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Solute interactions in pure vanadium and V–4Cr–4Ti alloy

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Abstract

Room temperature electrical resistivity and microhardness measurements were performed on cold-worked pure vanadium, solution annealed and cold-worked V–4Cr–4Ti alloy and fusion weld material over the isochronal annealing temperature range from 200°C to 1200°C. The results suggest that Ti solutes in the vanadium alloy interact with interstitial O, C and N elements at temperatures of 200°C and higher. This interaction lowers the effective diffusivity of the interstitials in the alloys, which shifts the interaction of interstitials with dislocations to higher temperatures as compared to the cold-worked vanadium. Over temperature ranges associated with recovery and recrystallization, general trends showed that the hardness decreased and resistivity first decreased but then increased in each material. Microstructural changes caused by precipitation and by reduction in dislocation density during recrystallization may account for most of the differences observed in the measured properties of each material. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Vanadium alloys with compositions near V–4Cr–4Ti have received significant attention in the past eight years due to their attractive combination of good thermal conductivity and strength along with low ductile-to-brittle transition temperature (DBTT) in the unirradiated condition. Based on current thermomechanical processing practices, the large heats (>500 kg) of vanadium alloys that have been fabricated over the past five years have contained interstitial impurities such as O, C and N solutes in cumulative concentrations ranging from 400 to 700 appm. Several studies have shown that a portion of the interstitials react with Ti solutes to form globular-shaped Ti-oxycarbonitride (Ti-OCN) precipitates [1]. In addition, other precipitates including a platelet-shaped Ti-oxide have been reported to form in alloys containing high O levels, which are encountered in weld and oxidation studies [2,3]. The remaining unreacted interstitial content is dissolved in the bcc matrix of the vanadium alloy. However, both the dissolved and precipitated interstitials can significantly affect the thermomechanical processing and the mechanical properties of vanadium alloys. The Ti-OCN precipitates can affect the grain size distribution during processing [4], while the dissolved interstitials can increase the DBTT for fracture [5] and are implicated in the dynamic strain aging (DSA) phenomena that occur over the temperature range from 300°C to 700°C [6]. Therefore, the purpose of this study is to advance the understanding of interactions between Ti and interstitial O, C and N solutes by measuring the electrical resistivity and hardness of vanadium and V–4Cr–4Ti alloys from room temperature up to 1200°C.

2. Experimental

The physical property measurements were performed on type SS-3 sheet tensile specimens of unalloyed vanadium (heat #820642) and V–4Cr–4Ti (heat #832665), which were from heats fabricated by Oremet–Wah Chang. The tensile specimens had nominal lengths of 25.4 mm and gage dimensions of 0.76 × 1.52 × 7.6 mm^3 and were electro-discharge machined from thin plates of vanadium or V–4Cr–4Ti. The vanadium specimens were prepared from a 3.175 mm thick, 50% cold-worked (CW) plate. The V–4Cr–4Ti specimens were prepared

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from a 3.81 mm thick, 40% CW plate. Half of the tested specimens were annealed at 1000°C for 2 h in a vacuum of $<\sim 3\times 10^{-7}$ Torr followed by furnace cooling. The weld specimens were prepared from a 0.76 mm thick section that was cut from the fusion zone of a gas tungsten arc (GTA) welding of a 6.35 mm thick V–4Cr–4Ti plate.

The isochronal annealing experiments were conducted using six specimens from the CW vanadium, CW V–4Cr–4Ti and annealed V–4Cr–4Ti and three specimens from the GTA weld. Measurements were performed at room temperature following each isochronal annealing at temperatures between 200°C and 1200°C for 1 h. The specimens were wrapped in tantalum foil and the annealings were performed in a vacuum of $\sim(0.7\text{–}1.2)\times 10^{-6}$ Torr using a constant heating rate of 10°C/min and furnace cooling. Table 1 shows the results of the chemical analysis for interstitial O, C and N on specimens before annealing and after the final annealing at 1200°C.

