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MECHANICAL PROPERTIES OF, AND PHASE TRANSFORMATION IN,
V-Cr-Ti-O SOLID SOLUTIONS*

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V-Cr-Ti-O SOLID SOLUTIONS*

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Abstract

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 in the alloys. X-ray diffraction indicated a phase transformation from body-centered-cubic (bcc) to tetragonal in the highly stressed lattice because of O incorporation. Cr depletion was observed near alloy grain boundaries, based on back-scattered-electron images and electron-energy-dispersive spectra. Elastic modulus and Vickers hardness also increased in O-enriched V-Cr-Ti alloys. Hardening in the alloys results from O atoms on face-centered interstitial sites in the bcc sublattice and the formation of very fine coherent oxide particles. O or N diffusion occurs via the interstitial sublattice of the 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 typical of oxides, nitrides, or carbides, or obtainable by ion-beam irradiation of metals.

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INTRODUCTION

Several vanadium-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/inert gas environments. Contamination of the processing environment by trace levels of O₂, N₂, H₂O, CO₂, etc., leads to the formation of a hard ceramiclike near-surface region on the alloys. In some applications, surface modification by controlled additions 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 (i.e., VO₂, and V₂O₃) that of the alloys (≈1910°C), except for the low-melting V₂O₅ (690°C) phase. Formation of V₂O₅ must be avoided in all thermomechanical and surface modification 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 oxygen and/or nitrogen and the physical properties of V-Cr-Ti alloys, namely (a) surface oxygen 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 nitrogen charging of the near-surface region of V-4Cr-4Ti: Oxygen and/or nitrogen charging of the near-surface region of the alloy was carried out in flowing 99.999% Ar and/or N₂ that contains ≤5 ppm O₂, ≤5 ppm H₂O, and a total impurity content of ≤20 ppm, 550 to 1030°C for 17 to 96 h. Oxygen and nitrogen pickup by the alloys was determined by weight-change measurements.

X-ray diffraction and related studies: X-ray diffraction on the surface of O-charged samples (25 x 25 x 1 mm) were used to investigate the relationship between hardness and oxygen 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 the specimens in O-charged regions. Vickers hardness was used to determine the depth 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.

Elastic modulus measurements: Elastic modulus measurements were performed by a simple pulse-echo technique on the 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 charging of V-Cr-Ti: When V or V-base alloys (e.g., V-Cr, V-Ti, C-Cr-Ti, or V-Cr-Al) oxidize in a high-oxygen environments, the low-melting V₂O₅ phase forms via cation outward diffusion, 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 in body-centered-cubic (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. Figure 1 shows the weight gain of V-4Cr-4Ti as a function of reciprocal temperature after a 70-h exposure to flowing high-purity Ar and N₂ (99.999%) that contained O as an impurity. At temperatures of 500 to 1030°C, the rate of O pickup by the alloy was greater than that of N. This could indicate that interaction energy between Ti in the alloy with O is greater than that with N. Also, the ionic size of N is larger than that of O. Diffusion coefficients of O and N in V indicate that O diffuses 10 to 1800 times faster than that of N. The activation energies for O and N (plus O) uptake by the alloy are 0.83 and 0.65 eV, respectively.

Figure 2 shows a back-scattered-electron image from the cross section of an O-charged specimen. The dark area indicates the low-atomic-number elements, i.e., the O-enriched area. Localized enrichment of O occurs in the grains and near grain boundaries. From EDS analysis, those areas enriched in O and Ti have a lower Cr content. However, localized Cr depletion did not occur during O-charging at $\leq 670^\circ\text{C}$, as shown in Fig. 2. 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 $\approx 2\text{--}3\%$, depending on position within the layer and exposure conditions.

