High-temperature nanoindentation behavior of Al/SiC multilayers

S. Lotfian , J.M. Molina-Aldareguia , K.E. Yazzie , J. Llorca and N. Chawla

Nanoscale Al/SiC composite laminates have unique properties, such as high strength, high toughness, and damage tolerance. In this article, the high-temperature nanoindentation response of Al/SiC nanolaminates is explored from room temperature up to 300°C. Selected nanoindentations were analyzed *postmortem* using focused ion beam and transmission electron microscopy to ascertain the microstructural changes and the deformation mechanisms operating at high temperature.

Keywords: high-temperature nanoindentation; metal–ceramic multilayer; Al/SiC

1. Introduction

Nanolaminate composites consisting of alternating layers of two materials are attractive materials due to their unique electrical, magnetic, optical, and mechanical properties [1–3]. These composites have been studied in many different layered combinations: metal–metal, metal–ceramic, and ceramic–ceramic. Several studies have shown that metal–ceramic systems, such as Al/SiC, display an attractive combination of strength, hardness, and toughness [4], which can be partially understood by the plastic deformation of the nanometer-thick metallic layers confined by the stiff ceramic layers. In previous studies [5,6], the mechanical behavior of Al/SiC nanolaminates was investigated at room temperature (RT) by means of nanoindentation. Recent progress in instrumented nanoindentation testing allows us to extend this analysis to high temperature to quantify the thermomechanical behavior of this class of materials. In this article, the mechanical response of Al/SiC nanolaminates was studied by means of high-temperature nanoindentation in the range 25–300°C. To understand the damage mechanisms under indentation loading at these temperatures, the indentations were studied extensively by focused ion beam (FIB) and transmission electron microscopy (TEM).

2. Experimental procedure

Al/SiC multilayer samples were synthesized by physical vapor deposition using magnetron sputtering. Details of the sputtering method are discussed elsewhere [1,4]. The samples were grown on a Si(1 1 1) substrate, and the individual layer thickness of Al and SiC were measured to be about 40 nm. A total of 40 (20 layers of Al and SiC each) layers were deposited.

Nanoindentation testing was carried out using a TI 950 Triboindenter™ (Hysitron, Inc., Minneapolis, MN). The indentation tip assembly consists of a Berkovich geometry diamond tip brazed to a low thermal expansion coefficient Macor® shaft, attached directly to the load transducer behind a heat shield. Nanoindentation testing was carried out at RT, 100, 200, and 300°C. Four different samples were cut from the same multilayer specimen, one for each test temperature. Each sample was placed on the heater plate and subsequently heated to the target temperature. The indenter was then put in contact with the sample using a small contact load (2 μN) and contact was maintained for at least 30 min before the first indentation test to allow for thermal stabilization of the system. Using this approach, typical drift rates of 0.1 nm/s were achieved. Two types of indentation tests were carried out: conventional loading–unloading up to a maximum load of 10 mN and multiple loading–unloading cycles to extract hardness and modulus as a function of indentation depth. The indentations were carried out at a loading rate of 1.0 mN/s with a hold period of 5 s at maximum load. The creep rate at the end of the hold period at maximum load was <0.1 nm/s, ensuring negligible creep effects on the determination of the elastic modulus from the unloading stiffness. On unloading, drift was measured by introducing 60-s hold segment at 10% of the maximum load. The drift rate was measured over the last 30 s of the hold segment. At least 10 indentations were performed at each temperature and the samples were kept at the test temperature for at least 4 h. After cooling down, nanoindentations were carried out at RT on each sample to measure the postannealing hardness and modulus. The load–displacement curves were analyzed using the Oliver and Pharr [7] method.

