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Effect of layer thickness on the high temperature mechanical properties of Al/SiC nanolaminates

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ABSTRACT

Composite laminates on the nanoscale have shown superior hardness and toughness, but little is known about their high temperature behavior. The mechanical properties (elastic modulus and hardness) were measured as a function of temperature by means of nanoindentation in Al/SiC nanolaminates, a model metal–ceramic nanolaminate fabricated by physical vapor deposition. The influence of the Al and SiC volume fraction and layer thicknesses was determined between room temperature and 150 °C and, the deformation modes were analyzed by transmission electron microscopy, using a focused ion beam to prepare cross-sections through selected indents. It was found that ambient temperature deformation was controlled by the plastic flow of the Al layers, constrained by the SiC, and the elastic bending of the SiC layers. The reduction in hardness with temperature showed evidence of the development of interface-mediated deformation mechanisms, which led to a clear influence of layer thickness on the hardness.

1. Introduction

Natural and synthetic composite laminates have demonstrated an excellent combination of strength and toughness [1]. Nanoscale multilayer or nanolaminates constitute a special case, when the layer thicknesses are reduced <100 nm. Nanolaminates in different combinations (metal–metal [2–5], metal–ceramic [6–9], and ceramic–ceramic [10–13]) have typically shown unique electrical [14], magnetic [15–17], optical [18,19], and mechanical properties [20,21], as a consequence of the nanoscale dimensions of the layers and/or the large interfacial area. Designing layered structures at nanoscale is therefore an attractive strategy for developing multifunctional materials to be used in different applications: wear resistant coatings, optical coatings for thermosolar energy generation, supercapacitors and/or electrical interconnects. Even in the latter examples, mechanical performance is crucial, because nanolaminate coatings will be often subjected to high stresses and temperatures under operation conditions. However, there is very little information available on the mechanical properties at high temperature of thin-films because of the experimental difficulties to carry out high temperature nanoindentation.

Progress in instrumented nanoindentation has opened the possibility to carry out nanoindentation and micropillar compression tests at high temperature [22–25] and these techniques were recently used to study the mechanical properties of Al/SiC nanolaminates, a model metal–ceramic nanolaminate. Previous work showed that Al/SiC nanolaminates with Al and SiC layer thicknesses of 50 nm presented very high room temperature strength [7,26–31], as a result of the constraint imposed by the stiff SiC layers on the plastic deformation of the Al nanolayers. However, the strength dropped quickly with temperature as a result of the large reduction in yield stress with temperature experienced by the Al nanolayers and the onset of interfacial sliding between layers [30,31], at least for equal thicknesses of the elastic SiC and plastic Al layers.

Following this line of research, this investigation was focused on the effect of temperature on the elastic modulus and hardness of Al/SiC nanolaminates as a function of the relative layer thicknesses of Al and SiC. To this end, nanolaminates with Al and SiC layer thicknesses in the range 2 to 100 nm were manufactured by magnetron sputtering and their Young's modulus and hardness were measured between 28 °C and 150 °C. The nanoindentation imprints were cross-sectioned using a focused ion beam (FIB) and analyzed by transmission electron microscopy (TEM) to ascertain the deformation modes as a function of layer thickness and temperature.

2. Materials and experimental procedure

The nanolaminates were fabricated by magnetron sputtering alternating layers of Al and SiC onto a single crystal silicon wafer (111).

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The sputter unit is made up of high vacuum chamber with dual sputter guns. Targets of pure Al (99.99%) and SiC (99.5%) (Kurt J. Lesker, Clairton, PA) were used for sputtering in Ar atmosphere at a working pressure of 3.0 mTorr (0.4 Pa). Al was sputtered using a DC sputter gun with a power of 95 W and SiC layers were deposited using identical argon pressure and an RF sputter power of 215 W. The targets were pre-sputtered for 10 min at 40 W for Al and 95 W for SiC to remove any oxides and contaminates prior to film deposition. With these conditions, the deposition rates were 7.5 nm min^{-1} for Al and 3.9 nm min^{-1} for SiC. The sample holder was continuously rotated during sputtering to obtain uniform layer thicknesses. The individual layer thicknesses were varied between 2 and 100 nm, and the total numbers of layers were selected to ensure total film thicknesses above 10 μm. The large total film thickness ensured negligible substrate effects during indentation testing. In order to investigate the effect of the individual layer thickness on the mechanical response, two series of samples were produced (see Table 1). In series 1, the SiC layer thickness was kept constant at 50 nm while the Al layer thickness varied between 10 and 100 nm; in series 2, the Al layer thickness was kept constant at 50 nm while the SiC layer thickness varied between 2 and 100 nm. The nanolaminates were named by their Al and SiC nominal layer thicknesses in nanometers, e.g. Al10SiC50 refers to a nanolaminate containing 10 nm thick Al layers and 50 nm thick SiC layers. The last column in Table 1 indicates the volume fraction of Al in each nanolaminate, according to the nominal layer thicknesses.

