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CHARACTERIZATION OF STRUCTURE AND MECHANICAL PROPERTIES OF MoSi₂-SiC NANOLAYER COMPOSITES

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ABSTRACT

A systematic study of the structure-mechanical properties relationship is reported for MoSi₂-SiC nanolayer composites. Alternating layers of MoSi₂ and SiC were synthesized by DC-magnetron and rf-diode sputtering, respectively. Cross-sectional transmission electron microscopy was used to examine three distinct reactions in the specimens when exposed to different annealing conditions: crystallization and phase transformation of MoSi₂, crystallization of SiC, and spheroidization of the layer structures. Nanoindentation was employed to characterize the mechanical response as a function of the structural changes. As-sputtered material exhibits amorphous structures in both types of layers and has a hardness of 11GPa and a modulus of 217GPa. Subsequent heat treatment induces crystallization of MoSi₂ to form the C40 structure at 500°C and SiC to form the α structure at 700°C. The crystallization process is directly responsible for the hardness and modulus increase in the multilayers. A hardness of 24GPa and a modulus of 340GPa can be achieved through crystallizing both MoSi₂ and SiC layers. Annealing at 900°C for 2h causes the transformation of MoSi₂ into the C11_b structure, as well as spheroidization of the layering to form a nanocrystalline equiaxed microstructure. A slight degradation in hardness but not in modulus is observed accompanying the layer break-down.

INTRODUCTION

Enhancement of mechanical properties of nanoscale materials has been predicted and observed in a number of multilayer structures [1-2]. Specifically, metal-metal systems have shown increased yield and fracture strength [2-3]. The availability of fine scale high strength materials may extend the applications of multilayered films into high temperature environments, such as protective surface coatings for high temperature structural applications. Therefore, the transformation of phases and the stability of layering are particularly important. This study examines both issues for MoSi₂-SiC multilayer structures.

MoSi₂ is a potential matrix material for high temperature structural composites due to its high melting temperature and good oxidation resistance at elevated temperatures [4]. The two major drawbacks for structural applications are inadequate high temperature strength and poor low temperature ductility. The need for composite additions has become the focus of extensive investigations in recent years [5]. On the other hand, SiC, being elastically hard and brittle, has been used as a reinforcing second phase in various intermetallic and ceramic compound matrices. Specifically, the addition of SiC whiskers has provided significant improvement in the high temperature yield strength of MoSi₂ [6].

In a previous report [7], it was shown that these MoSi₂-SiC multilayers exhibit superior oxidation resistance and significant hardness increase through annealing at 500°C. In this study, we have systematically investigated both the evolution of phases and the stability of layers by varying the heat treating conditions. By monitoring the changes in hardness and modulus with different structural changes, a trend in the structure-mechanical properties relationship can be established in these multilayers.

EXPERIMENTAL PROCEDURE

Alternating layers of MoSi₂ and SiC were prepared by sputter deposition at a pressure of 1.33Pa with an argon flow of 10sccm/min. Prior to deposition the chamber was evacuated down to a pressure of 10⁻⁴ Pa. Silicon (111) substrates were used for most of the depositions. MoSi₂ was sputtered from a planar magnetron target at a DC power of 100-200W. Silicon carbide was sputtered from a SiC diode target at an rf power of 130-200W. The deposition rates of MoSi₂ and SiC were 32 and 7nm/min, respectively, at a power of 200W. The MoSi₂-SiC layered composites were prepared by cyclically passing the samples beneath the two targets at such a rate and target power that the constituent SiC layers had a nominal thickness of 3nm and MoSi₂ layers 10nm. A total of 90 sublayers of each kind were produced for each film. The multilayers were then annealed at 500, 600, 700, 800°C for 1h and 900°C for 2h, respectively, in a vacuum of 10⁻⁸ torr.

Investigation of the surface hardness was performed using an indentation load-depth sensing apparatus, commercially available as a Nanoindenter™ [8,9]. This instrument directly measures the load on a triangular pyramid diamond indenter tip as a function of displacement from the surface. Hardness is determined from the load data using the relation:

$$H=L(h)/A(h),$$

where L(h) is the measured load, and A(h) is the projected area of the indent as a function of the plastic depth h. The area function is determined by an iterative process involving indents into materials of known isotropic properties [9]. Measurements were made under a constant load rate of 20mN-sec⁻¹ to a nominal depth of 70nm. Typically nine indents were made on each sample and the data averaged. The depth of the indents was chosen to be less than 10% of the total thickness of the nanolayered composites [10]. As discussed by Doerner and Nix [11], the actual depth of the indent includes the plastic depth as well as the elastic recovery of the material as the indenter is removed. Following their analysis, we used the unloading portion of the curve to estimate the elastic contribution to the total displacement. This analysis assumes a homogeneous material, rather than a layered surface structure, but the limitation on the depth of the indentation should validate this assumption.

