

PHYSICAL PROPERTIES OF O- AND N-CONTAINING V-Cr-Ti ALLOYS*

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SUMMARY

Incorporation of O in the surface of V-Ti-Cr alloys has been investigated in controlled environments at 550-750°C, and tests were performed to determine the physical properties of V-Cr-Ti-O solid solutions. The amount of O in the alloys has been determined by weight-change measurements. Microhardness was used to determine O depth profiles of the alloys. X-ray diffraction indicated a phase transformation from body-centered-cubic (bcc) to tetragonal in the lattice that was highly stressed because of O incorporation. Back-scattered-electron images and electron-energy-dispersive spectra revealed Cr depletion near alloy grain boundaries. Elastic modulus and Vickers hardness increased in O-enriched V-Cr-Ti alloys. Hardening of the alloys results from O atoms on face-centered interstitial sites in the bcc sublattice and the formation of very fine coherent oxide particles. Oxygen or N diffusion occurs via the interstitial sublattice of bcc V-base alloys and is accompanied by the formation of homogeneous oxide or nitride phases via internal oxidation or nitridation. The O,N-enriched surface region exhibited the extraordinarily high Vickers hardness of ≈ 18 GPa (1800 kg/mm^2), a value that is typical of oxides, nitrides, or carbides, or that is obtainable by ion-beam irradiation of metals.

INTRODUCTION

Several V-base alloys exhibit good high-temperature creep strength, low ductile-to-brittle transition temperatures, and high resistance to neutron irradiation damage.¹ However, thermomechanical processing to produce alloys in plate, sheet, and tubular form requires high-temperature annealing in vacuum or inert gas environments. Contamination of the processing environment by trace levels of O₂, N₂, H₂O, CO₂, etc., leads to formation of a hard ceramiclike near-surface region on the alloys. In some applications, surface modification by controlled addition of O, N, or C, with and without the formation of ceramic compounds within the substrate, could be desirable. Modification of the surface region of V-base alloys by diffusion of O, N, or C into the interstitial sublattice has been investigated under conditions in which V-O, V-N, or V-C ceramic compounds do not form at the alloy/gas interface. Most of these compounds have melting points greater than (VN, 2320°C) or comparable to (VO₂ and V₂O₃) that of the alloys ($\approx 1910^\circ\text{C}$), except for the low-melting V₂O₅ (690°C) phase. Formation of V₂O₅ must be avoided in all thermomechanical and surface-modifying processes. The hardness and elastic modulus of V-Cr-Ti-O solid solutions have been investigated.

EXPERIMENTAL PROCEDURE

Several experimental methods were used to explore the relationship between O and/or N and the physical properties of V-Cr-Ti alloys, namely (a) surface O charging of the alloys, followed by evaluations by optical metallography, transmission- and scanning-electron microscopy (TEM and SEM); (b) X-ray diffraction, energy-dispersive electron spectroscopy (EDS), secondary-ion mass spectroscopy (SIMS), and microhardness tests; and (c) elastic modulus measurements.

Oxygen and/or N charging of the near-surface region of V-4Cr-4Ti. Oxygen and/or N charging of the near-surface region of the alloy was carried out in flowing 99.999% Ar and/or N₂ that contained ≤ 5 ppm O₂, ≤ 5 ppm H₂O, and a total impurity content of ≤ 20 ppm, at 550-1030°C for 17-96 h. Oxygen and N pickup by the alloys was determined by weight-change measurements.

X-ray diffraction and related studies. The surface of O-charged samples (25 x 25 x 1 mm) was subjected to X-ray diffraction to investigate the relationship between hardness and O content of the materials. To determine X-ray parameters as a function of depth, the specimen surface was polished with a diamond paste. Secondary-ion mass spectroscopy studies were performed on cross sections of O-charged regions of the specimens. Vickers hardness was used to determine the depth of O or N diffusion into the alloys. TEM of O-enriched regions was performed to confirm the presence of a small cluster phase in this region.

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Elastic modulus measurements. Elastic modulus measurements were performed by a simple pulse-echo technique on O-charged small samples (25 x 25 x 1 mm). Because of relatively low attenuation, 15 MHz elastic waves were used.