3. Results and discussion

Representative load–displacement curves at each test temperature are plotted in Figure 1a, while the hardness evolution with contact depth is shown in Figure 1b. In this figure, the data for each temperature correspond to the average value from five multiple loading-unloading curves, while the error bars represent one standard deviation. It is evident that the test temperature had a marked influence on the indentation response, especially at 200°C and above. Figure 1b shows that hardness slightly increases with contact depth in the range between 100 and 400 nm, ruling out any substrate effects. For very shallow indents, below 100 nm, lower hardness values were measured probably due to the surface roughness of the multilayers. The evolution of hardness and elastic modulus with temperature is shown in Figure 2 (full symbols). Both exhibited a marked reduction with temperature, particularly at and above 200°C. The drop in modulus was much larger than the one that could be expected from the temperature dependence of the elastic moduli of Al and SiC. The RT moduli of Al and SiC are 70 and 277 GPa, respectively [2]. The modulus of SiC

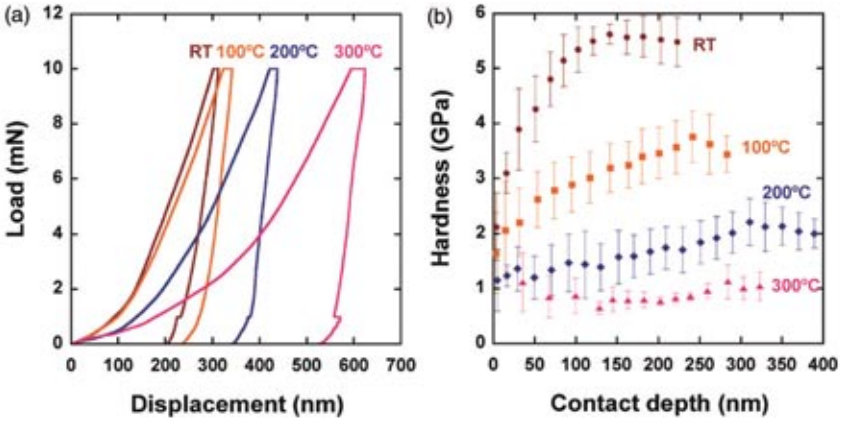

Figure 1. (a) Representative load–displacement curves for the different test temperatures. (b) Hardness versus contact depth at each test temperature.

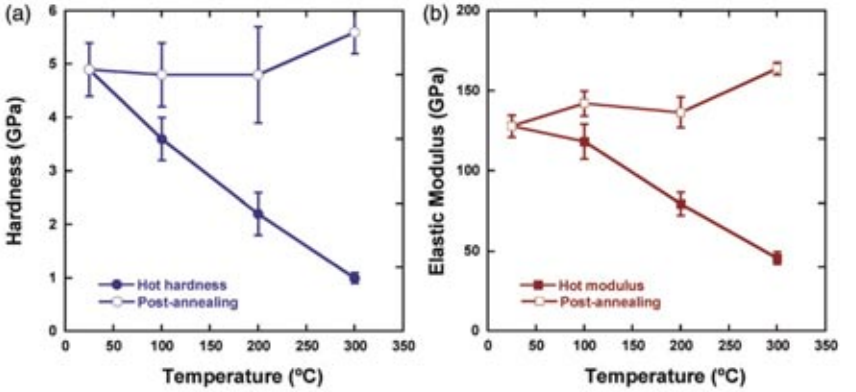

Figure 2. (a) Hardness and (b) elastic modulus as a function of test temperature, in full symbols. The open symbols represent the postannealing hardness and modulus at RT.

studied here is somewhat lower than that of the bulk because the SiC layers are amorphous. The elastic modulus of Al drops by 20% at 300°C [8], while the reduction in bulk SiC elastic modulus at this temperature should be negligible [9]. Therefore, the reduction by ≈50% of the Al/SiC multilayer elastic modulus at 200°C has to be attributed to changes in the microstructure and/or the deformation micromechanisms. Interestingly, the RT hardness and modulus of samples annealed at 100, 200, and 300°C during the 4 h were comparable to those measured in the as-received samples, as shown in Figure 2 (open symbols), and exhibited a slight increase at 300°C, presumably due to new phases developed, as will be shown below. Nevertheless, this demonstrates the need of high-temperature nanoindentation to ascertain the thermal stability of nanostructured coatings. Traditionally, the hardness after annealing has been used as a parameter to assess the thermal stability of coatings. However, in this particular case, postannealing nanoindentation of

Al/SiC did not reveal any effect of temperature on mechanical properties, while high-temperature nanoindentation did show marked differences.