As-deposited and annealed multilayers were made into cross-sectional transmission electron microscopy (XTEM) specimens and were examined using conventional and high resolution transmission electron microscopy (HRTEM) on a Phillips CM30ST microscope operating at 300kV. Optical diffractograms were taken from the lattice images; the patterns were then analyzed to identify the phase and orientation of each pattern.

RESULTS

Microstructural Characterization

Fig. 1(a) shows the XTEM image of the as-deposited multilayers. The average layer thickness was estimated to be 15nm and 2.7nm for MoSi₂ and SiC layers respectively. Selected area diffraction (SAD) patterns taken from the multilayered region revealed the amorphous structure as is represented by the diffuse rings in Fig. 1(b). Annealing the multilayers at 500°C for 1h induces crystallization of the amorphous MoSi₂ to form the hexagonal C40 structure which is a metastable structure of MoSi₂ [12]. SiC, on the other hand, remains amorphous.

Fig. 2(a), taken after annealing at 700°C, shows that the layer structure is preserved. Careful examination of the SAD pattern (Fig. 2(b)) indicates the presence of a few extra spots (indicated by circles) superimposed on the continuous ring patterns of the polycrystalline C40 structure. Analysis of the extra spots discloses that these extra reflections can be matched to the 6H structure and possibly other polytypes of α-SiC. XTEM image of an 800°C 1h-annealed multilayers is shown in Fig. 3(a). The two major differences between the 700° and 800°C annealed specimens are that the MoSi₂ layer dimension changes and the SiC layer morphology changes.

The average grain size within the MoSi₂ layers has increased by ~20% from 15nm to 18nm. The SiC layers have broken down to form discontinuous segments. Fig 3(b) shows a HRTEM image of the layer structure. It can be seen that some parts of the SiC layers (originally ~2.7nm thick) have spheroidized to form equiaxed shaped grains (grain size ~18nm) and extended into the original MoSi₂ layers. As a result, the grains in the MoSi₂ layers has grown outward towards the adjacent MoSi₂ layers to take up the space originally occupied by the layered SiC. In addition to the change in layer morphology, evidence from the SAD pattern suggests the onset of the phase transformation of MoSi₂ to the stable tetragonal C11_b structure.