RESULTS AND DISCUSSION

Oxygen and/or Nitrogen Charging of Near-Surface Region of V-4Cr-4Ti

When V or V-base alloys (e.g., V-Cr, V-Ti, V-Cr-Ti, or V-Cr-Al) oxidize in high-O environments, the low-melting V_2O_5 phase forms via outward diffusion of cations, even in the presence of O-active elements such as Y, Si, Al, etc.^{2,3} It is well known that O can be incorporated into the interstitial sublattice of bcc V and its alloys.⁴ In the bcc lattice of V-Cr-Ti, O can occupy interstitial sites within the lattice up to several atomic percent. Weight gain of V-4Cr-4Ti specimens was determined after 70-h exposures to flowing high-purity Ar and N_2 (99.999%) that contained O as an impurity. At temperatures of 500-1030°C, the rate of O pickup by the alloy was greater than that of N. This could indicate that the energy of interaction between Ti in the alloy and O is greater than that between Ti in the alloy and N. Also, the atomic size of N is larger than that of O. Diffusion coefficients of O and N in V indicate that O diffuses 10-1800 times faster than N. The activation energies of O and N (plus traces of O as impurity) uptake by the alloy are 0.83 and 0.65 eV, respectively.

Analysis of a back-scattered-electron image from the cross section of an O-charged specimen revealed that the dark area indicates elements with low atomic numbers, i.e., the O-enriched area. Localized enrichment of O occurs in the grains and near grain boundaries. From EDS analysis, areas enriched with O and Ti contain less Cr. However, localized Cr depletion did not occur during O charging at $\leq 670^\circ\text{C}$. Based on metallographic information and weight gain data, the depth of the O-charged layer can be controlled by exposure temperature and time in a flowing Ar atmosphere. Oxygen concentration in the near-surface layer was calculated from weight gain, surface area, and thickness of the hardened region; it ranged from 250 ppm (as-received) to $\approx 2-3\%$, depending on position within the layer and exposure conditions.

Microhardness Tests on O, N*-Charged V Alloys

Hardness profiles across the O-charged region and at $\geq 200 \mu\text{m}$ below the surface of V-4Cr-4Ti specimens were obtained after exposure to flowing Ar at several temperatures. Hardness at the interior of the specimen charged with O at 550°C is higher than that of the as-received specimen. Presumably, O penetration was greater at 550°C than at higher temperatures. An O-blocking mechanism could be involved at high temperatures; for example, local Ti migration or Cr depletion was detected by EDS analysis near grain boundaries. If Ti migrates to grain boundaries or to the surface via cation diffusion, residual O in the alloy will follow Ti, and, as a result, enrichment of O near grain boundaries or at the surface will occur. Because hardness is directly related to O concentration in the alloy, the amount of O pickup by the alloy in the near-surface region in relation to the exposure temperature increases in the order $615 > 685 > 703 > 750 > 550^\circ\text{C}$.

X-Ray Diffraction Studies

To determine whether the hardening mechanism involves primarily occupation of interstitial sites by O or formation of small particles of V-O, Ti-O, or V-Ti-O, TEM and X-ray diffraction were performed on the near-surface region of an O-charged V-5Cr-5Ti specimen that was exposed to pure Ar for 21 h at 650°C .

Figure 1 is a TEM photomicrograph of a surface that reveals small particles of coherent oxide. The TEM study supports a hardening mechanism whereby O and/or N lead to internal oxidation or nitridation at elevated temperatures. Coefficients of thermal expansion (CTE) of dilute solid solutions of O in V-O,

*We expect O and a very small amount of N contamination in the system. SIMS analysis indicated only contamination, but measured microhardness was very high.

Ti-O, or V-Ti-O are probably not much higher than those of V and the alloys, $\approx 9.2 \times 10^{-6}/\text{K}$. However, the CTEs of small coherent particles of oxide, nitride, oxynitride, or carboxynitride present in the alloy at high temperatures are probably lower than those of the alloy matrix, and, during cooling from high temperatures, stresses develop that are due to the difference in CTE of the coherent particles and the matrix. This effect seems to be more significant in V-base alloys than in other alloy systems, e.g., Ni-base alloys.⁵ X-ray peaks that tend to broaden because of strain that originates from small particles in the alloy (Fig. 3) provide evidence that hardening occurs by incorporation of interstitial impurities.

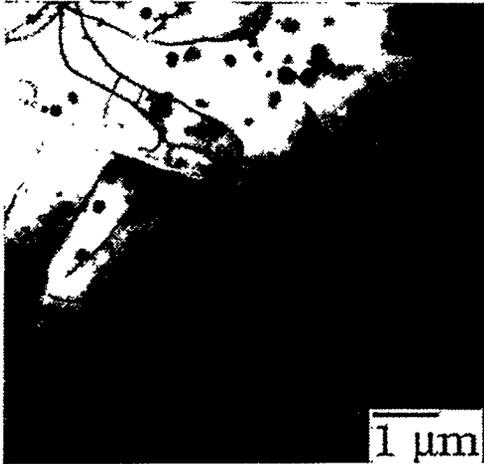


Figure 1.
TEM photomicrograph of O-charged region of V-5Cr-5Ti after exposure to Ar for 21 h at 650°C.