The electrical resistivity measurements were performed on the specimens using a four-point probe technique covered in ASTM Standard Method of Test for Resistivity of Electrical Conductor Materials, ASTM B 193-87 (reapproved 1992) and described by Zinkle et al. [7]. The resistivity data consisted of five measurements per specimen, which were averaged and corrected to a reference temperature of 20°C. The typical standard error of the mean was ±0.5 nΩ m for five resistivity measurements per specimen and ranged from ±0.3 to ±1.4 nΩ m for resistivity measurements of specimens within each category. The microhardness measurements were performed using a Vickers pyramidal indenter with a 1 kg load. Generally, between 2 and 4 indents per specimen were made near the end tab region of the SS-3 tensile specimens. The CW and annealed specimens of the V–4Cr–4Ti alloy consistently showed less scatter in hardness values as compared to CW vanadium and GTA weld specimens; the typical standard error was ±3 DPH for the alloy, ±5 DPH for the CW vanadium and ±8 DPH for the weld specimens. The largest scatter was measured at lower temperatures before sufficient recovery and recrystallization processes had occurred.

3. Results

3.1. Initial microstructures

The microstructures of the specimens prior to the isochronal annealings have been summarized in previous studies for the V–4Cr–4Ti alloy [1] and the GTA welded alloy [2]. In general, these studies have shown that the microstructure of the annealed V–4Cr–4Ti alloy consisted of fully recrystallized grains with a mean size of 23 μm (±2 μm), while the CW V–4Cr–4Ti alloy consisted of elongated grains containing dense dislocation substructures. Both the CW and annealed alloys contained a low number density and inhomogeneous distribution of globular-shaped Ti-OCN precipitates that were <1.0 μm in size. The fusion zone of the GTA welded alloy consisted of large columnar grains containing a moderate dislocation density and an inhomogeneous distribution of platelet-shaped Ti-OCN precipitates that were located primarily on dislocations.

A quite different microstructure was encountered for specimens of the CW vanadium. It was found that these specimens consisted of large grains which were several centimeters in size, containing dense dislocation substructures. Thus, the SS-3 tensile specimens were essentially single- or bi-crystals. The large grain size occurred as a result of not including a thermomechanical step to break up the coarse grain size of the cast ingot during processing of the plate. Therefore, care should be given in interpreting the measured hardness and resistivity data of these specimens, since the measurements do not include effects of grain boundaries and grain size, which will affect the mechanical and physical properties of materials.

3.2. Measured properties

Fig. 1 shows the behavior of the measured hardness and resistivity for specimens of CW vanadium, CW and annealed V–4Cr–4Ti and the welded alloy over the temperature range from 200°C to 1200°C. The data are shown as changes in properties measured at room temperature after each isochronal annealing from the reference room temperature values. At room temperature,

Table 1
Chemical analysis of vanadium, V–4Cr–4Ti alloy and weld before and after the isochronal annealing experiments

Material	Sample condition	O (wppm)	N (wppm)	C (wppm)
50% CW vanadium	SS-3	340	177	198
	Annealed SS-3	320	222	157
40% CW V–4Cr–4Ti	Ingot	310	85	80
	Annealed SS-3	492	109	196
Annealed V–4Cr–4Ti	Ingot	310	85	80
	Annealed SS-3	390	102	165
GTA weld	As-welded SS-3	457	95	235
	Annealed SS-3	484	108	225

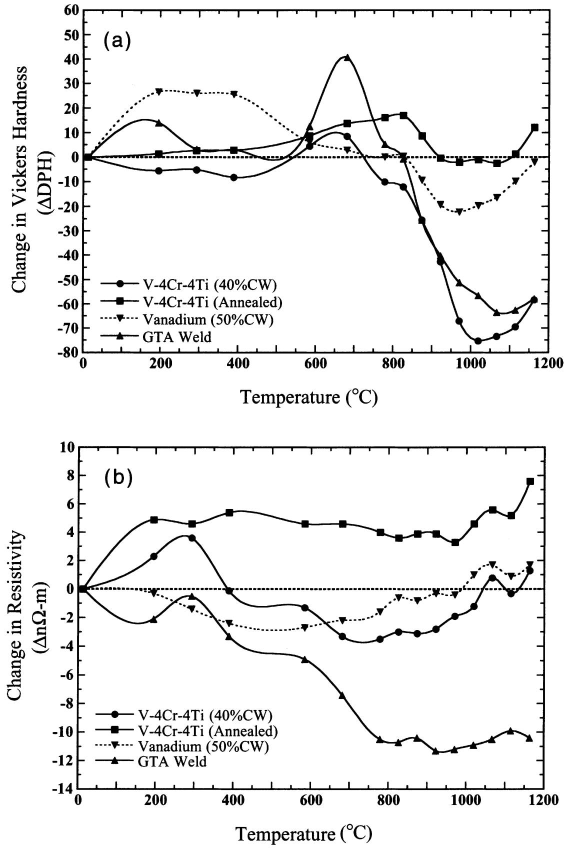

Fig. 1. Changes in the measured room temperature (a) hardness and (b) electrical resistivity after each isochronal annealing.

