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A STUDY OF NITRIDE FORMATION DURING THE
OXIDATION OF TITANIUM-TANTALUM ALLOYS

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A Study of Nitride Formation During the Oxidation of Titanium-Tantalum Alloys

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Abstract:

The oxidation rates of Ti rich titanium-tantalum alloys are significantly lower in air than in oxygen. This nitrogen effect has been shown to be associated with the formation of a nitride layer at or near the scale-metal interface. In the present work we used transmission electron microscopy and microdiffraction to identify the nitrides formed on Ti5Ta and Ti40Ta (5 and 40 weight percent Ta alloys) during identical exposures. In both alloys the nitride develops in contact with the oxygen stabilised α -phase in the substrate. In Ti5Ta a continuous layer of TiN forms, while in Ti40Ta a discontinuous layer of Ti₂N interspersed with Ta₂O₅ (formed from the Ta rich β -phase) is formed. The nitride layer acts as an oxygen diffusion barrier, reducing the dissolution of oxygen in the substrate.

Introduction

Most of the previous studies of the oxidation of Ti-Ta binary alloys were conducted in either pure oxygen or laboratory air. The only exception was Chen and Rosa¹ who performed experiments on Ti-4.37%Ta in both pure oxygen and air environments, where they reported lower oxidation rates in air. They did not discuss the mechanism by which nitrogen reduced the oxidation rate. However, they did report that TiN was detected near the scale/metal interface using x-ray diffraction. We have observed that the presence of nitrogen in the atmosphere consistently results in reduced oxidation rates of alloys containing from 5 to 60 weight percent tantalum.² In this paper, in order to further elucidate the effect of nitrogen on the oxidation mechanism, we present the results of an investigation of the structure and composition of the nitride layer using cross sectional TEM.

Materials and Experimental Procedures

All of the previous studies which reported their alloy fabrication technique used arc-melting. Arc-melting was initially utilized in this work as well but problems were observed with metal loss and gross inhomogeneity of the ingot. These effects may help account for the erratic results observed in other studies. In order to obtain optimum homogeneity and control over composition, the alloys used in this study were produced by plasma torch melting cold-pressed slugs of 99.9%+ Ta powder mixed with Ti sponge powder in the appropriate proportions. Complete details of the sample preparation are discussed in our previous paper.³ Coupons of each alloy were studied using thermogravimetric analysis (TGA). Each experiment ran for 16 hours in either pure oxygen, argon-20% oxygen, or nitrogen-20% oxygen. Because of the thick oxide scales and oxygen embrittled layers formed on these alloys after the 16 hour TGA experiments, specimens of Ti5Ta and Ti40Ta intended for cross sectional TEM were exposed in N₂-20% O₂ in a horizontal tube furnace for 2 hours at 1000° C. This exposure was chosen to minimize the thickness of the scale and oxygen embrittled substrate, while still maintaining a scale which is generally comparable to that developed at longer times. These 2 mm thick specimens were then cut into strips, the oxidized surfaces were glued face to face, ground and polished using standard metallographic techniques, and finally ion milled to the final thickness for TEM examination.

Results

Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM)

In order to put this study in perspective, we briefly review some of our previous observations of the effect of nitrogen on the oxidation of Ti5Ta and Ti40Ta. Fig. 1 shows TGA curves of these alloys exposed for 16 hours at 1000° C in Ar-20% O₂ or N₂-20%O₂. Scanning electron micrographs of these same samples in cross section are shown in Fig. 2. X-ray maps of Ti, Ta, N and O from the oxide metal interface of the Ti40Ta

specimen exposed in N_2 -20% O_2 are shown in Fig. 3. From these figures the effect of nitrogen on the oxidation mechanism can be readily observed. The gravimetric data show that the substitution of nitrogen for argon results in roughly a factor of 2 reduction in weight gain. In cross section it is apparent that the oxide scales are nearly the same thickness but the oxygen stabilised α -phase layer (in the Ti5Ta) or the two phase α - β layer (in the Ti40Ta) below the oxide-metal interface is much thinner in the specimens exposed in the atmosphere containing nitrogen. The nitrogen x-ray map shows that there is an increased concentration of nitrogen at or near the scale-metal interface. There is obviously less overall oxygen dissolution in the substrate, but the scale seems to grow outward at a comparable rate in both atmospheres. Therefore the nitride layer apparently acts as an oxygen diffusion barrier. To positively identify the structure and location of this presumed nitride layer we thus used cross sectional TEM, as discussed below.