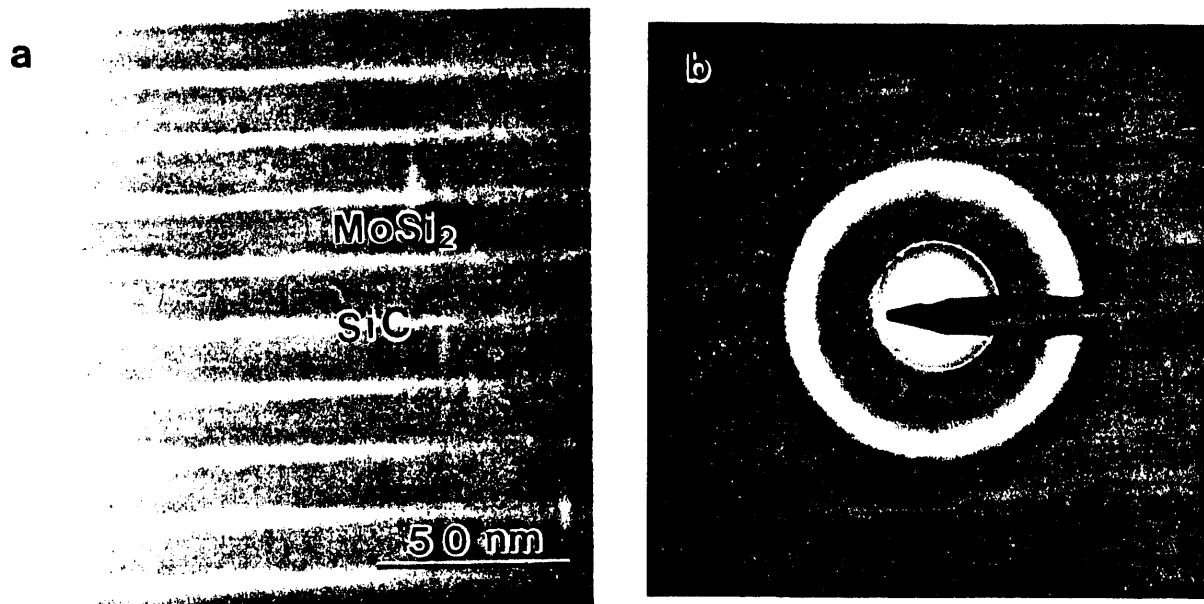


Fig. 1(a) XTEM micrograph showing the as-sputtered MoSi₂-SiC multilayers. Darker layers are MoSi₂, and the lighter layers are SiC. Fig. 1(b) Corresponding SAD pattern showing the amorphous structure in both layers.

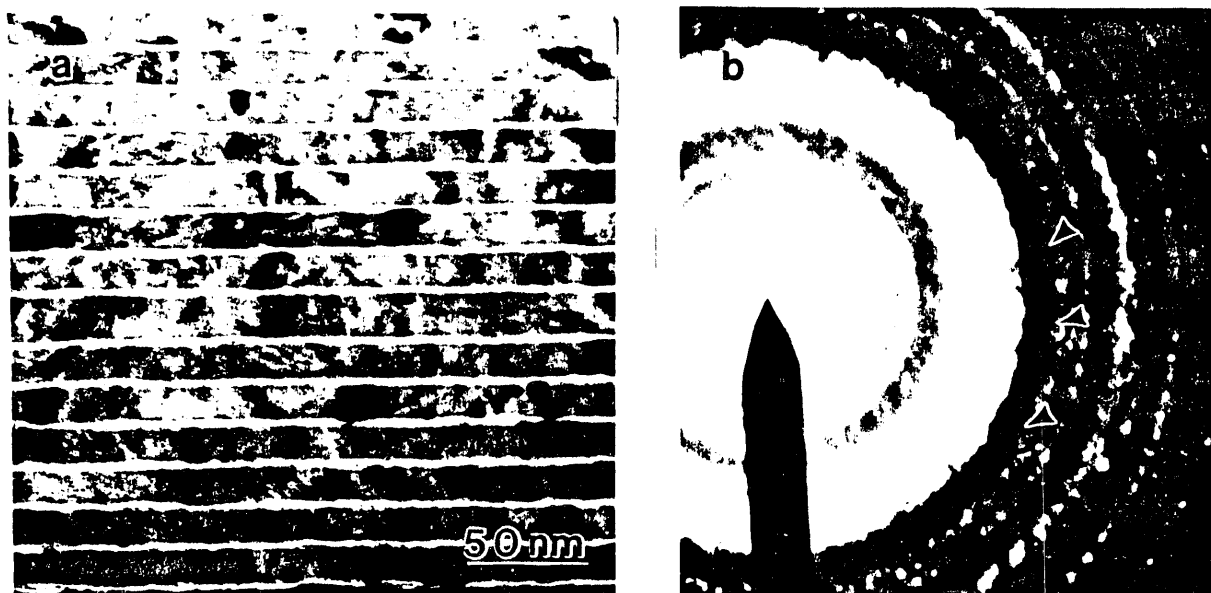


Fig. 2(a) Layered structure of MoSi₂-SiC multilayers annealed at 700°C for 1h. (b) SAD pattern showing extra spots corresponds to 6H structure and possibly other polytypes of α -SiC (indicated by circles) superimposed on polycrystalline rings of C40-MoSi₂.

900°C annealing for 2h has caused the break-down of the layered structure to form an equiaxed nanocrystalline composite. Fig. 4(a) shows a dark field image of the composite. The average grain size is in the range of 30nm, while there are a few larger grains (indicated by arrows) having diameters between 200 and 400nm. Some of the very large grains were identified to be 6H-SiC. The SAD pattern indicates that all of the C40 phase MoSi₂ has transformed at this temperature to form the stable C11_b structure. Fig. 4(b) shows a lattice image of an interface between a MoSi₂ grain ($d_{002}=3.92\text{\AA}$) and a 6H-SiC grain ($d_{10\bar{1}4}=2.17\text{\AA}$). The interface is free of any glassy phase.