the lowest hardness was measured for the CW vanadium (116 DPH) followed by the annealed V–4Cr–4Ti (140 DPH) and the highest hardness was measured for the CW V–4Cr–4Ti (210 DPH) and weld (213 DPH). The same trend was observed for resistivity; which was 219.1 nΩ m for the CW vanadium, 285.1 nΩ m for the annealed V–4Cr–4Ti, 286.3 nΩ m for the CW V–4Cr–4Ti, and 294.2 nΩ m for the weld.

The results showed that, for the CW vanadium specimens, the hardness increased sharply and the resistivity decreased slightly over the temperature range from 200°C to 400°C. The magnitude of the hardness increase was ∼26 DPH. However, the hardness decreased above 400°C, reached a minimum at ∼1000°C, and increased with increasing temperature above 1000°C. The resistivity reached a minimum between ∼400°C and 600°C and then increased slowly with increasing temperature.

For the annealed and CW V–4Cr–4Ti specimens, the measured properties showed similar trends for hardness, but opposite trends for resistivity below ∼800°C. The measured hardness did not change significantly from room temperature to ∼400°C but showed minor maxima at 700–800°C in both specimens. The hardness decreased with increasing temperature above ∼800°C and both specimens showed minima at 1000–1100°C. The behavior in resistivity was significantly different between the annealed and CW specimens. For the annealed specimens, the resistivity increased by ∼5 nΩ m after annealing at 200°C and remained positive up to 1200°C. Although the resistivity increased ∼3.6 nΩ m with temperature up to 300°C for the CW specimens, it then decreased with increasing annealing temperature. The resistivity reached a minimum between 700°C and 800°C and subsequently increased up to 1200°C in the CW specimens.

The measurements for the weld specimens showed similar behavior in hardness, but significantly different behavior in resistivity compared to the annealed and CW V–4Cr–4Ti specimens. The hardness showed minor and major maxima at 200°C and 700°C, respectively, and a minimum near 1100°C. The resistivity decreased continuously relative to room temperature with increasing annealing temperature and reached a minimum at ∼283.5 nΩ m, where it then remained nearly constant from 800°C to 1200°C.

4. Discussion

There have been few systematic studies of property changes in the V–4Cr–4Ti alloy over temperature ranges corresponding to those of thermomechanical processing and proposed applications. An exception to this was the study by Loomis et al. [8], who investigated hardness changes in cold-worked V–Ti and V–Cr–Ti alloys from room temperature up to 1200°C. In their study, hardness maxima were observed in an 85% CW alloy (V–4Cr–4Ti) at three temperature ranges: 180–250°C, 420–800°C and 1050–1200°C. However, a hardness maximum was only observed in the 40% CW alloy at ∼700°C in this study. The reason for these differences may be related to the indenter load, which was 1 kg in this study compared to 50 g used by Loomis et al. The larger load is more representative of bulk property behavior, while the smaller load would be more sensitive to the surface property behavior of test specimens.

The observed differences in the properties of specimens from 200°C to 400°C can be rationalized based on interactions between mobile interstitial solutes and both dislocations and Ti solutes. In this temperature range, recovery processes of dislocation substructures in the CW specimens may not be very active [9]. However, the interstitial solute atoms are mobile. Published diffusion data for pure vanadium [10] indicate that O and C are mobile at temperatures below 200°C and N is mobile below 300°C. Based on the diffusion data, the calculated diffusion distance for O and C is >10 nm (for 1 h) above