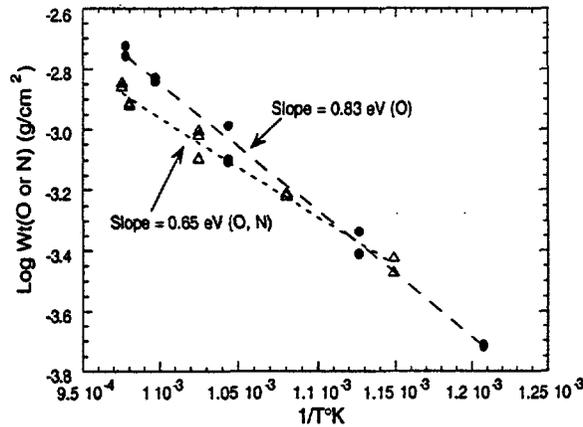


Fig. 1. Weight gain of V-4Cr-4Ti vs. reciprocal temperature after exposure to flowing Ar and N₂ for 70 h.



Fig. 2. Back-scattered electron image from cross section of O-charged V-5Cr-5Ti specimen.

Microhardness tests on O,(N)-charged V-alloys: Figure 3 shows Vickers hardness profiles across the O,(N)-charged region of V-5Cr-5Ti specimens after exposure to high-purity Ar for 40 h at 670, 880, and 1030°C. The high hardness of the near-surface region can be attributed to interstitial O,N atoms in the bcc lattice of the alloy. O,(N)-charging experiments were performed on pure V, V-10Cr, and V-20Ti specimens in the same atmosphere to obtain more insight into the hardening phenomenon. Figure 4 shows the dependence of room-temperature Vickers hardness on exposure temperature (490–890°C) in high-purity Ar for 24 h. Pure V showed the highest hardness among the different specimens, but the O,(N)-charged V-10Cr sample appeared to be more brittle during indentation. These materials exhibited higher hardnesses than did nitrided Ni-Cr alloys, which had a Vickers hardness of 450 kg/mm² [5]. Figures 5a and 5b show hardness profiles across the O-charged region and at ≥200 μm below the surface of V-4Cr-4Ti specimens, respectively, after exposure to

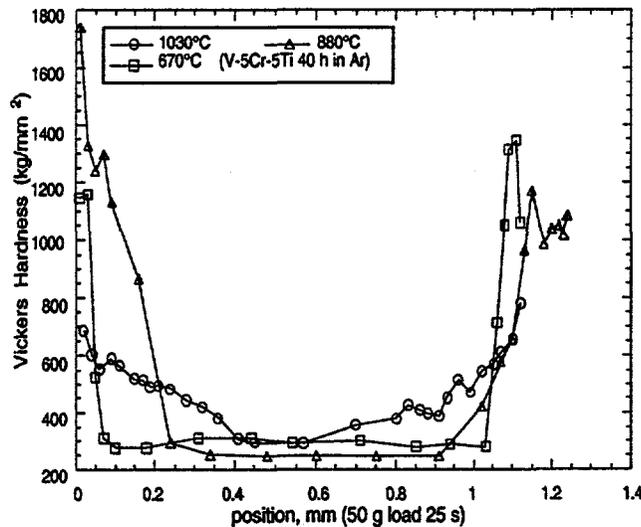


Fig. 3.

Vickers hardness profiles from cross sections of V-5Cr-5Ti specimens exposed to Ar for 40 h at 670, 880, and 1030°C

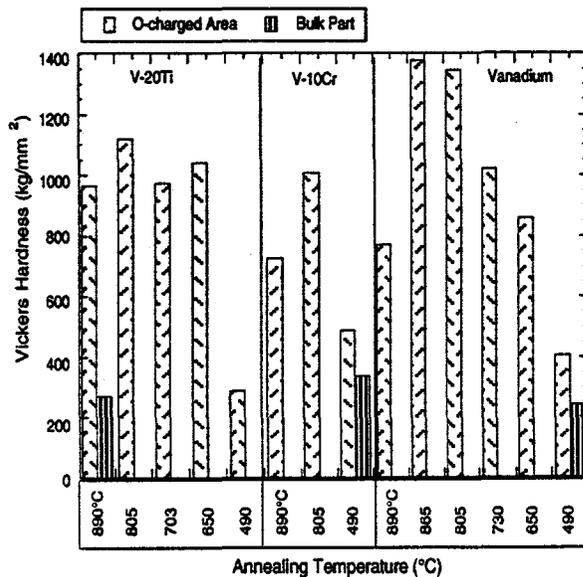


Fig. 4.