Transmission Electron Microscopy (TEM)

PEELS (Parallel Electron Energy Loss Spectroscopy) was used first to locate the nitrogen rich layers in both alloys. As can be seen from the PEELS scan shown in Fig. 4 taken from the nitride layer in the Ti40Ta specimen, the nitrogen rich layers were always found to be associated with Ti. Quantification of this particular spectrum gave a calculated Ti:N ratio of 1.99:1. No significant concentrations of O or Ta were found in this layer in either alloy.

In the Ti5Ta, the nitride layer appeared to be continuous. It was found at the scale-metal interface between continuous layers of oxygen stabilised α -phase in the metal and overlain by TiO_2 . Fig. 5 shows a TEM micrograph of the nitride layer along with a microdiffraction pattern taken from the grain labeled in the micrograph. The phase was identified from the microdiffraction pattern as TiN. No other phases were identified in the nitride layer.

In the Ti40Ta the nitride layer was found to be present predominantly in contact with the Ti rich oxygen stabilised α -phase in the substrate. Breaks in the nitride were found to

usually contain Ta_2O_5 in contact with Ta rich β -phase. The oxide overlaying the nitride/oxide layer was a very fine grained mixture of TiO_2 and Ta_2O_5 . A bright field TEM micrograph of the nitride layer along with a microdiffraction pattern taken from the grain labeled in the micrograph is shown in figure 6. The nitride layer in this case was identified from microdiffraction patterns as Ti_2N . This identification was repeated several times and no other nitride species was identified. This was further confirmed by the quantitative PEELS results mentioned above.

Discussion

In both Ti5Ta and Ti40Ta the nitride layer was found in contact with the oxygen stabilised α -phase layer in the substrate. The α layer in the substrate was continuous in the Ti5Ta alloy. The scale in the Ti5Ta contains only rutile, and the substrate below the metal oxide interface is continuous α -phase, suggesting that all points along the scale metal interface are equivalent, particularly with respect to the activity of the various species. Therefore it is reasonable that the nitride layer in Ti5Ta is also found to be a continuous single phase, in this case TiN. After 2 hours of exposure the substrate below the scale metal interface of the Ti40Ta was a mixture of α and β phases, both of which were saturated with oxygen. Therefore it is not surprising that the nitride layer is found to be discontinuous. The fact that the nitride formed in this case is Ti_2N rather than TiN suggests that the reduced oxidation rate associated with the formation of the nitride layer, cannot be attributed solely to the unique properties (ionic conductivity etc.) of a particular nitride. Rather, the nitrogen effect must be associated more with the physical barrier that the nitrogen rich layer presents to the transport of oxygen into the substrate. This may be compared to the well known nitrogen effect observed in γ -TiAl. In TiAl the presence of nitrogen in the atmosphere results in accelerated oxidation.⁴ This effect has been described by Rakowski et al.⁵ as resulting from the formation of a discontinuous layer of TiN (in Al_2O_3) at the scale/metal interface, which is subsequently oxidized to TiO_2 . This mechanism seems applicable to the nitrogen effect in TiTa alloys as well, however in this case since there is no element present which forms a slow growing protective oxide layer,

the nitride layer is actually more protective than the oxide (TiO_2). The observation that the nitride layer is found in contact with the Ti rich HCP α phase, suggests that there is a critical concentration of Ti required to maintain the nitride layer.

Conclusions

Exposure of TiTa alloys in a mixture of oxygen and nitrogen results in significantly slower oxidation kinetics compared to exposure in a nitrogen free environment. This is due to the formation of a nitride layer at the scale metal interface which consists of predominantly titanium nitrides. TiN is the nitride phase observed in Ti5Ta at 1000°C , while Ti_2N is found in Ti40Ta, predominantly in contact with the Ti rich oxygen stabilized α phase in the substrate. The nitride layers act as oxygen diffusion barriers but apparently do not impede the transport of Ti or Ta from the metal into the growing scale. This effect is thought to be due to the combination of the nitride acting as a physical barrier to the transport of oxygen and dissolution of nitrogen in the α -phase. The nitride is maintained at a near constant thickness dictated by the oxygen activity gradient in the scale. New nitride grows into the α -phase at the scale-metal interface while the nitride is oxidized to TiO_2 at the nitride-oxide interface.