To quantify the physical mechanisms responsible for the mechanical response, selected indentations were cross sectioned using a FEI Quanta FIB workstation and further thinned down for TEM analysis using a FEI Tecnai F20. Figure 3 shows two indentation cross sections at (a) RT and (b) 300°C. The small imprint of the 10-mN indentation at RT is pointed out by the arrow and the typical microstructure of Al/SiC multilayers is observed. Both Al (light gray) and SiC (dark gray) layers were 40 nm in thickness and the layers were wavy (albeit continuous) due to the inherent columnar growth of the Al layers. Although SiC is brittle, the SiC layers exhibited a considerable compliance due to their small thickness and sandwiching effect between the ductile Al layers. No cracking was observed at this indentation load, but it is known from previous studies [1] that the SiC layers tend to crack at RT at larger indentation depths. The residual imprint at 300°C was much larger at the same indentation load (Figure 3b) as the hardness was reduced by a factor of five in comparison with the RT value (Figure 2a). This drop in hardness could be attributed to several factors.

First, the flow stress of nanostructured Al grains decreases rapidly with temperature and the indentation load has to be mainly borne by the SiC layers as Al exhibits significant plastic flow. This led to the cracking of the SiC layers, especially at columnar boundaries (marked with white arrows in Figure 3b), further reducing the strength (as well as the stiffness) of the nanolaminate. Finally, it should be noted that the cracks in SiC layers tested at high temperature were always filled in by Al that plastically flowed to fill the gap (see detail in Figure 3c). This is an indication of the development of a self-healing mechanism in these nanolaminates, which results from the small size of the Al grains (easy flow at high temperature) together with small layer thickness.

Second, the FIB cross section at 300°C (Figure 3b) revealed many dark areas indicative of the development of some chemical reaction between Al and SiC. Moreover, the SiC layers appear much thinner, enforcing the reaction hypothesis. Very little is known about the reactivity and diffusivity between Al and SiC when the layers are at the nanoscale [10] and a detailed analysis is beyond the scope of this

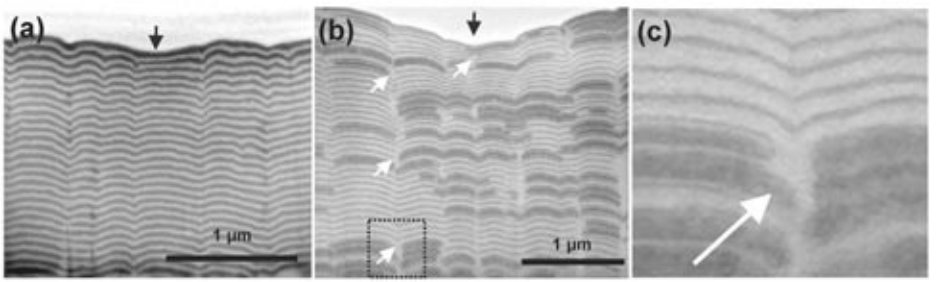

Figure 3. Scanning electron microscope (SEM) images of indentation cross sections (a) at RT (dark gray: SiC; light gray: Al) and (b) at 300°C. Some reaction between Al and SiC can be observed at 300°C (dark areas). The white arrows in (b) indicate areas where the SiC layers have broken and the Al has plastically flown to heal the cracks, as shown in more detail in (c).

