**MICROSTRUCTURE AND MECHANICAL PROPERTIES OF NITRIDED
MOLYBDENUM SILICIDE COATINGS**

TITLE:

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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF NITRIDED MOLYBDENUM SILICIDE COATINGS.

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ABSTRACT

Mo-Si-N films with a high nitrogen concentration were produced by sputter-deposition in the presence of nitrogen plasma. The chemical composition was determined with Rutherford backscattering and nuclear reaction analysis. The ratio of Mo to Si was 1:2 in the coatings with a nitrogen concentration of 50 %. The microstructure of the as-deposited coatings on a silicon substrate was amorphous and no crystallization was found after annealing up to 1000 °C, although some relaxation was observed in X-ray diffraction. This was confirmed in high-resolution transmission electron microscope examination. The hardness of the Mo-Si-N films was 18.8 GPa as determined with a nanoindenter. This is significantly higher than that of MoSi₂ films, 11.2 GPa. The hardness of the Mo-Si-N films increased to 24.4 GPa after annealing at 800 °C, which is approximately the same as the hardness of the high-temperature tetragonal phase of MoSi₂, 25.5 GPa. Similarly, the modulus of the as-deposited Mo-Si-N film was higher (257 GPa) than that of the MoSi₂ film (222 GPa). However, only a slight increase in the modulus of the Mo-Si-N film was found after annealing at 800 °C, whereas the modulus of the crystallized tetragonal MoSi₂ was 382 GPa. No cracking was found in the Mo-Si-N films even after annealing at 1000 °C.

INTRODUCTION

The excellent oxidation resistance of molybdenum disilicide (MoSi₂) is widely known, as is its lack of ductility at low temperatures [1]. This disadvantage restricts the extensive use of MoSi₂ as a structural material. When applied as a coating, a more ductile base material can be used, and in this way the problem may be partly avoided. However, thermal stresses due to a mismatch of thermal expansion coefficients may result in cracking which will eventually degrade the good protective properties. In addition, possible transformation stresses in a coating can also result in cracking.

Reinforcement with particulates or fibers, such as TiB₂, Al₂O₃, and SiC [2,3], or combination with a ductile phase such as tantalum [4] have been used to reduce the low-temperature brittleness of MoSi₂. In these cases, at best an improvement in the fracture toughness from 2.7 to 4.9 MPa/m^{1/2} was reported [4]. Recently a new approach, refinement of the microstructure down to the nanometer scale, has been used to enhance the mechanical performance of materials. In our previous work, we have reported the deposition and characterization of MoSi₂/SiC composite coatings [5]. Layered nanostructures were produced by sputter deposition. The main purpose of the SiC layers was to prevent a crystal growth of MoSi₂. Silicon carbide was chosen as a constituent because of the thermodynamic stability of a MoSi₂/SiC pair [6]. However, no improvement in room temperature toughness was observed, although indentation fracture measurements indicated different fracture behavior when compared to that of a single MoSi₂ layer.

Cracking of the MoSi₂/SiC composite coatings was, however, reduced during oxidation at relatively low temperatures. In fact a reduction of 66% in the crack line density was observed as compared to the cracking of a single MoSi₂ coating with approximately identical thickness. The

composite coating still possessed good oxidation resistance, but differences were detected in the oxidation mechanism [7].

Previous experience suggests the possibility of cracking can be reduced by improving the ductility of the coating, by attaining an enhanced compatibility of elastic and thermal expansion properties between the base material and the coating, or by avoiding phase transformations. In this work we have successfully applied most of these principles by producing amorphous molybdenum silicide with a significantly higher crystallization temperature than usual. This was obtained by nitrogen alloying simultaneously during the sputter deposition.

EXPERIMENTAL PROCEDURE AND MEASUREMENTS

Single crystal silicon wafers and unalloyed carbon steel were employed as substrates. Prior to deposition the steel samples were mechanically polished, degreased in TCE, acetone and isopropanol, and finally sputter cleaned. A 1:50 HF:H₂O solution was used to remove the native oxide of the silicon wafers. Depositions on the silicon substrates were used to determine the chemical composition of the coatings (using Rutherford backscattering (RBS) spectroscopy and the 429 KeV resonance of the reaction $^{15}\text{N}(p,\alpha-\gamma)^{12}\text{C}$ [8] (NRA)), in nanoindentation measurements, in transmission electron microscopy (TEM), and in x-ray diffraction (XRD) examinations. Oxidation, corrosion, and thermal cracking measurements were performed on the steel samples. In this paper we report on the results obtained concerning the coatings on the silicon substrates.

