement curves of the Al/SiC microtensile tests performed at 90° and 0° orientations with respect to the layers are plotted in Fig. 7.15 (a) and (b), respectively. The arrow on each curve indicates the sudden failure of the specimen. Some of the tests at 90° (Fig. 7.15a) were interrupted at several steps, like the Al₅₀SiC₅₀ case, or either unloaded, as the example shown for Al₁₀₀SiC₁₀₀, to acquire high resolution SEM images. The tests carried out at 0° were performed without interruption up to final failure (Fig. 7.15b).

The microtensile specimens displayed a brittle response in both loading directions unlike the behavior in compression, where the fracture process was gradual.

7.4 Mechanical behavior of Al/SiC nanolaminates under tension

Figure 7.15: Microtensile stress-displacement curves of Al/SiC nanolaminates tested at (a) 90° and (b) 0° .

Attempts to measure the strain just before fracture by DIC yielded strain levels below the resolution of the SEM images. However, based on the shape of the curves, the microtensile tests carried out at 90° show a non-linear behavior, while the ones carried out at 0° are linear up to fracture. Therefore, some limited Al plasticity cannot be ruled out at 90° , although the overall behavior is still very brittle. The difference between 0° and 90° orientations is not surprising, considering that the layers deform under isostrain conditions in the former, and therefore, the SiC sustained most of the load. On the contrary, isostress conditions prevailed in the latter and the stress levels on the Al layers were much higher. Intriguingly, the tensile strength of the 90° and 0° microtensile specimens was independent of the layer thickness. The tensile strengths determined at 0° and 90° are listed in Table 7.3, as a function of layer thickness. In all cases, the nanolaminates at 90° failed at ≈ 1.3 GPa, while the tensile strength was significantly lower, ≈ 0.6 GPa, at 0° loading. Therefore, the tensile properties are very different from the compressive behavior reported in the previous chapter. Not only the failure strengths are much lower under tension, but the behavior is very brittle, and independent of the layer thickness. Analysis of the fracture surfaces might help to understand the failure modes of the nanolaminates under tension.

7.4 Mechanical behavior of Al/SiC nanolaminates under tension

Table 7.3: Tensile strength of the Al/SiC nanolaminates tested at 90° and 0° loading directions.

Nanolaminate	Tensile Strength (GPa)	
	90°	0°
Al100SiC100	1.28	0.61
Al50SiC50	1.3	0.63
Al10SiC10	- ¹	0.61

7.4.2 Fracture modes under tension

In order to ascertain the tensile fracture mechanisms, the fractured microtensile specimens loaded at 90° and 0° were cross-sectioned by FIB and analysed in the TEM. The cross-section of the Al50SiC50 nanolaminate fractured at 90° is shown in Fig. 7.16 (c), while a higher magnification image of the fractured cross-section is included in Fig. 7.16 (d). The fracture path seems to follow the Al/SiC interfaces, as pointed by the white arrows. Similar results were found for Al100SiC100 and Al10SiC10, as shown in Fig. 7.16 (a,b) and (e,f). They indicate that, the tensile strength of the Al-SiC interfaces controls the nanolaminate tensile strength when loaded under tension perpendicular to the layers. This explains the lack of influence of the layer thickness on the strength. From these results, the Al-SiC interface tensile strength should be of the order of ≈ 1.3 GPa. This is the first time the tensile strength of Al/SiC interfaces is measured. Previous attempts to measure the shear strength of Al-SiC interfaces Mayer *et al.* (2015) yielded values of the order ≈ 0.69 GPa. This represents a shear to tensile interface strength ratio of 0.5, which is deemed reasonable.

The cross-section of the Al50SiC50 nanolaminate fractured at 0° is shown in Fig. 7.17 (c), while a higher magnification image of the fractured cross-section is included in Fig. 7.17 (d). The fracture path in this case follows a pre-existing columnar boundary, and similar results were also found for the rest of the nanolaminates, as seen in Fig. 7.17 (a,b) for 100 nm and in Fig. 7.17 (e,f) for 10 nm. The

¹Unfortunately, even though the tests were also carried out for Al10SiC10, problems with the *in-situ* machine during testing prevented the acquisition of the load-displacement curves in this case.