Nanoindentation tests were carried out using a NanoTest™ platform III (Micro Materials, Wrexham, UK) with a Berkovich diamond tip. Nanoindentation testing was performed at 28 °C, 50 °C, 100 °C, and 150 °C. Samples were bonded to the heater plate using a high temperature adhesive and then both, sample and indenter were heated independently to the target temperature. Independent heating of tip and sample is the best way to control thermal drift, so that drift rates lower than 0.01 nm s^{-1} can be achieved prior to testing. Indentations were carried out with a loading rate of 10 mN s^{-1} up to a maximum load of 100 mN. The maximum load was held constant for a dwell period of 5 s at maximum load prior to unloading at 20 mN s^{-1}. The creep rate was computed in all cases at the end of the hold period and it was always below 0.1 nm s^{-1}, ensuring negligible creep effects on the determination of the elastic modulus from the unloading stiffness. Upon unloading, thermal drift was measured again by introducing a 60-second hold segment at 10% of the maximum load. The drift rate was measured over the last 40 s of the hold segment.

At least 8 indentations were performed at each temperature and the samples were kept at the test temperature for at least 3 h. The load–displacement curves were analyzed using the Oliver and Pharr method [32]. Selected indentations were characterized by atomic force microscopy (AFM), using a Park XE-150 instrument (Park Systems, Suwon, Korea) to carry out a more detailed analysis of the indentation contact area and to study pile-up/sink-in effects.

The microstructure of the nanolaminates was characterized using a dual beam FIB (FEI, Nova 200 NanoLab). To ascertain the deformation modes, selected indentation imprints were cross-sectioned and observed by TEM, using a JEOL JEM 3000 microscope.

Table 1
Number of layers and layer thicknesses of the Al/SiC nanolaminates.

Series	Sample	Thickness (μm)	Number of layers	t_{Al} (nm)	t_{SiC} (nm)	V_{Al}
S1	Al10SiC50	15	250	10	50	0.17
	Al25SiC50	13.3	200	25	50	0.33
	Al50SiC50	14	150	50	50	0.50
	Al100SiC50	12	100	100	50	0.67
S2	Al50SiC2	12.8	289	50	2	0.96
	Al50SiC10	12.3	250	50	10	0.83
	Al50SiC25	13	200	50	25	0.67
	Al50SiC100	14	100	50	100	0.33

3. Results

3.1. Layer morphology

Representative TEM bright-field images of the cross-section of various nanolaminates are shown in Fig. 1. They include (a) Al50SiC50, (b) Al50SiC2, (c) Al50SiC10 and (d) Al10SiC50. The SiC layers were amorphous in all cases while the Al layers were nanocrystalline, with columnar grains whose average width (parallel to the layers) was of the order of 2–3 times the layer thickness. The interfaces between Al and SiC were chemically abrupt, with no evidence of chemical reactions, but physically rough as a result of the competitive columnar grain growth during deposition of each Al layer. The layer roughness was not large enough to break up the layered structure, even in the case of the Al50/SiC2 nanolaminate, where the SiC layers were only 2 nm thick (Fig. 1(b)). The actual layer thicknesses, as measured by TEM, compared well with the nominal layer thicknesses and were uniform through the entire thickness of each nanolaminate. All nanolaminates were apparently pore free, except for laminate Al10/SiC50, that showed evidence of porosity, presumably aligned along columnar grain boundaries, as indicated by the arrows in Fig. 1(d). This TEM image was recorded at slightly under focused conditions to reveal the Fresnel contrast associated with the pores.

3.2. High temperature nanoindentation

Representative load–indentation depth curves at room temperature of three different nanolaminates are plotted in Fig. 2. They correspond to, Al10SiC50, Al50SiC50 and Al50SiC10 and the Al volume fraction was 0.17, 0.50 and 0.83, respectively. As expected, the resistance to the indenter penetration decreased with the Al volume fraction due to the much higher hardness of SiC. The maximum indentation depth was always below 1200 nm and, therefore, within 10% of the total laminate thickness, which is a widely accepted rule-of-thumb to avoid substrate effects in the indentation response. Similar curves to those shown in Fig. 2 were analyzed using the Oliver and Pharr method [32] to compute the hardness and the elastic modulus of different nanolaminates. The Poisson's ratio of each nanolaminate was estimated as the average of the direct and the inverse rule of mixtures assuming that the Poisson's ratio of Al and SiC were 0.34 and 0.14, respectively [31,22,33]. The hardness and elastic modulus of all the nanolaminates are summarized in Table 2.

It is well known that the Oliver and Pharr method [32] may not provide accurate values of the hardness and elastic modulus if significant pile-up takes place around indentations. In order to confirm the applicability of the Oliver and Pharr method in these nanolaminates, the contact area was measured using AFM from the surface profile of indentation imprints in all samples at different temperatures. The topography results showed no significant pile-up around the indentations, as illustrated in Fig. 3 for selected indentations, confirming the accuracy of the data included in Table 2.

3.3. Deformation mechanisms

Fig. 4 shows an indentation cross-section in the Al50SiC10 nanolaminate. Remarkably, the layered structure was preserved in the deformed region and the strain imposed by the indenter was accommodated by the plastic deformation of the Al layers, plus the elastic deflection of the SiC layers. No dislocations could be found in the Al layers, but their thickness was reduced under the indented area, evidencing that they deformed plastically under the constraint of the stiff and hard SiC layers. It is also worth noting that the SiC layers underwent substantial bending under the indenter, because their small thickness allowed large elastic deformations without fracture. Nevertheless the SiC layers could not always accommodate the shear deformation imposed by the indenter, and were broken, as shown by the arrow in Fig. 4(b). Similar