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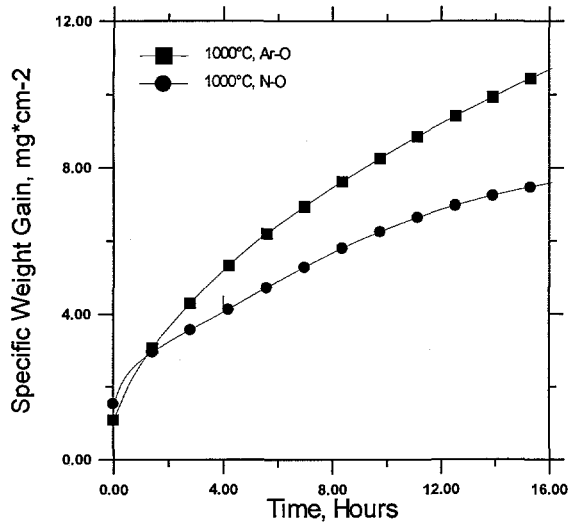


Fig. 1a TGA data from exposure of Ti5Ta in Ar-20%O₂ and N₂-20% O₂ at 1000° C

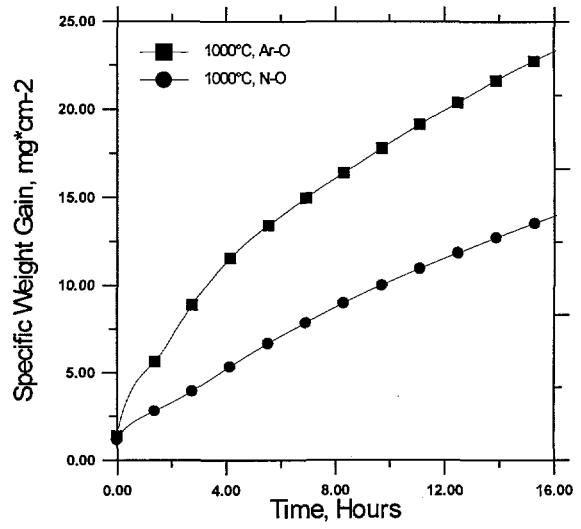


Fig. 1b TGA data from exposure of Ti40Ta in Ar-20%O₂ and N₂-20% O₂ at 1000° C

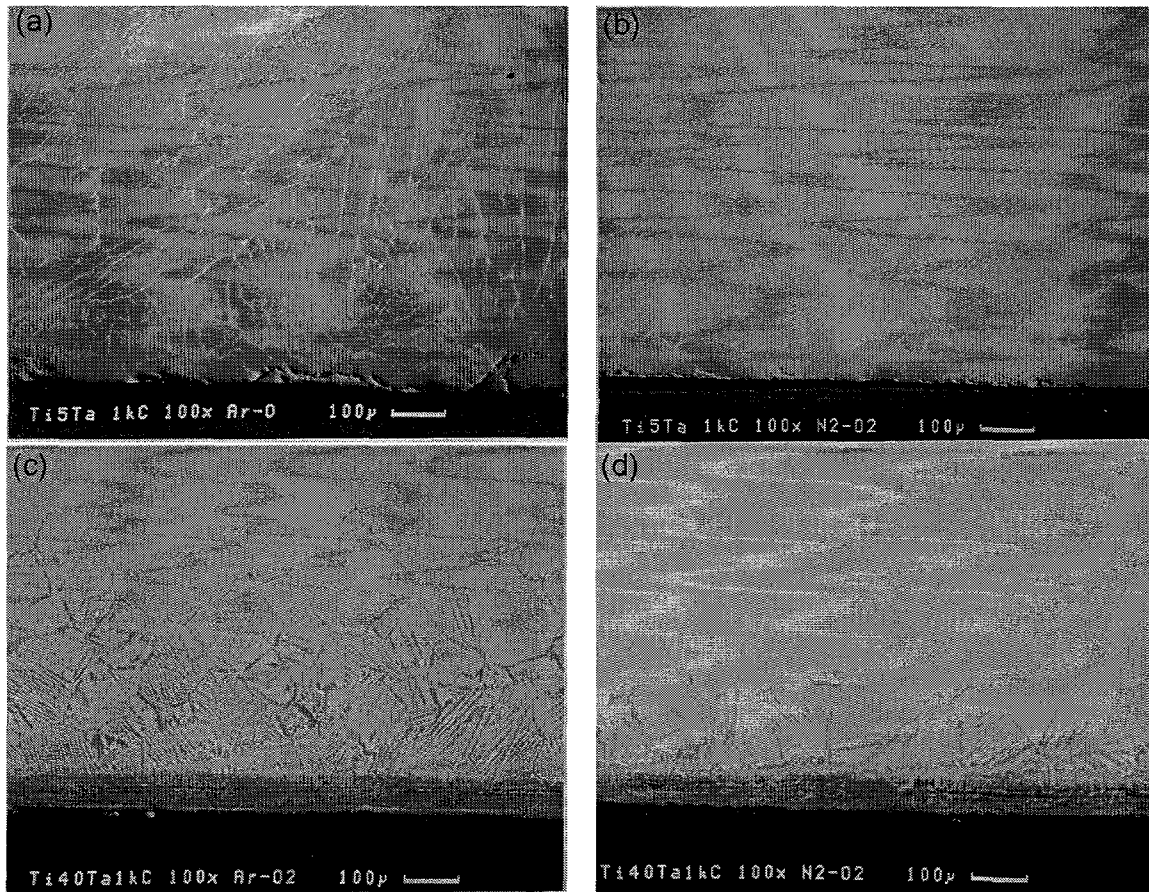


Figure 2. SEM micrographs of cross sectioned Ti5Ta (top, a and b) and Ti40Ta (bottom, c and d) exposed in either Ar-20%O₂ (a and c) or N₂-20%O₂. The penetration of oxygen into the substrate, as indicated by the depth of the oxygen stabilised α phase, is significantly less reduced in the nitrogen bearing atmosphere.