~180°C, and for N, this distance occurs above ~275°C. Therefore, interstitial solutes can diffuse to dislocations and form atmospheres. The occurrence of DSA in vanadium over the temperature range from 150°C to 400°C [11] provides evidence of interstitial solute atmosphere formation. In addition, the DSA phenomenon is associated with an increase in the ultimate tensile strength and work hardening rate. Since hardness is a material property that is generally viewed as resistance to plastic deformation [12], the formation of atmospheres may be responsible for the hardness increase observed for CW vanadium. The simultaneous decrease in resistivity above 200°C is in agreement with this scenario since interstitial solute atoms are effectively removed from the matrix as the atmospheres are formed. However, it is not clear why the resistivity did not decrease at 200°C since the hardness increased at this temperature. This observation will require further studies including TEM analysis in order to gain a better understanding.

The results suggest that an interaction existed between Ti solute and interstitial solutes since no significant hardening was measured in the V–4Cr–4Ti alloys over the same temperature range of 200–400°C. This interaction would depend on the mobility of interstitial solutes since Ti is essentially immobile in vanadium below 500°C [13]. Indirect evidence of this interaction has collectively been obtained from previous studies. Nakajima et al. [14] observed a lower O diffusivity in a V–5Ti (at.%) alloy than in vanadium (i.e. $d = \sim 11$ nm at 475°C for 1 h compared to ~180°C for equivalent time and distance in unalloyed vanadium). Shikama et al. [15] observed internal friction peaks in the temperature range from 240°C to 375°C in V–Ti alloys that were attributed to either Ti–O or Ti–N interactions [4]. In addition, the DSA phenomenon was observed in the V–4Cr–4Ti alloy above ~300°C [4], which was ~150°C higher than the lower temperature limit of DSA in vanadium. It is presumed that an interaction would have shifted the temperature range associated with the formation of atmospheres by lowering the diffusivity of interstitial solutes. Thus, the interaction is expected to change the hardness property behavior of Ti-containing alloys.

The resistivity data of the alloys measured over the temperature range from 200°C to 400°C are difficult to interpret. This is especially true for specimens of the welded alloy since their microstructures consist of both the heat affected zone (HAZ) and the fusion zone, which typically show differences in compositional segregation effects, formation and distribution of precipitates and deformation structures. Nevertheless, it seems reasonable to assume that the measured resistivity is based on a cumulative effect between one that results from the binding of interstitials to immobile Ti atoms and the other from the formation of atmospheres around dislocations. In the former case, clustering can occur over short distances since the point density of Ti atoms is much higher than the lineal density of dislocations. It is possible that clustering and binding of interstitials to Ti atoms may increase the resultant local strain field of the complex compared to the individual solutes. If this idea is correct, then a high density of these complexes would cause an increase in resistivity. This explanation is the only reasonable one that can account for the increase in resistivity observed in the annealed alloy, which had the lowest dislocation density. For the latter case, the formation of atmospheres causes the removal of interstitial solutes from the matrix that should then lower the local strain field of the interstitial by occupying dilatational sites near the dislocation core. This mechanism requires longer diffusion distances and is more likely to occur at higher temperatures. Assuming that both mechanisms were active, the small resistivity maxima observed at 300°C and subsequent decrease at 400°C would suggest that binding between Ti and interstitial solutes (resistivity increase) occurred at lower temperatures and atmosphere formation (resistivity decrease) occurred at higher temperatures in both the CW and welded alloys. Although this concept is consistent with the resistivity data, it is not consistent with the hardness data. For example, it is unclear why atmosphere formation caused an increase in hardness as the resistivity decreased whereas, in the CW and welded alloys, the same mechanism did not cause an increase in hardness. It may be that solid solution hardening due to Cr and Ti increased the mechanical properties to such an extent that the hardness was relatively insensitive to these microstructural changes.