article. In any case, our initial TEM studies suggest that chemical reaction between the Al and the SiC layers did take place at 200°C and profusely at 300°C. Figure 4a shows a high magnification bright-field (BF) image of an area where one of this dark layers was located (indicated by the white arrow). The selected area diffraction pattern (SADP) in Figure 4b shows the expected Al diffraction rings plus several rings that can be attributed to either Al_4C_3 or Al_4SiC_4, common reaction products between Al and SiC. According to previous works on SiC-particle-reinforced Al composites [11], the common reaction product between Al and SiC is Al_4C_3 through the following reaction:

$$4Al + 3SiC \rightarrow Al_4C_3 + 3Si \quad (1)$$

but these results were obtained at higher temperatures and with crystalline SiC particles of much larger size. Therefore, other reactions such as

$$4Al + 4SiC \rightarrow Al_4SiC_4 + 3Si \quad (2)$$

cannot be ruled out. In both cases, carbides plus some free Si are expected as reaction products resulting in interface embrittlement. The energy-dispersive X-ray spectroscopy mapping of Figure 4c of the nanolaminate tested at 300-°C multilayer clearly shows the thinning of the SiC layers together with regions in which a complete layer of Al has been substituted by Si and carbides as a result of the reaction process (marked with white arrows). Thus, extensive chemical reaction between Al and SiC, leading to brittle reaction products, should also be responsible for the reduction in hardness and modulus beyond 200°C. It should be noted, however, that annealing of the nanolaminates for 4 h at high temperature did not modify either the hardness or

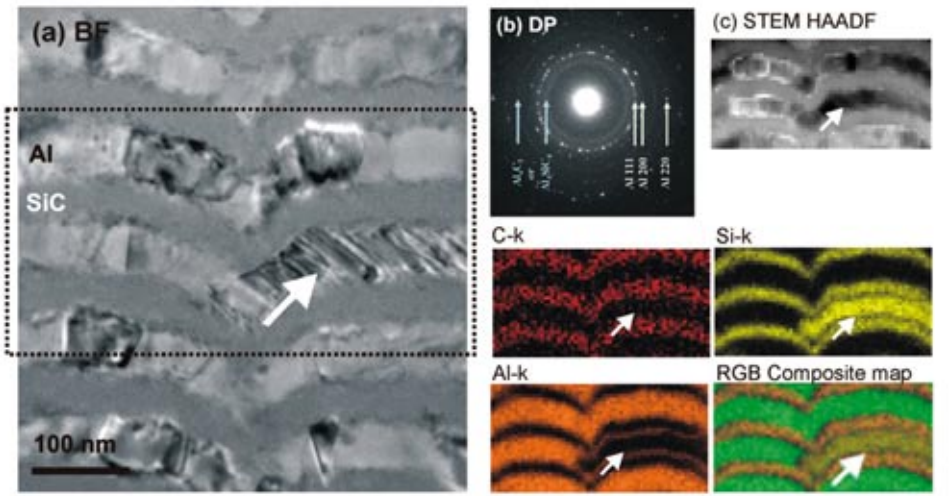

Figure 4. (a) BF TEM image of the Al/SiC nanolaminate after annealing at 300°C. The white arrow indicates one of the layers that appear dark in the SEM image of Figure 3b. (b) SADP, indicating the presence of reaction products between Al and SiC. (c) The elemental maps measured in the dashed rectangle indicate that the dark layer corresponds to a Si-rich area, presumably as a reaction product between Al and SiC.

the modulus (Figure 2) at RT, so apparently these are not severely modified by the interface embrittlement. Therefore, the flow stress of Al together with the chemical reactions at the interface determines the high-temperature nanoindentation behavior of the Al/SiC nanolaminates.

4. Conclusions

In summary, the hot hardness and modulus of Al/SiC nanolaminates were stable at temperatures up to 200°C, after which they dropped, while the postannealing hardness and modulus remained unchanged. FIB and TEM studies showed two mechanisms responsible for hardness and modulus drop with temperature, namely cracking of the SiC layers during high-temperature indentation and extensive chemical reaction between Al and SiC. The analysis of the samples deformed at high temperature also suggested the development of a self-healing mechanism in the Al/SiC nanolaminates as the Al plastically flowed to close the cracks induced in the brittle SiC layers. Finally, the results presented here demonstrate the need of high-temperature nanoindentation to ascertain the high-temperature properties of Al/SiC nanolaminates, as no microstructural changes could be inferred from the postannealing hardness and modulus at RT, which remained unchanged.

Acknowledgements

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