Vickers hardness from cross sections of V-20Ti, V-10Cr, and nonalloyed V specimens in near-surface and center regions after exposure to Ar for 24 h at 490–890°C

flowing Ar at several temperatures. Surface hardnesses of these specimens were not as high as those in Figs. 3 and 4. 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

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

550°C than that 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 (Fig. 3) 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. Figure 5(c) shows the integral of hardness–depth profile in the near-surface region versus depth at various temperatures. 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°C > 703°C > 750°C > 550°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.

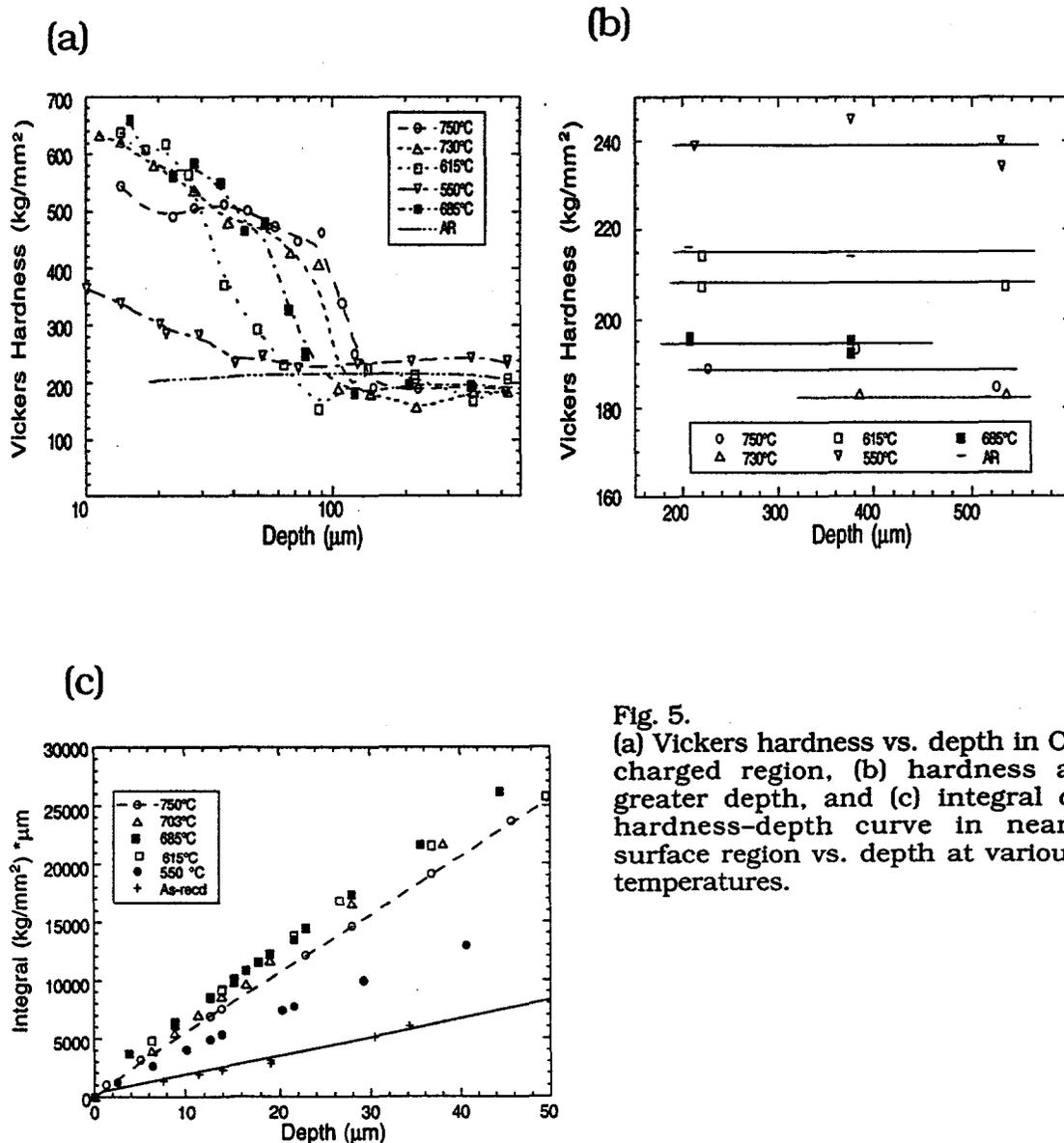


Fig. 5. (a) Vickers hardness vs. depth in O-charged region, (b) hardness at greater depth, and (c) integral of hardness–depth curve in near-surface region vs. depth at various temperatures.

Figure 6 is a TEM photomicrograph of the 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 the elevated temperatures. Coefficients of thermal expansion (CTE) of dilute solid solutions of O in V-O, Ti-O, or V-Ti-O are probably not much higher than that of V and the alloys, $\approx 9.2 \times 10^{-6}/\text{K}$. However, small coherent particles of oxide, nitride, oxynitride, or carboxynitride present in the alloy at high temperatures probably have lower CTEs than the alloy matrix, and during cooling from high temperatures, stresses develop due to the difference in CTE between coherent particles and the matrix. This effect seems to be more significant than in other alloys systems, e.g., Ni-base alloys [6]. X-ray peaks tend to broaden due to strain that originates from small particles in the alloy (Fig. 6). This provides evidence that hardening occurs by incorporation of interstitial impurities in the alloys.

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. Figure 7 shows SIMS profiles for O and V from the cross section of an O-charged V-5Cr-5Ti specimen. The X-ray spectrum from this specimen did not show significant broadening; only the X-ray lattice parameter of the bcc structure increased. Figure 8 shows the X-ray diffraction spectrum from the surface of the specimen after $\approx 20 \mu\text{m}$ of the O-charged layer was removed by polishing. Figure 9 shows the d-spacing of (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 will follow Ti, and enrichment of O near grain boundaries or the surface will occur.

The X-ray lattice parameter could also increase due to vacancy formation (Fig. 9). However, X-ray diffraction profiles in Fig. 10 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 oxygen partial pressure ($p\text{O}_2$) 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 (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.



Fig. 6.
TEM photomicrograph of O-charged
region of V-5Cr-5Ti after exposure to Ar
for 21 h at 650°C.