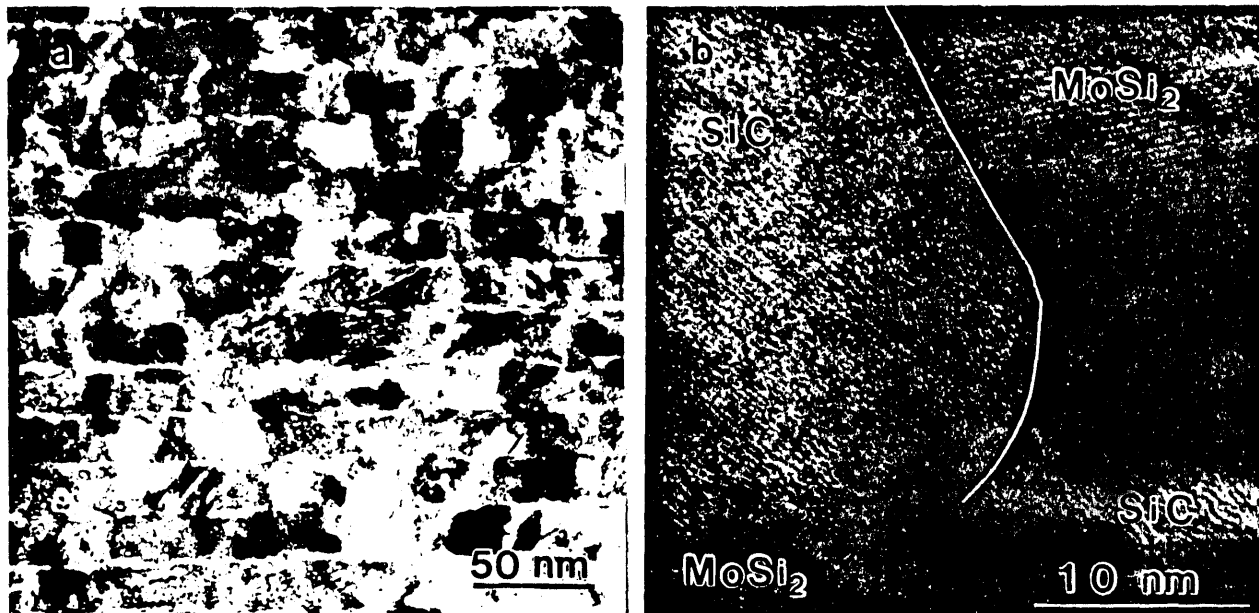


Fig. 3 (a) XTEM micrograph of an 800°C 1h-annealed multilayers. (b) HRTEM image showing evolution of layered structure: spheroidization and growth of SiC into the original MoSi₂ layer.