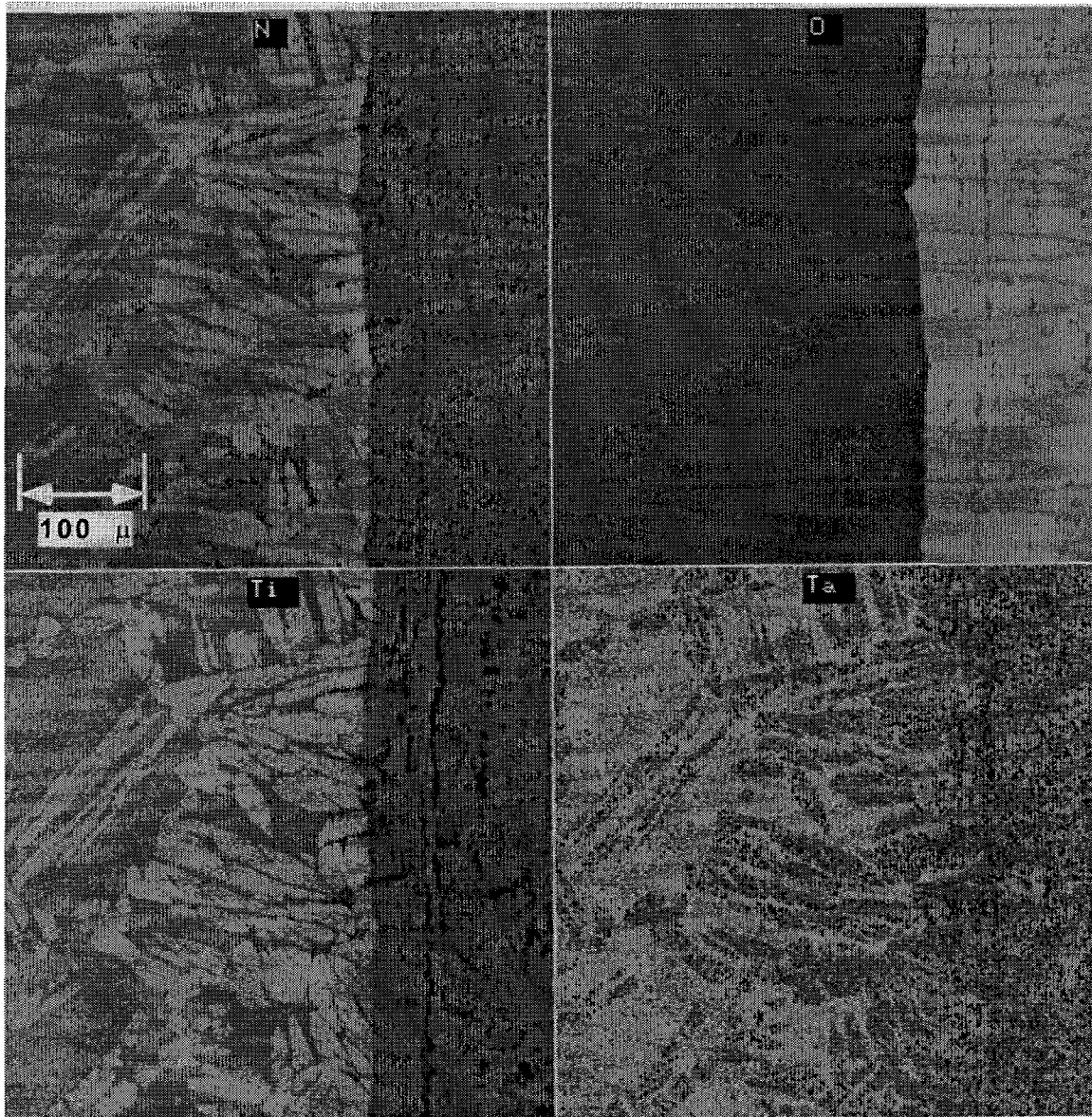


Figure 3: Digital x-ray maps of N, O, Ti, and Ta measured at the scale metal interface region of a specimen of Ti40Ta exposed for 16 hours at 1000° C in N₂-20%O₂. There is a clear enhancement of the nitrogen signal at the scale metal interface. This was verified by point scans at the interface where the effect of the interference of Ti with N (Ti L1 with N K α) was subtracted.

