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and Tantalum Using High-Energy Resonant Helium Backscattering

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**OXIDATION STUDIES OF YTTRIUM IMPLANTED COPPER,
MOLYBDENUM AND TANTALUM USING HIGH- ENERGY RESONANT
HELIUM BACKSCATTERING**

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The $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ resonance at 8.8 MeV was used to determine the oxidation rates of Y implanted Cu, Mo and Ta. At back angles this resonance has an uniform cross section of ≈ 25 times the coulomb cross section over an energy range of ≈ 0.6 MeV, allowing the surface oxidation of metals to be easily determined without the necessity of weighing the samples. Oxidations were made at 200 °C, 400 °C and 500 °C for Cu, Mo and Ta respectively and for times ranging from 10 min to 10 h. At short times the oxidation is enhanced in the Y implanted materials as compared to unimplanted materials. However, as the oxidation times increase the oxidation rate in the implanted materials fall, and in the case of Cu and Ta the total amount of oxygen in the implanted samples eventually becomes lower than that of the unimplanted samples. In all cases Y implantation strongly effects the oxidation process. For Ta and Cu retardation of grain boundary oxidation occurs. For Mo, implantation produces a discrete oxide layer which grows in a layer-by-layer manner. These data indicate that the Y-Cu and the Y-Ta oxides are more passivating than their unimplanted counterparts.

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1. Introduction

Ion implantation has several attributes which distinguish it as a means of oxidation protection. Ion implantation alters only the top few microns of a material, and, unlike traditional forms of alloying, it is unlikely to change the bulk materials properties. In contrast to oxidation resistant coatings, ion implantation will not alter the dimensions of the treated specimen. Finally, stresses which can occur between the coating and base material are not of great concern since ion implantation creates a composition gradient near the surface of the material.

This study was performed for two reasons: The first was to evaluate the effect of Y ion implantation on the oxidation of Mo, Ta and Cu. Yttrium was chosen for its known ability to produce passivating oxides. In addition, Y is immiscible with Mo and Ta making ion implantation the only possible means for alloying. In contrast, Y alloys readily with Cu. The second was to demonstrate the use of high-energy resonant backscattering of alpha particles to determine the amount of oxidation.

2. Experimental Procedure

Commercial purity Cu (.049 in thick), Mo (.030 in.) and Ta (.030 in.) were cut into 1 cm² specimens. One surface of each specimen was polished with successively finer diamond pastes, and finally, to a mirror finish with a suspension of Cr₂O₃ and Linde B powder.

One half the polished surface was masked with an Al sheet while the other half was implanted with a dose of 3×10^{16} of 160 keV Y⁺ ions for the Cu and Mo and 200 keV for the Ta specimens. The projected range was calculated by TRIM¹ to be $\approx 350 \text{ \AA}$. All implantations were performed with the sample stage and a surrounding cryoshield cooled by flowing liquid nitrogen to limit both the Y interaction with the specimens and surface contamination during implantation.

The oxidations were carried out at ambient pressure in a quartz cylinder tube furnace under oxygen flowing at a rate of ≈ 0.2 SCFH. Because each specimen had an implanted and unimplanted region both received identical anneals. Copper was oxidized at 200 and 400 C, Mo at 400 C and Ta at 500 C. Oxidation times ranged from 10 min to 10 hr.

High-energy resonant backscattering analysis was performed at the Los Alamos Ion Beam Materials Laboratory with a National Electrostatics Corp. 9SDH-2 tandem accelerator. He⁺⁺ ions with an incident energy of 8.8 MeV bombarded the specimen and

were detected at a scattering angle of 167° . At this energy a wide, flat resonance in the $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$ reaction allows for enhanced oxygen detection over a range of 8.2 to 8.8 MeV. The usefulness of this resonance for oxygen analysis has been previously demonstrated by Barbour et al.² and Martin et al.³ In addition, the scattering from Y and Ta is known to be Coulomb⁴ but non-Rutherford for Cu. The oxygen cross section is $\approx 25\times$ the Coulomb cross section at 8.8 MeV. To enhance the measurement of the oxygen concentration as a function of depth the specimens were tilted at an angle of 60° with the incident beam (except for 600 min Ta which had 0° tilt). The spectra were normalized to the simulation of RUMP⁵ for the unoxidized metal. The amount of oxidation was determined by integrating the oxygen peaks in the spectra and then applying the O cross section at 8.8 MeV to obtain the number of O atoms/cm². The amount of oxygen in the specimens was measured prior to annealing and found to be negligible.