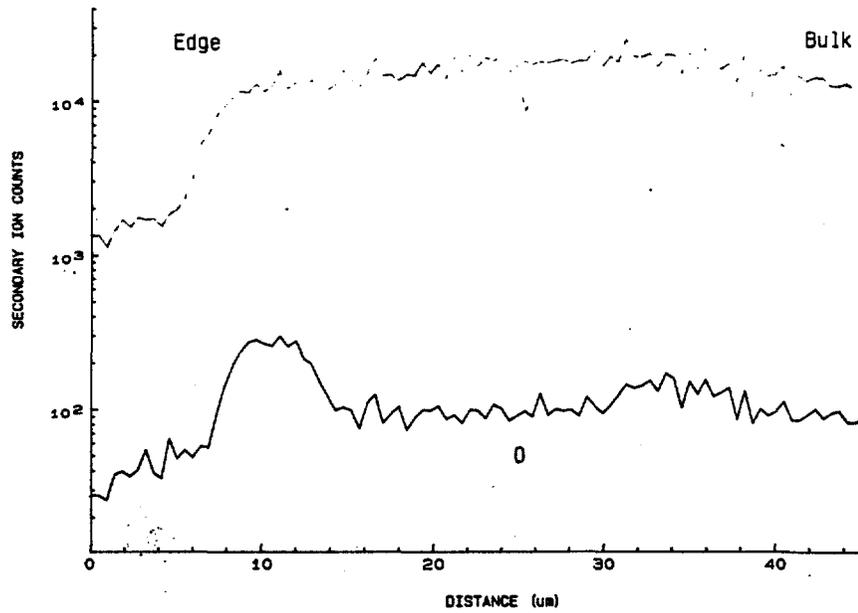


Fig. 7. O and V profiles by SIMS from cross section of V-5Cr-5Ti specimen.

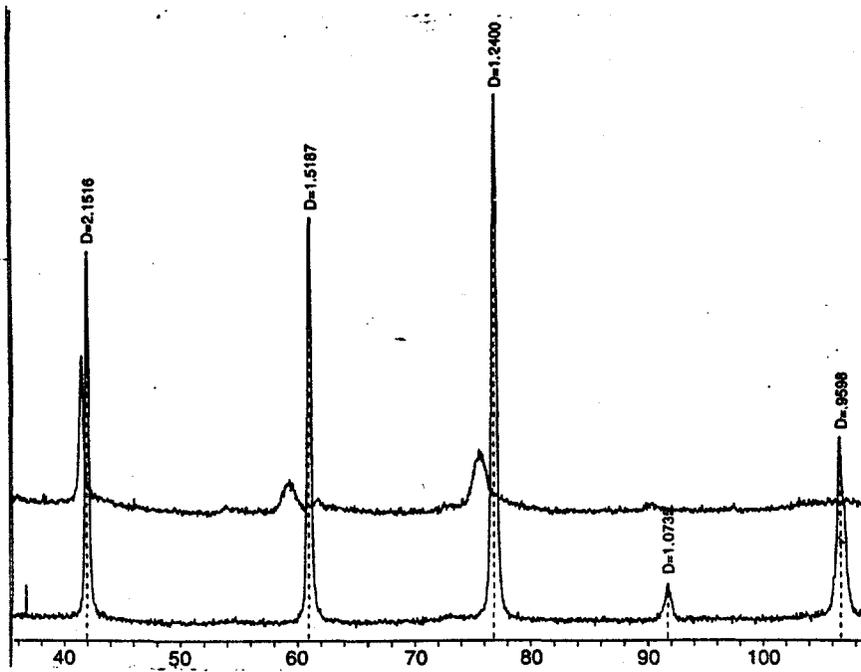


Fig. 8. X-ray diffraction spectra from as-received (bcc) and O-charged (stress, tetragonal phase) V-5Cr-5Ti specimens.