However, hardening can also be explained by an alternative mechanism. When O or N is incorporated into an alloy by a solid-state diffusion process at elevated temperatures and the alloy is cooled, impurities can become trapped in interstitial positions. The X-ray spectrum from this specimen did not show significant broadening; only the X-ray lattice parameter of the bcc structure increased. Based on the Vickers hardness versus O-charged depth of the near-surface region at various temperatures, we can write the following equation:

$$\text{Log } K_c = 2.77 - 1615/T \text{ (K)} \quad (\mu\text{m}/\text{h}^{1/2}),$$

where K_c is the rate constant for the O-affected depth $x = K_c t^{1/2}$.

Figure 2 shows the X-ray diffraction spectrum from the surface of a specimen after $\approx 20 \mu\text{m}$ of the O-charged layer was removed by polishing, and the d-spacing of the (110) and (200) planes as a function of depth. The results indicate that the variation of interstitial O in the alloy with depth can be directly related to the average strain distribution with position. In general, all d-spacings decreased with depth. However, as mentioned previously, if Ti migrates from the bulk to grain boundaries or to the surface, then residual bulk O follows Ti, and enrichment of O near grain boundaries or the surface occurs. The X-ray lattice parameter could also increase because of vacancy formation (Fig. 2).

X-ray diffraction profiles in Fig. 3, from the near-surface region of an O-charged sample, reveal phase transformation from a bcc to a tetragonal phase. Oxygen charging at low temperatures produces more separation of the ratio of the a/c spacing in the lattice. It is possible that the high-purity Ar maintains a constant O partial pressure (p_{O_2}) over the range of temperatures and stabilizes the tetragonal phase in the alloy. Lower temperatures should increase the thermodynamic stability of this phase, and less relaxation (diffusion) should occur. Therefore, the difference in a/c is larger (produces more distortion) at low temperatures. During heating, stress relaxes at the free surface and if the tetragonal phase is present within bulk regions of the bcc lattice, it could generate active diffusion/reactive sites during thermal cycling.