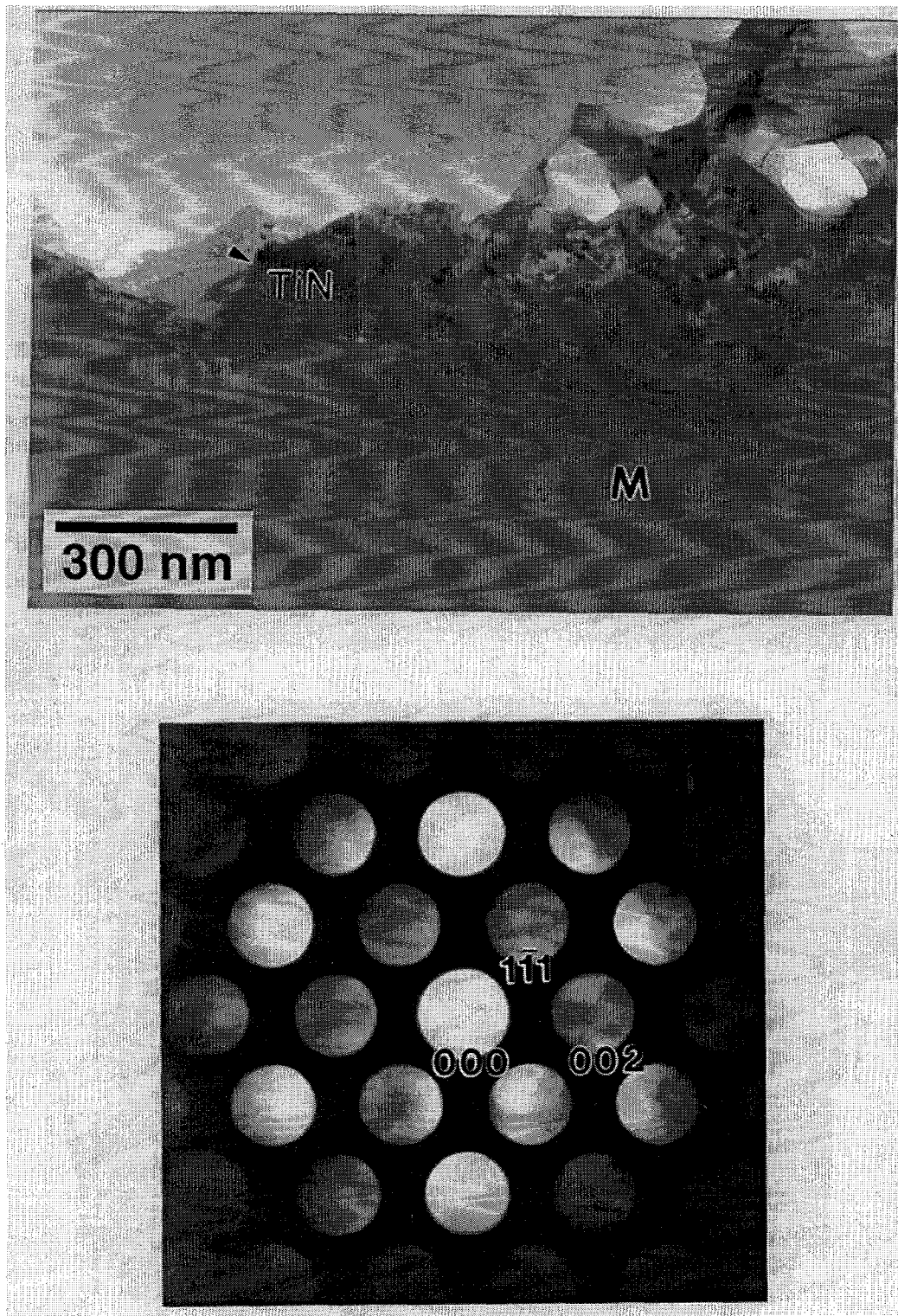


Figure 5. Cross sectional TEM of Ti5Ta exposed in N_2 -20% O_2 for 2 hours at 1000° C. TEM bright field micrograph (top) and [110] zone axis microdiffraction pattern (bottom) taken from the grain labeled in the micrograph.