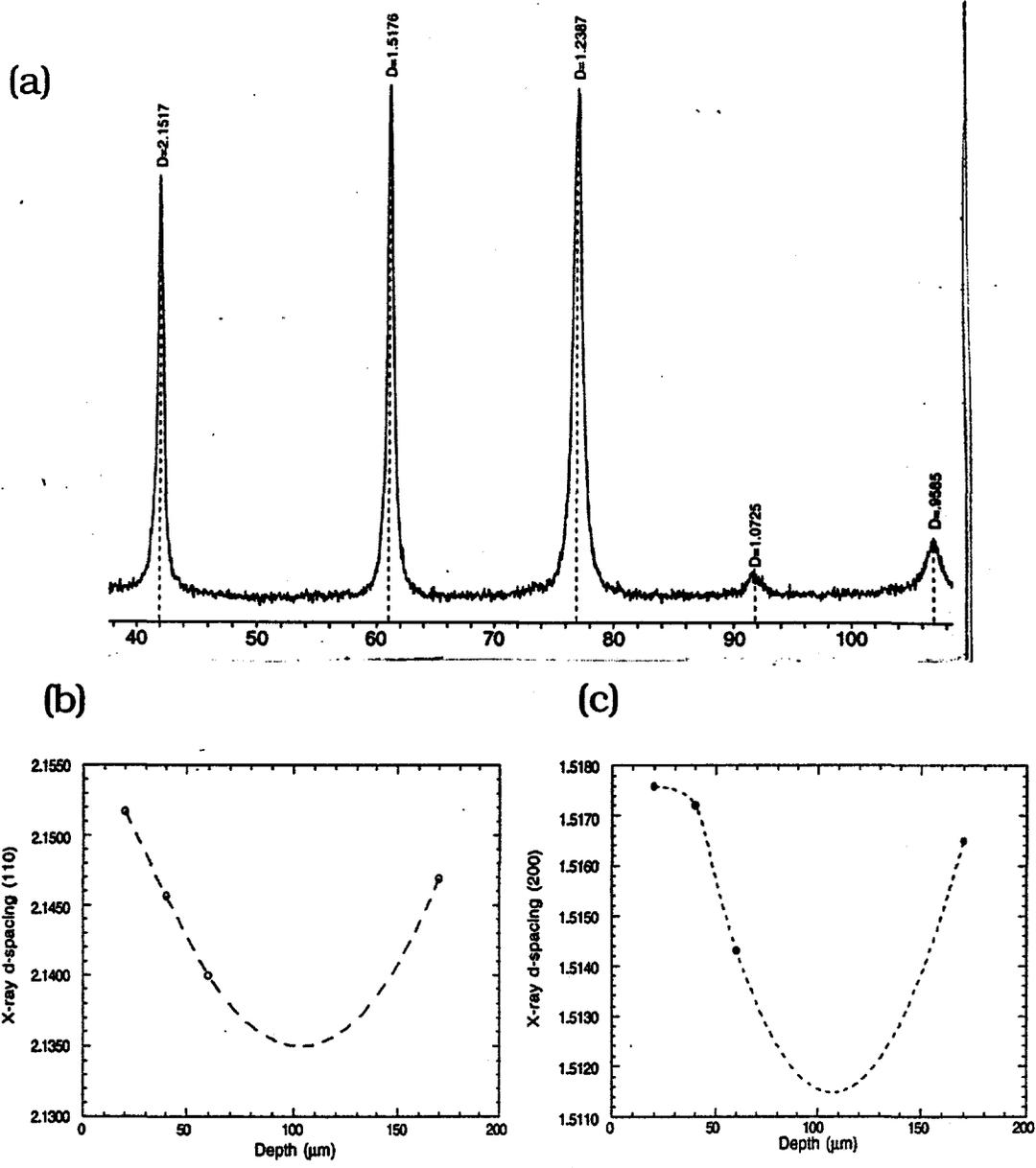


Fig. 9.
 (a) X-ray diffraction spectrum for V-CR-5Ti after removal of $\approx 20 \mu\text{m}$ of O-charged layer, (b) X-ray d-spacing of (110), and (c) (200) plane as a function of depth.

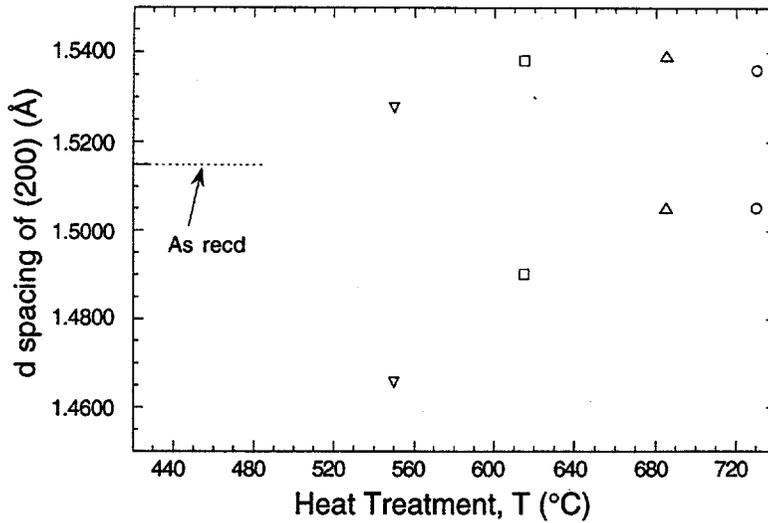


Fig. 10. Splitting of X-ray d-spacing (200) vs. temperature of O-charging. As-received (black dot) is bcc.