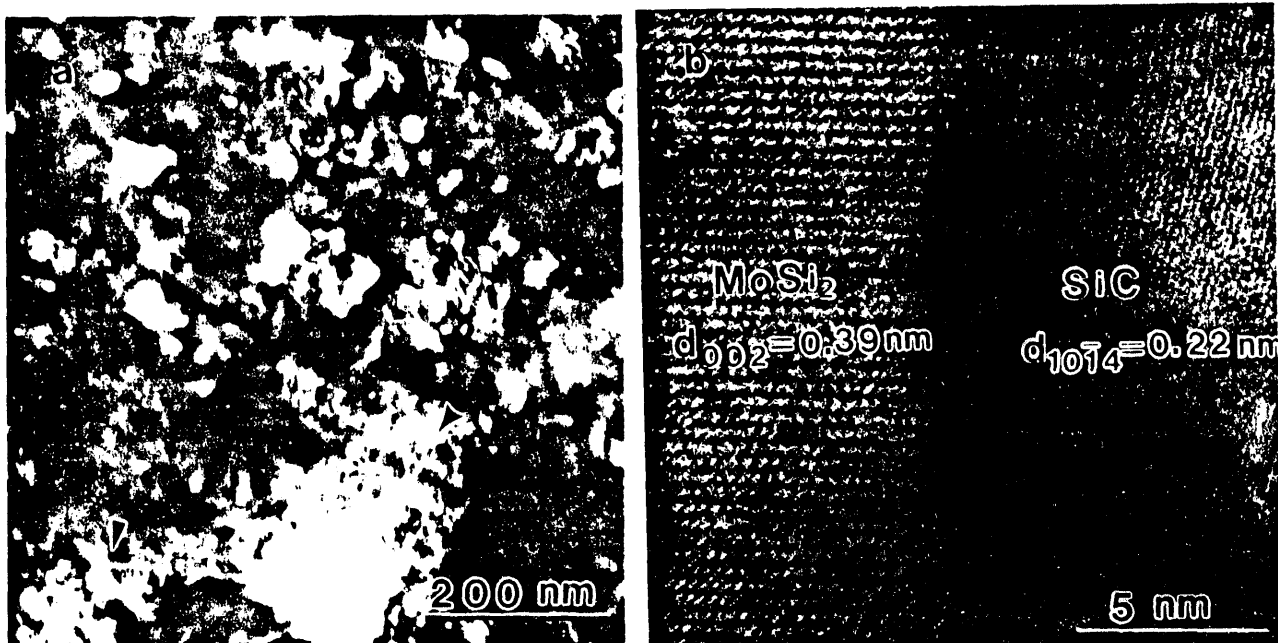


Fig. 4(a) Dark field image of a 900°C 2h-annealed composite showing equiaxed microstructure. The average grain size is ~30nm with a few large grains (as indicated by arrows) in the 300nm range. (b) HRTEM lattice image of an interface between two neighboring grains of C11_b-MoSi₂ ($d_{002}=3.92\text{\AA}$) and 6H-SiC ($d_{10\bar{1}4}=2.17\text{\AA}$).

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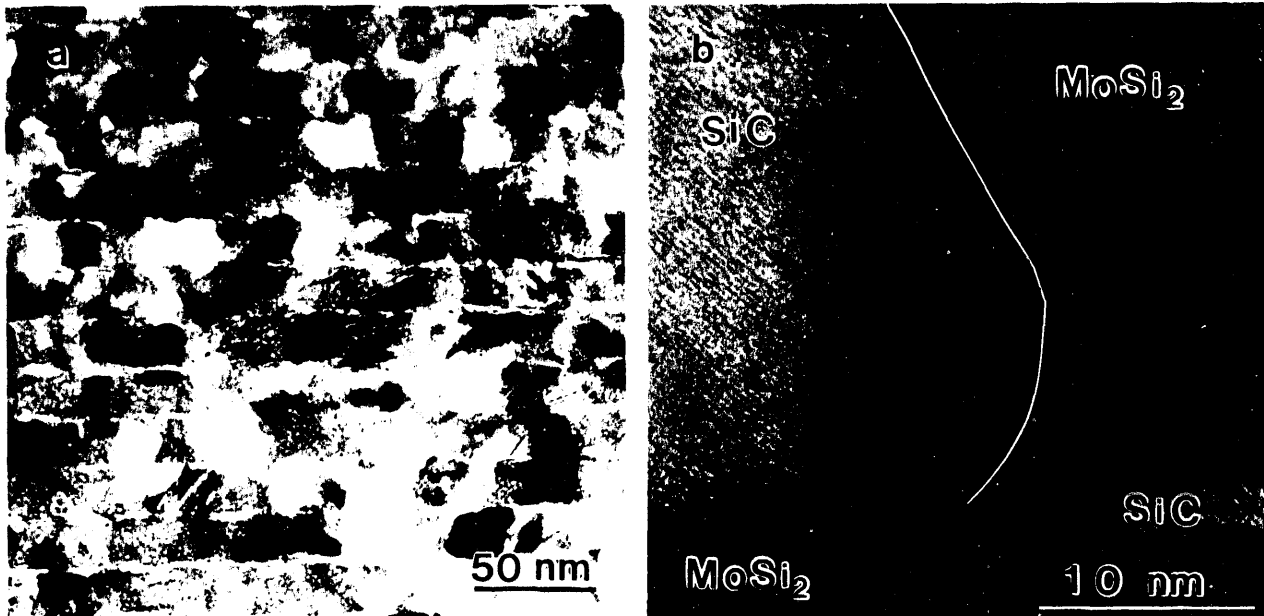


Fig. 3 (a) XTEM micrograph of an 800°C 1h-annealed multilayers. (b) HRTEM image showing evolution of layered structure: spheroidization and growth of SiC into the original MoSi_2 layer.