Figure 7.16: TEM cross-sectional characterization of Al/SiC nanolaminate after the microtensile tests at 90°: (a, b) Al₁₀₀SiC₁₀₀, (c, d) Al₅₀SiC₅₀ and (e, f) Al₁₀SiC₁₀.

results yield a tensile fracture strength of ≈ 0.69 GPa for the columnar boundaries, relatively weaker than the Al-SiC interfaces, independently of the layer thickness. This suggests that the columnar boundaries are similar in all cases. The fact that

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the columnar boundaries are weaker than the Al-SiC interfaces also explains why those boundaries, trigger failure in compression, specially when the loading axis is parallel to the layers.

Figure 7.17: TEM cross-sectional characterization of the Al/SiC nanolaminate after the microtensile tests at 0°: (a, b) Al100SiC100, (c, d) Al50SiC50 and (e, f) Al10SiC10.

CHAPTER 8

Conclusions and Future Work

8.1 Conclusions

This doctoral thesis has been devoted to the fundamental study of the deformation, strengthening and fracture mechanisms of an Al/SiC metal-ceramic nanolaminates made up of layers with a large mechanical mismatch. The following main conclusions can be drawn from this investigation:

Yield stress of ultra-thin Al layers:

1. The yield stress of the Al layers showed a large “the thinner, the stronger” size effect at ambient temperature. The characteristic length controlling the plasticity of the Al layers was found to be the smallest between the layer thickness and the grain size. In any case, the yield stress of the Al layers was compatible with a deformation mechanism controlled by the glide on single dislocations confined within individual grains, as confirmed by *in-situ* TEM studies.
2. A dramatic reduction in the yield stress of the Al layers was found at 100°C. The reduction in yield stress increased for the thinnest Al layers. This resulted in an inverse size effect at 100°C: the yield stress of the 100 nm thick

8.1 Conclusions

Al layers was four times higher than the 25 nm thick ones. These results were found to be compatible with plastic deformation mechanisms controlled by grain boundary and interface diffusion at 100°C, which limit the strength of the ultra-thin Al layers at high temperature.

Strain hardening mechanisms in Al/SiC nanolaminates:

1. Micropillar compression tests on Al/SiC nanolaminates also showed a strong “the thinner, the stronger” size effect for the Al/SiC micropillars, even stronger than that found on the hardness results. In particular, the stress-strain curves showed that the layer thickness reduction increased considerably the rate of strain hardening and the maximum compressive strength of the micropillars.
2. The constraint imposed by the SiC layers on the deformation of the Al layers was responsible for the large strain hardening rate observed. The constraint encountered by the Al layers in the micropillar compression tests depended on the ratio between the Al layer thickness, t_{Al} , and the micropillar radius, R .
3. The effect of constraint is very important in nanolaminates when the layers have a large mismatch in stiffness and strength. Therefore, a direct comparison between the nanoindentation and micropillar compression results is not possible because the differences in constraint between both tests.

Anisotropic fracture mechanisms of Al/SiC nanolaminates in compression:

The fracture mechanisms that limit the maximum strength of Al/SiC nanolaminates in compression depend on loading direction with respect to the layer orientation:

1. For loading perpendicular (90°) to the layers, the maximum compressive strength was mainly controlled by cracking of the SiC layers perpendicular

to the layers. The maximum compressive strength increased with layer thickness reduction from 100 nm to 25 nm because the fracture stress of the SiC layers increase with layer thickness reduction as a result of the reduction in the size of pre-existing cracks. The maximum compressive strength for 10 nm thick layers was smaller than expected from the Griffith criterion, which might be due to the weakening effect of pre-existing columnar boundaries in this case. As a result of this fracture mechanism, the fracture strength was found to be pillar size dependent, with the smaller pillars being stronger.