Elastic modulus measurements on O-charged specimens: 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. 11, and the data are replotted in Fig. 12 in terms of the change in elastic modulus with the amount of either O or O, N in the V-4Cr-4Ti samples.

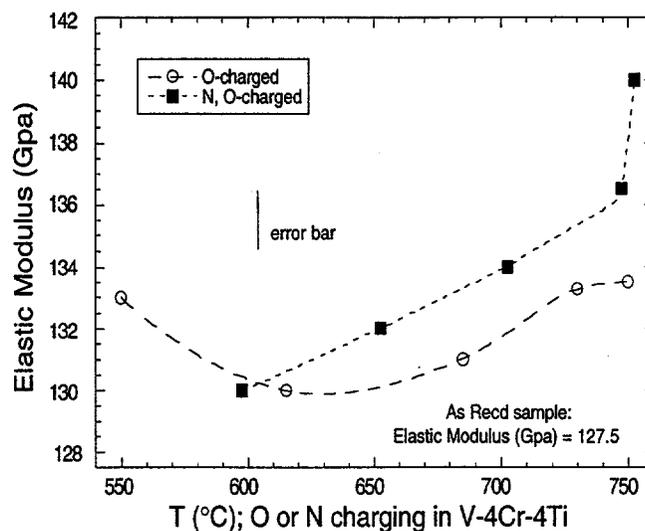


Fig. 11. Room-temperature elastic modulus of V-4Cr-4Ti vs. temperature of O or N charging.

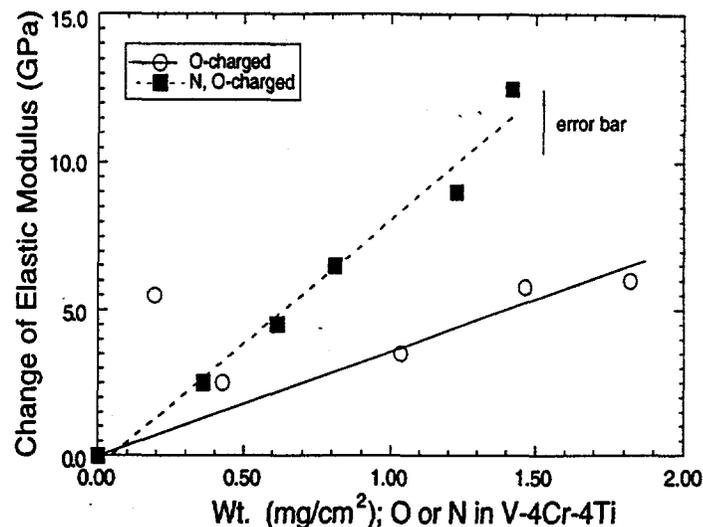


Fig. 12. Change in elastic modulus of V-4Cr-4Ti vs. weight gain during either O or O,N charging.

SUMMARY

Incorporation of O and N in the surface of V-Ti-Cr alloys has been investigated in controlled environments at 550-750°C. For the same exposure time and temperature, O pickup exceeded that of N in the alloys, as determined by weight-change measurements; however, N produced a higher degree of hardening in the alloys. X-ray diffraction indicated a phase transformation from body-centered-cubic (bcc) to tetragonal 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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KEY WORDS

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Vickers hardness
Phase transformation
SIMS depth profile
Elastic modulus