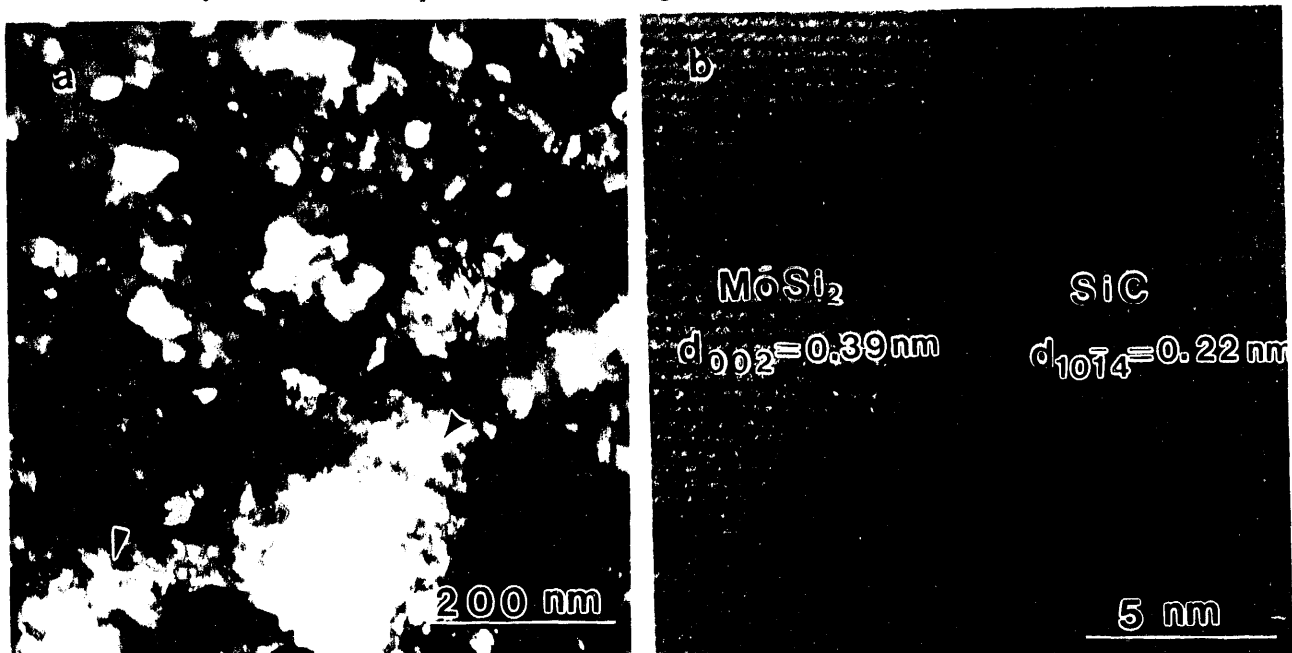


Fig. 4(a) Dark field image of a 900°C 2h-annealed composite showing equiaxed microstructure. The average grain size is $\sim 30\text{nm}$ with a few large grains (as indicated by arrows) in the 300nm range. (b) HRTEM lattice image of an interface between two neighboring grains of C11_b- MoSi_2 ($d_{002}=3.92\text{\AA}$) and 6H-SiC ($d_{10\bar{1}4}=2.17\text{\AA}$).

The average grain size within the MoSi₂ layers has increased by ~20% from 15nm to 18nm. The SiC layers have broken down to form discontinuous segments. Fig 3(b) shows a HRTEM image of the layer structure. It can be seen that some parts of the SiC layers (originally ~2.7nm thick) have spheroidized to form equiaxed shaped grains (grain size ~18nm) and extended into the original MoSi₂ layers. As a result, the grains in the MoSi₂ layers has grown outward towards the adjacent MoSi₂ layers to take up the space originally occupied by the layered SiC. In addition to the change in layer morphology, evidence from the SAD pattern suggests the onset of the phase transformation of MoSi₂ to the stable tetragonal C11_b structure.