Sputter deposition was carried out at a pressure of 1 Pa with an argon and nitrogen flow of 10 sccm/min. The nitrogen gas concentration in the flow was 50 %. Prior to deposition the chamber was evacuated down to a pressure of 10^{-4} Pa. Molybdenum silicide was sputtered from a planar magnetron MoSi₂ target with a diameter of 100 mm at a DC power of 200 W. The deposition rate was 27 nm/min. MoSi₂ coatings without nitrogen were also deposited onto the same substrate materials for reference. The thickness of the coatings varied from 1.2 μm to more than 3 μm .

In order to investigate the effect of heat treatment on the microstructure, the hardness and elastic properties, and the cracking of the coatings, annealing was performed in a quartz tube furnace at a temperature range of 450 - 1000 °C. Both the as-sputtered and annealed (1 h at 800 °C) Mo-Si-N coatings were made into cross-section TEM (XTEM) specimens using M-bond 610 for structural characterization. The specimens were examined using conventional and high-resolution transmission electron microscopy (HRTEM) on a Phillips CM30ST microscope operating at 300 kV. Thermal cracking was examined with a scanning electron microscope (SEM). The hardness and elastic properties were determined with a commercially available nanoindentation instrument.

RESULTS AND DISCUSSION

In Fig. 1 RBS spectra from as-deposited Mo-Si-N films are shown. The molybdenum to silicon ratio corresponds well to that of the sputtering target, $[\text{Mo}]:[\text{Si}] = 1:2$. The nitrogen concentration, determined from NRA, was 50 at. % and the concentration profile very uniform, as can also be seen in Fig. 1.

An isothermal section of the Mo-Si-N ternary phase diagram at 1400 °C is given in reference [9]. In the Mo-Si-N system silicon nitride Si₃N₄ can coexist with both MoSi₂ and MoSi₃ but no molybdenum nitride is stable without excess nitrogen at temperatures above 1000 °C. The third silicide of the Mo-Si system is Mo₃Si. Nitrogen is considered as practically insoluble in MoSi₂. The composition of our coatings is located quite close to silicon nitride

(Si_3N_4) on the isothermal section of the Mo-Si-N phase diagram. In fact, in ESCA measurements, a strong chemical interaction between silicon and nitrogen was observed, whereas in the MoSi_2 films the only bond type was the silicide type between silicon and molybdenum. It should be noted that chemical interaction between silicon and nitrogen is much stronger (heat of formation -25.6 kcal/g-at. [10]) than that between silicon and molybdenum (heat of formation -9.3, -8.5, and -5.8 Kcal/g-at for MoSi_2 , Mo_5Si_3 , and Mo_3Si respectively [11])

Fig. 1. RBS spectrum and nitrogen distribution of the Mo-Si-N coating.

The microstructure of both the as-deposited MoSi_2 and Mo-Si-N films was amorphous as determined by XRD. After annealing at 500 °C in a vacuum furnace, MoSi_2 films crystallize to a hexagonal structure, which is the stable phase of molybdenum disilicide at low temperatures. Nitrided Mo-Si-N films are still amorphous after annealing, as indicated by the broad diffuse feature in the spectrum. Even after annealing at 1000 °C the microstructure of these films remains amorphous. However, changes in the shape of the amorphous feature of the Mo-Si-N after annealing at high temperatures can be observed, which relate to a relaxation of the structure. This was also confirmed by TEM results. HRTEM observation of the as-deposited films revealed the amorphous structure as shown in Fig. 2(a). Fig. 2(b) shows the corresponding selected area diffraction (SAD) pattern. The diffuse rings indicate the presence of an amorphous structure which is consistent with the observation in (a). By measuring the diameter of the innermost ring and converted to the real space spacing using the known camera constant, the nearest neighbor distance was estimated to be 2.30 Å.