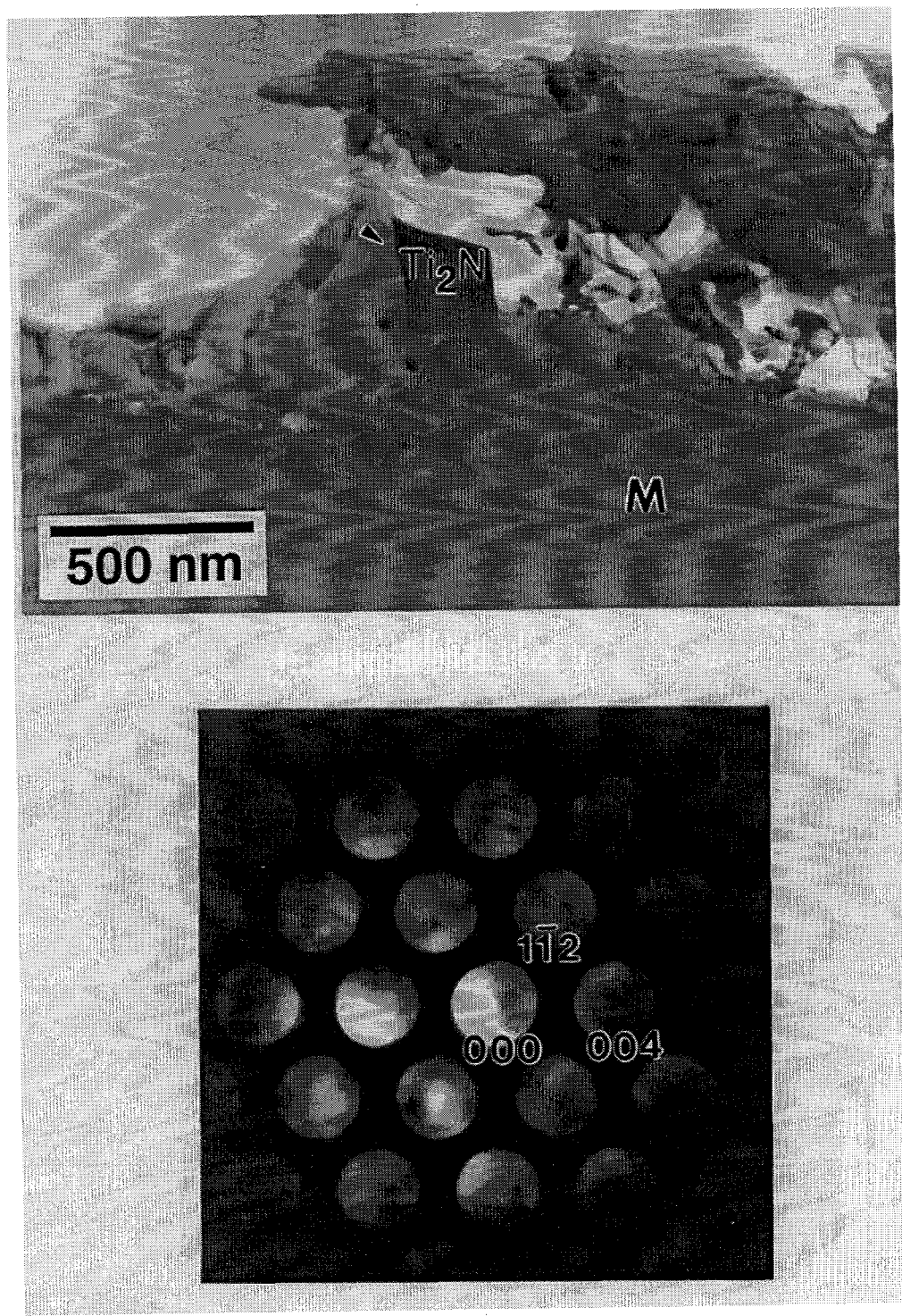


Figure 6. Cross sectional TEM of Ti40Ta exposed in N₂-20%O₂ for 2 hours at 1000° C. TEM bright field micrograph (top) and [110] zone axis microdiffraction pattern (bottom) taken from the grain labeled in the micrograph.

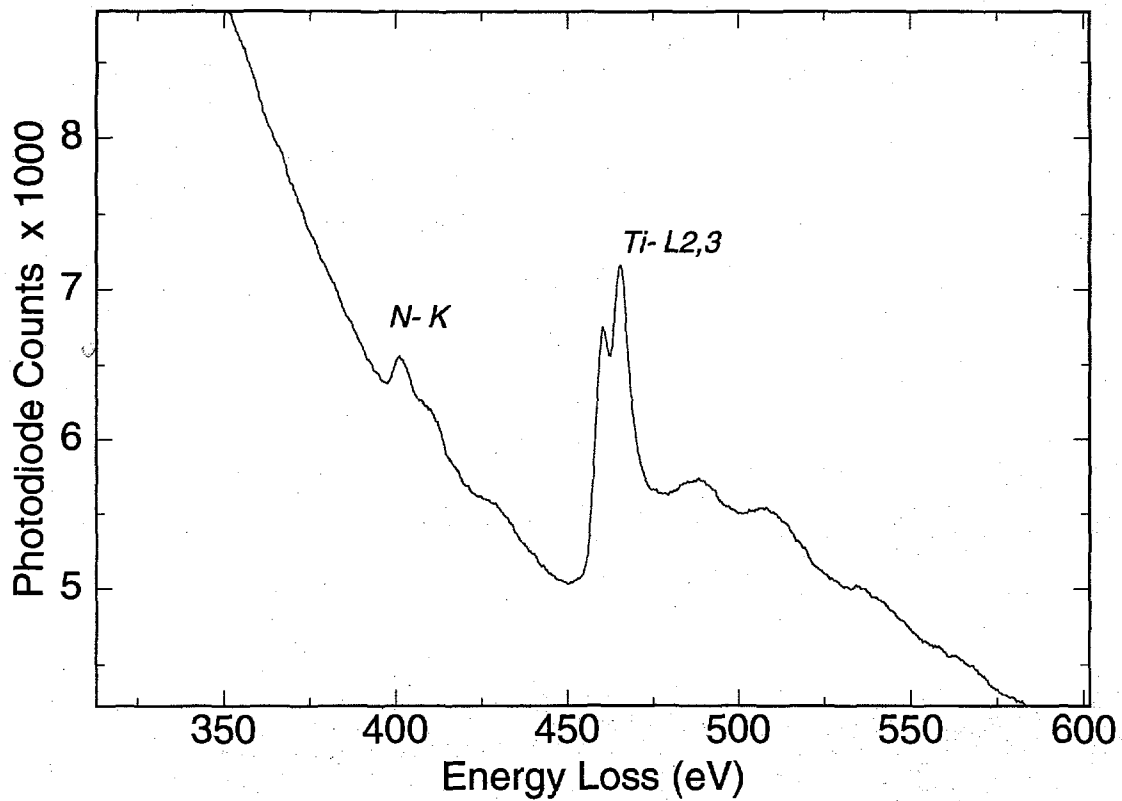


Figure 4. Parallel Electron Energy Loss (PEELS) spectrum measured from the nitride layer formed on Ti40Ta after 2 hours at 1000° C. The Ti:N ratio was calculated from this spectrum to be 1.99:1 which confirms the identification of Ti_2N as the nitride phase formed in this case. The concentrations of O and Ta detected in the nitride layer were too low to quantify.