3. Results

Molybdenum

Backscattering data from the region of the spectra near the oxygen signal from both unimplanted and implanted Mo oxidized at 400C for various times are shown in fig. 1. The data consistently shows greater oxidation in the implanted regions than in the unimplanted regions both of which were oxidized under similar conditions. Both the implanted and unimplanted specimens saturate to the stoichiometry $\text{Mo/O} \approx 1/3$. However the shapes of the O signals differ significantly suggesting a difference in oxidation behavior between the implanted and unimplanted regions. In the unimplanted case the oxygen backscattered signal shows a slow accumulation of oxygen at the surface while also developing a low-energy tail. For the implanted Mo, the O signals show the evolution of a very discrete oxide layer with a constant stoichiometry of $\text{Mo/O} \approx 1/3$. Continued annealing results in a layer-by-layer growth of the surface oxide which saturates at a maximum thickness of $\approx 10,000 \text{ \AA}$.

Optical and scanning electron microscopy provided little insight into the oxide morphology or mechanisms of oxide formation. The implanted regions displayed a regular pattern of uniform and bright interference colors indicating a transparent oxide.

Tantalum

Backscattering data from the region of the spectra near the oxygen signal from both unimplanted and implanted Ta oxidized at 500C for various times are shown in fig 2. However, care must be taken in interpreting the Ta data because the low energy tails of the

data, particularly in the unimplanted specimens, exceed the width of the resonance, and exceeds the analytical capability of this method. The effect of this is to increasingly underestimate the amount of oxidation as the oxidation time increases. However, the data, although not quantitative, does give the trend in the oxidation rate. As in the Mo specimens, the implanted Ta has a higher initial oxidation rate. However, after the high initial rate the implanted Ta stops oxidizing until long annealing times while the unimplanted specimen develops a long oxygen tail. Note that the 600 min data was taken with a tilt angle of 0° . For both unimplanted and implanted specimens, a signal height analysis yields a stoichiometry of $\text{Ta/O} \approx 3/7$.

Optical microscopy shows that the implanted region quickly develops a coherent layer (probably an oxide) while the unimplanted region oxidizes initially by the formation of platlets extending along particular crystallographic planes, and later, by the formation of a blocky oxide on top of this. Ta oxidation has been well characterized by Kofstad R, and ?. Studies have indicated that initially TaO forms along the (100) planes and Ta_2O_5 forms on top of this. After 360 min. the implanted Ta forms oxide platlets along the interface between implanted and unimplanted regions of the specimen. After 600 min. these platlets appeared throughout the implanted region.

Copper

Initial Cu studies were performed at 400 C. The unimplanted specimens oxidized very rapidly and exhibited flaking and cracking even at times as short as 20 min. However, the implanted specimens exposed to identical treatment showed only slight oxidation which was evident only along the grain boundaries. Oxide flaking was not observed in the implanted samples for oxidation times up to 120 min.

To obtain a more quantitative analysis of Cu oxidation additional studies were performed at 200 C. Backscattering spectra in the region near the oxygen signal for both implanted and unimplanted Cu is shown in fig. 3. The spectra show that the implanted regions oxidize more rapidly initially. In a manner similar to the Ta results, the rate of oxidation in the implanted regions slows with respect to the unimplanted regions. Both implanted and unimplanted specimens display low-energy tails on the oxygen peaks with the tails more pronounced for the unimplanted specimens. For both unimplanted and implanted specimens at the higher oxidation times, a signal height analysis yields a stoichiometry of $\text{Cu/O} \approx 2/1$.

Optical microscopy of the implanted regions showed an initial bluish layer with no apparent grain structure while the unimplanted regions showed grain structure (probably

that of the underlying Cu). After 240 min. the implanted region had formed a grain structure similar to that of the unimplanted regions at earlier times.

