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TITLE SILICON-BASED COATINGS ON NIOBIUM METAL

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SILICON-BASED COATINGS ON NIOBIUM METAL

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ABSTRACT

Silicon coatings on niobium substrates were subjected to thermal, ion beam and laser mixing, and the effectiveness of the different methods for the synthesis of graded interfaces was compared. The resulting metal/silicon interfaces were characterized by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and Rutherford backscattering (RBS).

INTRODUCTION

Niobium alloys have become important in applications which require structural strength and high temperatures.¹ These alloys are not oxidation resistant, and require protection, especially in harsh environments. Silicon containing overlay coatings on alloys of nickel and iron have been shown to dramatically increase their resistance to oxidation and corrosion at high temperature.² Unfortunately these types of coatings tend to fail due to the formation of cracks induced by thermal stress at the substrate-coating interface. These cracks then serve as pathways for oxidation below the coating leading to catastrophic failure of the protective coating.

We have been concerned with the formation of oxidation and thermal-oxidation resistant coatings on niobium metal, as a model for more complex niobium based alloy systems.³ As part of this study we have investigated the preparation of graded interfacial layers between a niobium substrate and a silicon coating. A graded interface shows a smooth variation in the niobium and silicon concentrations, with the possibility of a constant

composition region. It is expected that these graded interfaces will have greater thermal and mechanical stability than the atomically sharp interfaces.

EXPERIMENTAL PROCEDURE

Elemental silicon (99.999% purity) was deposited by electron beam evaporation (background pressure $< 10^{-5}$ Torr) onto 2 mm thick polished niobium substrates. The substrates were sputtered with argon ions prior to and during the early stages of deposition to prevent the formation of native niobium oxide at the interface. The thickness of the coating (1800-2000 Å) was determined by RBS. One sample, A, was retained untreated while the remainder, B-H, was subjected to the following treatment. Two samples, B and C, were heated under vacuum ($< 3 \times 10^{-5}$ Torr), in a quartz tube furnace.⁴ Sample B was heated for 18 hours at 550°C, while sample C was treated to a two step anneal at 550°C and 850°C, 18 hours for each step. Two samples, D and E, were subjected to ion beam mixing with 400 KeV krypton ions at pressures below 2×10^{-7} Torr. Sample D was ion beam mixed at room temperature, and sample E was mounted on a hot stage and mixed at 300°C. Both samples were given a total dose of 3×10^{16} ions cm^{-2} which took a total of 20 minutes each sample.

Samples F-H were laser mixed in air with an excimer laser of 248 nm.⁵ A fixed spot size was used but different pulse energies produced fluences of 0.5 (F), 1.7 (G), and 2.5 (H) J cm^{-2} respectively.

The coatings were characterized by RBS, AES, XPS and low angle X-ray diffraction. RBS was carried out using 2.0 MeV He^+ ions at the Los Alamos Ion Beam Material Laboratory. AES were carried out on a Perkin-Elmer SAM-660. XPS spectra were acquired with a Surface Science Laboratories Model SSX-100 spectrometer with a monochromatized Al-K_α X-ray source ($10^{-8} - 10^{-9}$ Torr). A Guinier thin film diffractometer was used for low angle X-ray diffraction studies.

RESULTS AND DISCUSSION

The thermally annealed samples, B and C, were coloured blue (B) and purple (C). The SEM showed no significant difference between the thermally annealed samples and the untreated sample.

The AES sputter depth profiles of samples B-E and G are shown in Figure 1. The slightly broadened interfacial region in the low temperature (550°C) annealed sample, B (Figure 1b) as compared to the untreated sample, A (Figure 1a) is consistent with the slow diffusion of Nb and Si at temperatures below 800°C. Sample C not only shows a more pronounced diffusion region but possibly a constant composition region.

Figure 1. AES depth profile of silicon layers on niobium substrates: (a) untreated, (b) one step annealed, (c) two step annealed, (d) room temperature ion mixed, (e) 300°C ion mixed, (f) 1.7 J cm⁻² laser mixed.

The AES data shows that the room temperature mixed sample (Figure 1d) has a wider interface layer than that obtained from the one and the two step anneals but at a similar composition. Samples B, C and D do not show interface layers with well defined composition regions. The sample given the ion beam mixing at 300°C (E) has a nearly uniform interfacial layer composition (Figure 1e). No NbSi₂ could be detected by X-ray diffraction.

RBS spectra of samples D and E, subjected to ion beam mixing at room temperature and 300°C respectively, are shown in Figure 2. The spectra clearly show that more mixing takes place in the sample mixed at 300°C as compared to room temperature.

Figure 2. RBS spectra of the ion beam mixed samples, D and E, as compared to the as deposited sample, A.

The RBS spectra of the laser mixed samples F-H are shown in Figure 3 along with that of the as deposited sample (A). Sample G mixed with a fluence of 0.5 J cm⁻² does not show an obvious constant phase region, but shows mixing on a scale comparable to the 300°C ion mixed sample. By contrast the samples mixed at

1.7 Jcm⁻² and 2.5 Jcm⁻² show substantial mixing as well as regions of constant composition. AES depth profile analysis of sample G (Figure 1f) is consistent with the RBS data, while the XPS spectrum (Figure 4) and X-ray diffraction ($\phi=5^\circ$)⁶ of H confirm that the mixed zone to consist of polycrystalline NbSi₂.

Figure 3. RBS spectra of the laser mixed samples, F, G and H.

Figure 4. In 3d, curve fitted XPS spectral components for sample H. Peak positions and assignments are included (eV).

CONCLUSION

It is clear that ion beam and laser mixing are more effective than thermal annealing for the preparation of wide graded interfacial layers between niobium metal substrate and silicon coatings. In addition to a broad interfacial region, a constant composition mixed zone is produced by high energy laser mixing.

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