2. For loading parallel to the layers (0°), the maximum compressive strength was triggered by the onset of buckling of the layers and the formation of shear bands along pre-existing columnar boundaries. In this case, the effect of layer thickness on compressive strength was negligible and other microstructural features, like the waviness of the layers, seemed to control the strength.
3. For loading oblique to the layers (45°), the strength was also limited by the buckling of the SiC layers and the formation of shear bands along pre-existing columnar boundaries. The strength was also very dependent on the layer waviness.

Fracture toughness of Al/SiC micropillars:

The fracture toughness of Al/SiC nanolaminates was also determined by the micropillar splitting method. The results showed that:

1. The fracture toughness increased from $\approx 0.69 \text{ MPa}\sqrt{m}$ to $\approx 1.18 \text{ MPa}\sqrt{m}$ when the layer thickness decreased from 100 nm to 25 nm. The cracks propagated following a tortuous path with clear signs of crack deflection at the Al-SiC interfaces. The increase in fracture toughness was therefore attributed to the increase in interface density with layer thickness reduction.
2. The fracture toughness decreased to $\approx 0.96 \text{ MPa}\sqrt{m}$, however, when the layer thickness was further reduced to 10 nm. The cracks propagated in this case

8.2 Future work

along the pre-existing columnar boundaries, without evidence of Al plasticity and/or crack deflection at interfaces.

3. The results highlight the role of the Al-SiC interfaces and the pre-existing columnar boundaries on the fracture of the Al/SiC nanolaminates. These microstructural features limited the tensile strength of the nanolaminates. Irrespective of layer thickness, all nanolaminates were failed at a tensile stress of ≈ 1.3 GPa along the Al-SiC interfaces when loaded perpendicular to the layers and at a tensile stress of ≈ 0.69 GPa along the pre-existing columnar boundaries, when loaded parallel to the layers.

8.2 Future work

1. The strength of the Al/SiC nanolaminate is significantly weakened at 100°C, as shown in chapters 4 and 5, and this can be worse at even higher temperatures, as shown in Fig. 8.1. This is mainly due to the softening of the Al layers at a large homologous temperature (>0.4), which is also diffusion controlled (chapter 4). From the engineering perspective, developing a new metal-ceramic system that exhibits better mechanical properties is of vital importance. A good choice for this is to substitute Al with Ti to fabricate novel Ti/SiC nanolaminates. The novel system can be also used to verify whether the mechanisms obtained in current Al-SiC systems are robust in other metal-ceramic nanolaminates that have similar microstructures.
2. Nano-mechanical tests in this thesis (nanoindentation, micropillar compression, microtension, etc.) were carried out under quasi-static conditions, at a strain rate of $\approx 10^{-3}$ /s. As introduced in chapter 1, one of the main applications of metal-ceramic nanolaminate is to serve as wear-resistant coatings in aerospace engines where the compressor blades work always at extremely high speeds, which pushes the testing of the metal-ceramic nanolaminates into high strain rates and in small volumes. However, the dynamic mechanical properties of metal-ceramic nanolaminates are unknown. The available

Figure 8.1: High temperature mechanical properties of the Al/SiC nanolaminates by micropillar compression: (a) stress-strain curves and deformation modes at (b) 25°C, (c) 100°C, (d) 200°C and (e) 300°C.

stand-alone NanoTestTM system is able to perform nano-impacts in a small volume, which could be suitable for the dynamic testing of nanolaminates. Therefore, one interesting line of work in the future could be to explore the dynamic properties of metal-ceramic nanolaminates using the nano-impact testing method.

3. The fracture toughness is important for engineering application. This work used a novel micropillar splitting method to determine the fracture toughness of the nanolaminates, but other tests, including *in-situ* SEM/TEM observations, could provide more information to get a better understanding of the fracture mechanisms.