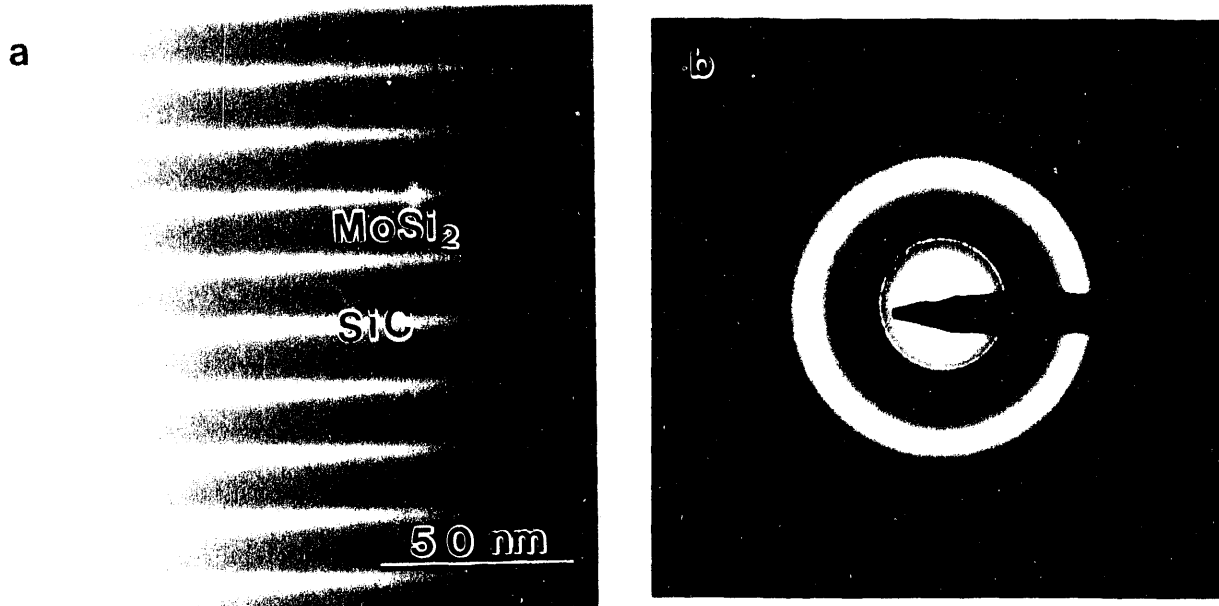


Fig. 1(a) XTEM micrograph showing the as-sputtered MoSi₂-SiC multilayers. Darker layers are MoSi₂, and the lighter layers are SiC. Fig. 1(b) Corresponding SAD pattern showing the amorphous structure in both layers.

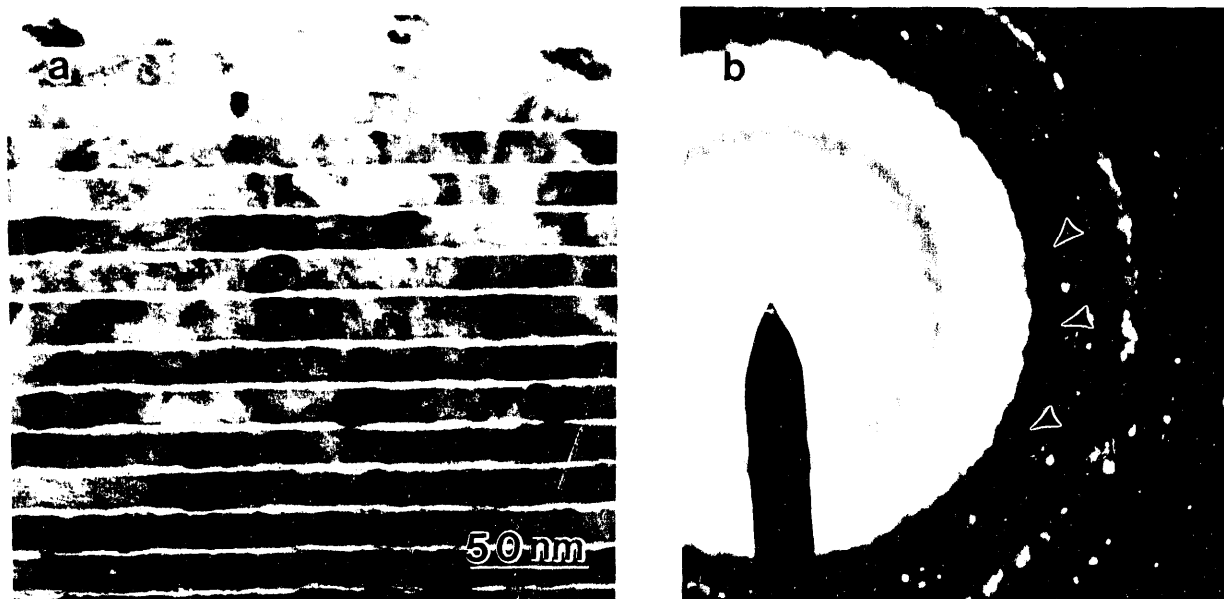


Fig. 2(a) Layered structure of MoSi₂-SiC multilayers annealed at 700°C for 1h. (b) SAD pattern showing extra spots corresponds to 6H structure and possibly other polytypes of α -SiC (indicated by circles) superimposed on polycrystalline rings of C40-MoSi₂.