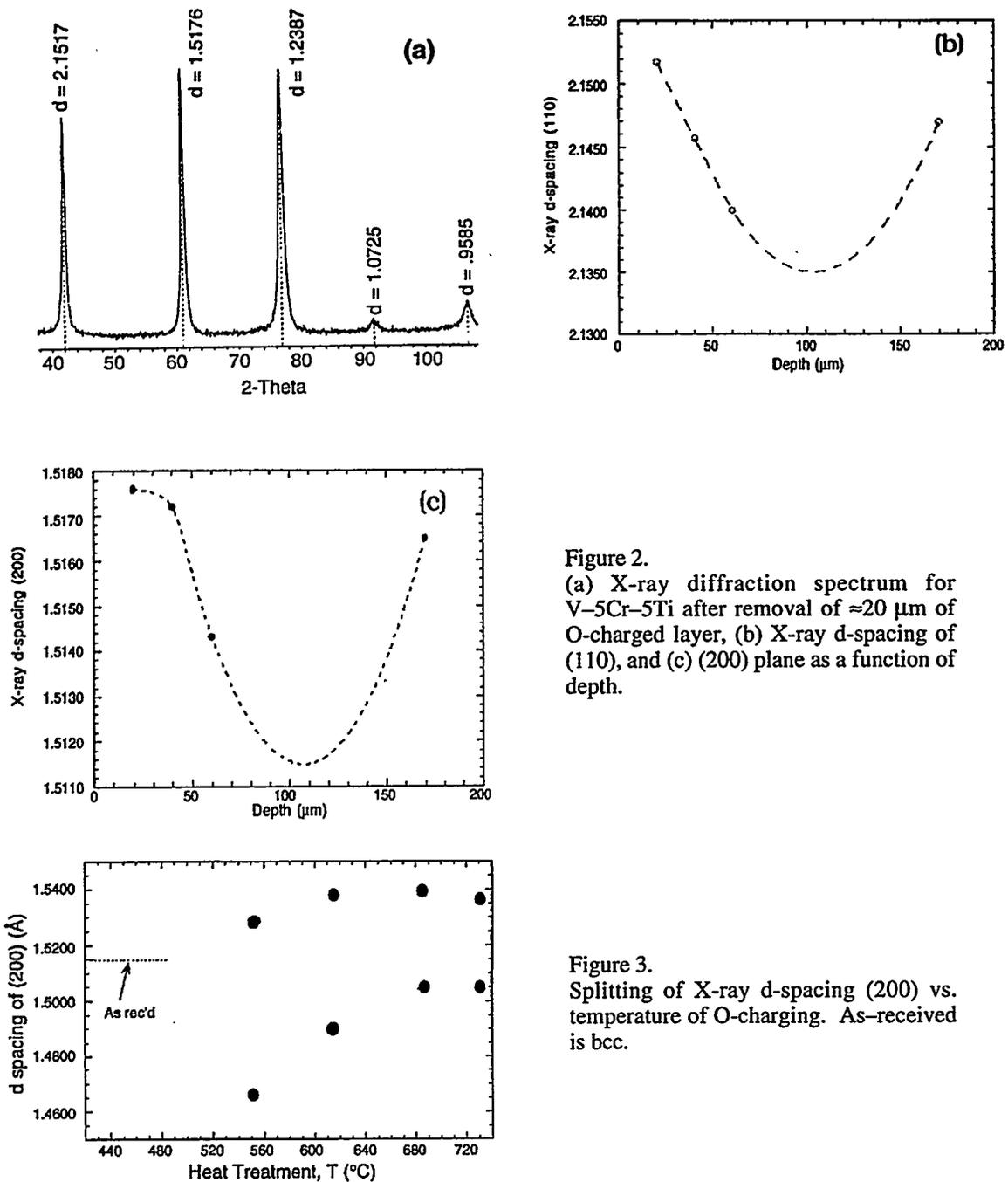


Figure 2.
 (a) X-ray diffraction spectrum for V-5Cr-5Ti after removal of $\approx 20 \mu\text{m}$ of O-charged layer, (b) X-ray d-spacing of (110), and (c) (200) plane as a function of depth.

Figure 3.
 Splitting of X-ray d-spacing (200) vs. temperature of O-charging. As-received is bcc.

Elastic Modulus Measurements on O-Charged Specimen

A relationship between hardness and impurity concentration in the V-Cr-Ti was developed from the results of TEM, SEM, X-ray diffraction, and hardness measurements. Elastic modulus measurements were performed on O- and O,N-charged samples at room temperature. Because of the relatively low attenuation of V-base alloys, 15 MHz elastic waves were applied. The results are shown in Fig. 4, and the data are replotted in Fig. 5 in terms of the change in elastic modulus with the amount of either O or O, N in the V-4Cr-4Ti samples.

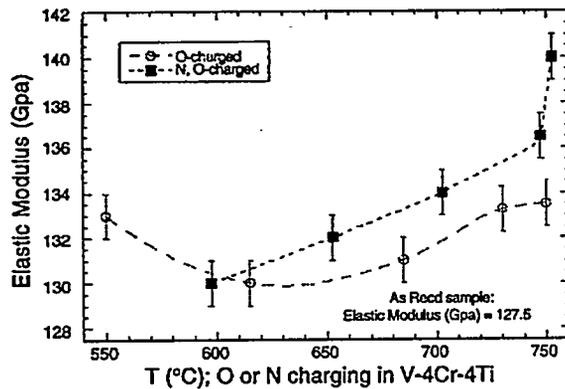


Figure 4.
Room-temperature elastic modulus of V-4Cr-4Ti vs. temperature of O or N charging.

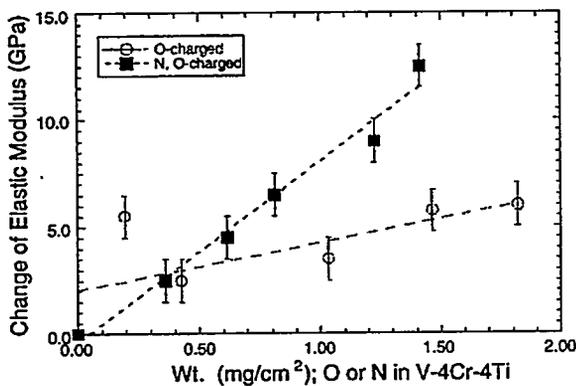


Figure 5.
Change in elastic modulus of V-4Cr-4Ti vs. weight gain during either O or O, N charging.

CONCLUSIONS

Incorporation of O and N in the surface of V-Ti-Cr alloys produced a high degree of hardening in the alloys. X-ray diffraction indicated a phase transformation from body-centered-cubic (bcc) to tetragonal phase and a highly stressed lattice because of O and N incorporation. O and N atoms occupied face-centered interstitial sites and sites between corners in the bcc sublattice. Elastic modulus and Vickers hardness also increased in O- and N-enriched V-Cr-Ti alloys.

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