CHAPTER 9

List of publications and conferences

1) Papers that are a direct result of this doctoral thesis

The work presented in this thesis has been already published or has been submitted for publication in the following papers:

1. **L.W. Yang**, C. Mayer, N. Chawla, J. Llorca, J.M. Molina-Aldareguía: Deformation mechanisms of ultra-thin Al layers in Al/SiC nanolaminates as a function of thickness and temperature. **Philosophical Magazine**, vol. 96, pp. 3336-3355, 2016.
2. C.R. Mayer, **L.W. Yang**, S.S. Singh, J. Llorca, J.M. Molina-Aldareguia, Y.L. Shen, N. Chawla: Anisotropy, size, and aspect ratio effects on micropillar compression of AlSiC nanolaminate composites. **Acta Materialia**, vol. 114, pp. 25-32, 2016.
3. C. Mayer, **L.W. Yang**, S.S. Singh, H. Xie, Y.-L. Shen, J. Llorca, J. Molina-Aldareguia, N. Chawla, Orientation dependence of indentation behavior in Al-SiC nanolaminate composites. **Materials Letters**, vol. 168, pp. 129-133, 2016.

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4. **L.W. Yang**, C. Mayer, N. Li, J.K. Baldwin, N. Mara, N. Chawla, J.M. Molina-Aldareguía, J. Llorca, Mechanical properties of metal-ceramic nanolaminates: effect of constraint and temperature, submitted to **Acta Materialia**.
 5. **L.W. Yang**, A.J. Palomares, N. Chawla, J. Llorca, J.M. Molina-Aldareguía. Role of layer thickness on the fracture toughness of Al/SiC nanolaminates, submitted to **Journal of Materials Science**.

2) Presentations at conferences

The work has also been presented in several international conferences:

1. **L.W. Yang**, C. Mayer, N. Chawla, J. Llorca, J.M. Molina-Aldareguía. Layer orientation and size effects on micropillar compression of Al/SiC nanolaminates. **ECI: Nanomechanical Testing in Materials Research and Development V**, October 5-11, 2015, Albufeira, Portugal.
2. **L.W. Yang**, C. Mayer, N. Chawla, J. Llorca, J.M. Molina-Aldareguía. Measuring the fracture toughness of metal-ceramic nanolaminates as a function of layer thickness and orientation, **IRPS**, May 30-June 1, 2016, Dresden, Germany.
3. **L.W. Yang**, C. Mayer, N. Chawla, N. Li, N. Mara, J.M. Molina-Aldareguía, J. Llorca. Mechanical properties of metal-ceramic nanolaminates: effect of constrain and temperature. **MRS Fall Meeting**, November 27-December 2, 2016, Boston, Massachusetts, USA.
4. C.R. Mayer, **L.W. Yang**, V. Carollo, J.K. Baldwin, N. Mara, J.M. Molina-Aldareguía, N. Chawla. Fracture toughness of Al/SiC nanolaminates: experiments and simulation. **TMS Annuual Meeting & Exhibition**, February 26- March 2, 2017, San Diego, CA.
5. J.M. Molina-Aldareguía, **Y. Lingwei**, C. Mayer, J. Llorca, N. Chawla. Layer thickness effects on the strength and deformation mechanisms of Al/SiC nanolaminates. **TMS Annuual Meeting & Exhibition**, February 14-18, 2016, Nashville, TN.

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6. C. Mayer, **L.W. Yang**, S. Singh, Y.L. Shen, J.M. Molina-Aldareguía, J. Llorca, N. Chawla. Anisotropy, size and aspect ratio effects in micropillar compression of Al-SiC nanolaminate composite. **TMS Annual Meeting & Exhibition**, February 14-18, 2016, Nashville, TN.
 7. M. Monclús, **Y. Lingwei**, J.M. Molina-Aldareguía, J. Llorca. High temperature mechanical behavior of nanoscale multilayers. **EUROMAT**, September 20-24, 2015, Poland.