Nanoindentation Measurements

The hardnesses and moduli of the multilayered composites determined by nanoindentation are listed in Table I. All indents have a penetration depth less than 10% of the total thickness to avoid any influence from substrate effects. The scatter of the data is in average less than 4% of the value averaged from the nine measurements. The measured hardness and modulus of the as-sputtered multilayer are 11GPa and 217GPa, respectively. A 500°C-1h anneal has increased the hardness by almost 80% (20GPa) and the modulus by 30% (290GPa). This effect is mainly due to the crystallization of the MoSi₂ layers. Another significant change in hardness and modulus occurred after a 700°C annealing for 1h. An increase in hardness to 24GPa and in modulus to 326GPa corresponds well with the evidence of the SiC layer being crystallized at temperature at or above 700°C in the multilayers.

Not much change in either hardness or modulus was detected by increasing the annealing temperature to 800°C even though the layering started to show signs of breaking down. After the layers spheroidized at 900°C, a slight decrease in hardness was observed from 23.8 to 21.6GPa, perhaps due to grain size effect, while the modulus remained at ~340GPa.

Table I Hardness and Modulus of MoSi₂-SiC Multilayered Films

Condition	Layer Structure	Phase: MoSi ₂ / SiC	Hardness (GPa)	Modulus (GPa)
As-Sputtered	Layered	Both Amorphous	11.5	217
500°C-1h	Layered	C40 / Amorphous	20.8	290
700°C-1h	Layered	C40 / α	24.0	326
800°C-1h	Partially Layered	C40+C11 _b / α	23.8	344
900°C-2h	Equiaxed	C11 _b / α	21.6	338

DISCUSSION

The phase transformation behavior of MoSi₂ layers within the multilayers agrees well with that of single phase MoSi₂ films [13,14]. It has been shown that, at ~500°C, the C40 structure crystallizes from the amorphous structure, while at temperatures above 800°C it starts to transform to the C11_b structure. This agreement suggests that the presence of SiC layers pose no influence on the crystallization process of MoSi₂ within the temperature range studied.

The clue to the onset of layer spheroidization was obtained by examining the 800°C 1h-annealed multilayers. The significant growth and coarsening of SiC into MoSi₂ layers, as compared to the relatively mild grain growth in MoSi₂ layers, suggests that the coarsening process may be favorable both thermodynamically and kinetically. One obvious driving force is the reduction in interfacial area/energy through spheroidization. It has also been shown that the carbon self diffusion rate through grain boundaries in SiC is several orders of magnitude larger than either carbon or silicon lattice diffusion [15]. On the other hand, the diffusion of Mo and Si in MoSi₂ is very slow below ~1200°C [16]. No quantitative comparison can be made of the self diffusion coefficients of Mo, Si and C due to the scarcity of comparable diffusion data. It can only be speculated that the abundance in interface area may provide favorable diffusion paths for C (and possibly also Si) to complete the growth process.

It has been demonstrated in this study that the mechanical properties are directly related to the crystallization process in multilayered films. Significant improvement in both hardness and modulus can be achieved through crystallization of both MoSi₂ and SiC layers while still maintaining the layering structure. A maximum hardness value of 24GPa was obtained, which is higher than either single crystal MoSi₂, 10GPa (nanoindentation) [17], or reaction sintered MoSi₂-

30v/oSiC, 14.2GPa (microindentation) [18]. One possible explanation for the high hardness value is the nanocrystalline structure of these films.

The preservation of the nanocrystalline structure (grain size ~30nm) after 900°C annealing may be attributed to two factors. One is the slow diffusion process in MoSi₂ at this temperature. Secondly, the presence of homogeneously distributed SiC among the matrix may be imposing constraints on the MoSi₂ grain boundaries to prevent severe grain growth. The maintenance of high hardness even after layer break-down shows the potential of the multilayers to be used for high temperature coating applications. Future experiments have been planned to investigate the effect of prolonged high temperature exposure on the mechanical properties.

CONCLUSIONS

Amorphous structures are present in the as-sputtered multilayers. Crystallization of MoSi₂ and SiC layers significantly increases the hardness and modulus. A maximum hardness of 24GPa and a modulus of 326GPa are obtained through annealing at 700°C for 1h where layered MoSi₂ (C40) and SiC (α plus other polytypes) remain stable. The onset of layer spheroidization starts when annealing at ~800°C. Increasing the temperature to 900°C for 2h causes the complete layer break-down to form a nanocrystalline equiaxed microstructure and the transformation of MoSi₂ to the C11b structure. A slight decrease in hardness is observed accompanying this structural change.

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