As discussed above, annealing the Mo-Si-N films at 800 °C for 1 h failed to crystallize the amorphous structure, as shown in Fig. 3(a). Fig. 3(b) shows the corresponding SAD pattern which confirms the amorphous nature of the structure. Even though Fig. 3 shows the amorphous structure, careful examination of the two structures reveals the difference in their detailed microstructure. After the 800 °C anneal, the amorphous structure seems to have a coarser microstructure and a different nearest neighbor spacing than the as-sputtered film. The latter difference is confirmed by comparing the diameters of the innermost ring on the SAD patterns. The ring diameter of the annealed film is 2.5% larger than the as-sputtered one, and corresponds to a nearest neighbor spacing of 2.25 Å. The decrease in the nearest neighbor spacing from 2.30 to 2.25 Å suggests that the annealing may have reduced the free volume in the as sputtered films and caused the densification of the coatings.

Fig. 2. (a) Cross-section TEM micrograph of an as-deposited Mo-Si-N coating.
(b) Corresponding SAD pattern.

Fig. 3. (a) Cross-section TEM micrograph of the Mo-Si-N coating annealed at 800 °C for 1 h
(b) Corresponding SAD pattern.

In Table 1, the mechanical properties of the as-deposited and heat treated Mo-Si-N films are shown. For comparison, the modulus and hardness of MoSi₂ films with different microstructures are given. The modulus of the as-deposited Mo-Si-N films is somewhat higher than that of the as-deposited MoSi₂ films. However, tetragonal MoSi₂ films have a significantly higher modulus, 382 GPa, reflecting the transformation to a crystalline phase. The fact that the modulus of the Mo-Si-N films remains fairly low may result in much lower residual and thermal stresses in these films. The value of the modulus of the Mo-Si-N coatings is, in fact, quite close to that of the most common steels, about 210 GPa.

Table 1. Mechanical properties of Mo-Si-N and MoSi₂ thin films.

Sample	Modulus [GPa]	Hardness [GPa]
As-deposited Mo-Si-N (amorphous)	257	18.8
Annealed 1 h @800 °C (amorphous)	273	24.4
As-deposited MoSi ₂ (amorphous)	222	11.2
Annealed 1 h @500 °C (hexagonal)	278	22.0
Annealed 1 h @900 °C (tetragonal)	382	25.5

Indentation measurements show that after annealing at 800 °C, the hardness of the Mo-Si-N films has increased from 18.8 to 24.4 GPa, while little difference in modulus was observed. The increase in hardness could be the result of the densification process discussed above. In any case, the hardness of the Mo-Si-N films is much higher than that of the amorphous MoSi₂ films. However, since no crystallization process is involved, one would not expect the elastic properties of the materials to change much, which is consistent with the small change in modulus observed in this case.

Thermal cracking was examined by annealing the samples at different temperatures in vacuum and viewing the possible cracking in a scanning electron microscope. In Fig. 4 SEM micrographs of the samples annealed at different temperatures are shown. Cracking is seen in the MoSi₂ coatings even after annealing at relatively low temperatures. In contrast, no cracking is observed on the Mo-Si-N coatings, even after annealing at 1000 °C. This absence of cracking may be due to several reasons. The modulus of the Mo-Si-N coating is closer to that of the substrate. There is no phase transformation (which could cause transformation stresses) in the temperature range investigated. Finally, the fracture toughness of amorphous material may be higher than that of crystalline material, although no direct evidence of this was obtained in the current experiments. This resistance to thermal cracking makes Mo-Si-N coatings very attractive for protective coatings in corrosive and hostile environments at elevated temperatures.

Fig. 4. SEM micrographs of MoSi₂ coating annealed at 600 °C and Mo-Si-N coatings annealed at 600 and 1000 °C.

CONCLUSIONS

Based on our observations, we can conclude that: i) molybdenum-silicon films with high nitrogen concentrations can be deposited by DC sputtering in the presence of a nitrogen plasma, ii) nitrogen significantly increases the crystallization temperature of molybdenum-silicon films, iii) the hardness and modulus of Mo-Si-N films are higher than those of amorphous MoSi₂ films; (after recrystallization into a tetragonal structure, the modulus of MoSi₂ films is greater than that of amorphous Mo-Si-N films), iv) thermal cracking of Mo-Si-N films is almost completely prevented at temperatures below 1000 °C.

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