4. Discussion

Previous investigations have studied the oxidation characteristics of various implanted materials including Ta⁶, Ti and Zr⁸, and Fe-24Cr⁹. It is difficult to determine the mechanism(s) by which an implanted species alters the oxidation characteristics. However, it is useful to consider the mechanisms by which oxidation resistance might be achieved. These have been reviewed by Dearnaley¹⁰ and are summarized as follows:

Oxides such as Al₂O₃ and Cr₂O₃ provide protection from further oxidation of the metal substrate as a result of their high cohesive energy and low vacancy concentration. A low vacancy concentration will result in a low rate of diffusion and oxidation, since oxidation takes place as a result of either cation or anion diffusion. Another means of protection may occur if the implanted atoms segregate to low strain energy locations such as grain boundaries or dislocations. Grain boundaries and dislocations provide fast diffusion paths for ions during oxidation and the segregation of the implanted species may block such paths. Another possibility is that the implanted species may increase the plasticity and/or adherence of the oxide scale and thereby reduce the cracking and flaking of an oxide as a result of thermal stresses. The improvement in the oxidation characteristics of Zr with the implantation of Cu ions was attributed to the substitution of Zr by Cu. It has been suggested that the smaller ionic radius of Cu allows dislocation climb at lower stresses. Finally, one must consider that the damage introduced by the implanted species may alter the nucleation and growth of the oxide. However, when Ta was implanted into Ta (180 keV, 3x10¹⁶/cm²)² it was shown that no significant effects were seen from the implantation damage.)

We know that Y is immiscible with Mo and Ta but alloys with Cu. In addition, the atomic volume of Y (19.8 cm³/mole) is nearly twice that of Mo (9.4 cm³/mole) and Ta (10.9 cm³/mole) and three times that of Cu (7.1 cm³/mole). Therefore, the grain boundaries and dislocations will be the most energetically favorable locations for Y in Mo and Ta. The situation for Cu is less clear since size effects may be balanced by the enthalpy of alloy formation to keep the Y in the bulk of the Cu.

Molybdenum

The low energy tails on the O backscattered signals suggest that the surface for oxidized, unimplanted Mo is becoming increasingly rougher or that oxidation is occurring

by grain-boundary diffusion. In the implanted Mo the oxidation mechanism has clearly changed. Initial diffusion is rapid and the evolution of discrete oxide layers of Mo/O are formed. Continued annealing results in a layer-by-layer growth of the surface oxide which saturates at a maximum depth of 10,000 Å. In all cases the total O uptake is greater for the implanted regions than for the unimplanted. The surface oxygen gain vs. annealing time for both unimplanted and implanted specimens is shown in fig. 4a and indicates that the unimplanted Mo accumulates O nearly linearly with time. In the implanted case, however, the oxide layer grows with a $t^{1/2}$ dependence for the first 40 min. before becoming almost constant.

Tantalum

The long low energy tails on the O backscattered signals for the unimplanted Ta as well as for the long annealing time implanted Ta indicate that a low concentration of O has diffused to large depths, possibly throughout the bulk of the specimens. Again grain boundary diffusion or surface roughness could be the cause. However, a change in mechanism for the implanted Ta, similar to the implanted Mo, is evident. In contrast to the Mo case, the O uptake in the implanted specimens is greatly reduced. This indicates that grain boundary blocking may be the predominate effect of Y in Ta. Fig. 4b shows the O gain vs time for Ta. As noted previously, quantitative analysis of the O in the unimplanted specimens was not possible.

Copper

Similar to the Ta, low energy tails on the O signals for both the implanted and unimplanted specimens indicate possible grain boundary diffusion. The O uptake is less for the implanted case, but not to the extent of the Ta. Saturation appears to be occurring for the highest times. Fig. 4c shows the O gain vs.time for Cu.

In all cases Y implantation strongly effects the oxidation process. For Ta and Cu retardation of oxidation occurs. For Mo, implantation produces a discrete oxide layer which grows in a layer-by-layer manner. These data indicate that the Y-Cu and the Y-Ta oxides are more passivating than their unimplanted counterparts.

This study also clearly shows the power of the 8.8 MeV $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$ high-energy resonant backscattering analysis technique to determine the surface oxidation in heavy metals. The shape of the oxygen concentration profile would not be easily determined by other methods.

5. Acknowledgements

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Figure Captions

1. Backscattering spectra near the oxygen signal from oxidized molybdenum, unimplanted and implanted. Specimen tilted 60° to beam.
2. Backscattering spectra near the oxygen signal from oxidized tantalum, unimplanted and implanted. Specimen tilted 60° to beam. Note the change of tilt angle (0°) for the 600 min specimen.
3. Backscattering spectra near the oxygen signal from oxidized copper, unimplanted and implanted. Specimen tilted 60° to beam.
4. Oxygen gain vs time for unimplanted and implanted molybdenum, tantalum and copper.

Oxygen Gain (10^{17} atoms/cm²)

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