3) Other papers

Additionally, the novel nanomechanical testing methods developed during this thesis have been used in other collaborative research projects, giving rise to the following publications:

1. **L.W. Yang**, H.T. Liu, R. Jiang, X. Sun, W.G. Mao, H.F. Cheng, J.M. Molina-Aldareguía: Weak interface enhanced high temperature fracture resistance of carbon fiber reinforced mullite matrix composites. **Journal of the European Ceramic Society**, vol. 37, pp. 2991-2996, 2017.
2. **L.W. Yang**, J.Y. Wang, H.T. Liu, R. Jiang, H.F. Cheng: Sol-gel temperature dependent ductile-to-brittle transition of aluminosilicate fiber reinforced silica matrix composite. **Composites Part B: Engineering**, vol. 119, pp. 79-89, 2017.
3. **L.W. Yang**, X.S. Zhang, H.T. Liu, M. Zu. Thermal resistant, mechanical and electrical properties of a novel ultrahigh-content randomly-oriented CNTs reinforced SiC matrix composite-sheet. **Composites Part B: Engineering**, vol. 119, pp. 10-17, 2017.
4. H.T. Liu*, **L.W. Yang***, X. Sun, H.F. Cheng, C.Y. Wang, W.G. Mao, J.M. Molina-Aldareguia: Enhancing the fracture resistance of carbon fiber reinforced SiC matrix composites by interface modification through a simple fiber heat-treatment process. **Carbon**, vol. 109, pp. 435-443, 2017.

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5. H.T. Liu*, **L.W. Yang***, S. Han, H.F. Cheng, W.G. Mao, J.M. Molina Aldareguía: Interface controlled micro- and macro- mechanical properties of aluminosilicate fiber reinforced SiC matrix composites. **Journal of the European Ceramic Society**, vol. 37, pp. 883-890, 2017.
 6. S. Han*, **L.W. Yang***, H.T. Liu, X. Sun, R. Jiang, W.G. Mao, Z.H. Chen: Micro-mechanical properties and interfacial engineering of SiC fiber reinforced sol-gel fabricated mullite matrix composites. **Materials & Design**, vol. 131, pp. 265-272, 2017.
 7. X.S. Zhang*, **L.W. Yang***, H.T. Liu, M. Zu. Thermal and oxidation resisted carbon nanotube reinforced SiC matrix composite-fiber with enhanced mechanical and electric properties. **RSC Advances**, vol. 7, pp. 23334-23341, 2017.
 8. Xiaomin Zhao, **Lingwei Yang**, Francisco Hueto Martin, Xiu-Qin Zhang, Rui Wang, De-Yi Wang, Impact of phenylphosphonate based flame retardant on epoxy/glass fiber reinforced composites (GRE): flammability, thermal stability and mechanical properties. **Composites Part B: Engineering**, vol. 110, pp. 1-9, 2017.
 9. Junhao Zhang, Qinghong Kong, **Lingwei Yang**, De-Yi Wang: Few layered Co(OH)₂ ultrathin nanosheet-based polyurethane nanocomposites with reduced fire hazard: From eco-friendly flame retardance to sustainable recycling. **Green Chemistry**, vol. 18, pp. 3066-3074, 2016.
 10. M.A. Monclús, M. Callisti, T. Polcar, **L.W. Yang**, J. LLorca, and J.M. Molina-Aldareguía: Selective oxidation -induced strengthening of Zr/Nb nanoscale multilayers. **Acta Materialia**, vol. 122, pp. 1-10, 2017.
 11. Yun Liu, Xi-Ran Zhao, Ya-Li Peng, Dan. Wang, **Lingwei Yang**, Hao Peng, Ping Zhu, De-Yi Wang: Effect of reactive time on flame retardancy and thermal degradation behavior of bio-based zinc alginate film. **Polymer Degradation and Stability**, vol. 127, pp. 20-31, 2016.

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