Recovery and recrystallization processes have been shown to occur in CW vanadium and V–Cr–Ti alloys over the temperature range from ~400°C to ~900°C [9]. In general, both hardness and resistivity are influenced by microstructural factors, such as dislocation density, grain size and precipitates, that depend on temperatures corresponding to these processes. For the CW vanadium, there was a slight decrease in resistivity between 400°C and 600°C followed by a gradual increase with higher temperatures. The possible reasons for this behavior could be the formation of dislocation substructures during recovery at the lower temperatures and the release of interstitial solutes from dislocation atmospheres caused by the decrease in dislocation density during recrystallization at the higher temperatures. The hardness results appear to support a recovery process above 400°C and a recrystallization process above ~800°C since it decreased sharply above each of these temperatures. However, hardness usually does not change appreciably during recovery since the dislocation substructure that develops during this process does not involve a significant loss in dislocation density [12]. It is possible that this discrepancy may be related to the large grain size and subsequent lack of grain boundaries in the

CW vanadium specimens. In this case, considerable softening could have occurred during recovery caused by discontinuous subgrain growth of the dislocation substructure since there would be essentially no resistance to this phenomenon by grain boundaries. Further work is still in progress in order to verify this softening mechanism. The results for the CW alloy did not show a change in hardness corresponding to recovery, but, instead, showed a maximum near 700°C followed by a significant decrease above 700°C that was consistent with recrystallization. The resistivity changes decreased over the corresponding temperature range below the hardness maxima near 700°C and increased over the temperature range related to recrystallization. The discussion provided above for CW vanadium based on dislocations and interstitial solutes can be applied to the CW alloy to explain the behavior in hardness and resistivity changes at temperatures higher than 700°C.

The results showed the occurrence of a maximum hardness near 700°C in specimens of the CW and welded alloys. The appearance of this maximum suggests that a precipitation reaction occurs involving Ti and interstitial solute atoms. This assumption is consistent with the results of a previous studies that showed precipitation of Ti-oxides in a V–1Ti alloy at 700°C [16]. Interestingly, the change in hardness at the maximum was larger for the welded alloy compared to the CW alloy. The reason for this difference is related to the large interstitial content of the welded alloys, as shown in Table 1, and to microstructural changes that occurred during welding. In the latter case, all prior precipitates that existed in the alloy plate were dissolved in the welded zone during welding. This would result in a larger concentration of interstitial solutes in solution in the matrix of the welded alloy compared to the CW alloy. This assessment is consistent with the larger decrease in resistivity that was observed for the welded alloy compared to the CW alloy. It should also be pointed out that the annealed alloy showed a hardness maximum, but it was not well defined and it occurred at a higher temperature, near 850°C. Provided that the hardness maximum is caused by precipitation, the reason for this higher temperature may partly be the low dislocation density in the annealed alloy. The low dislocation density could have an effect on both the bulk diffusivity of Ti and the nucleation behavior of the precipitates.

The dominant processes occurring above 900°C were related to recrystallization and grain growth. These processes typically cause the hardness to decrease. This trend appears to have occurred in all of the specimens in the 900–1000°C range. With the reduction in dislocation density during recrystallization, interstitial solutes would concurrently enter back into solution. For similar reasons as described previously, this scenario accounts for the decrease in hardness and gradual increase in resistivity that were observed for the CW vanandium and CW alloy during recrystallization. However, the annealed alloy and welded alloy also showed similar hardness decreases over this temperature range but neither showed any significant changes in resistivity. Thus, it is unclear what mechanisms are responsible for the property behavior observed in these specimens. The results also showed that a minimum in hardness occurred between 1000°C and 1100°C, followed then by a hardness increase up to 1200°C in all of the specimens. The resistivity also increased over this temperature range in all of the specimens except for those of the welded alloy. It is possible that contamination by interstitial elements may have occurred during the annealing of the specimens at temperatures above ~1100°C. This possibility is supported by the chemical analysis results shown in Table 1. Further work will be conducted to determine if contamination occurred at the higher annealing temperatures.

5. Conclusions

The results of this study showed that there are several processes which can affect the interactions between Ti and interstitial solutes in vanadium and V–4Cr–4Ti alloy over the temperature range from 200°C to 1200°C. These processes involve thermal activation such as diffusion, precipitation and dislocation cross slip and climb mechanisms. The measured hardness and resistivity data suggest that Ti solutes in the V–4Cr–4Ti alloy interact with interstitial O, C and N elements at temperatures of 200°C and higher. This interaction lowers the effective diffusivity of the interstitials in the alloys, which appears to shift the interaction of interstitials with dislocations to higher temperatures as compared to the cold-worked vanadium. At intermediate temperatures associated with recovery of deformation structures, the hardness and resistivity properties decreased with increasing temperature. The results indicate that a precipitation process may be occurring in the V–4Cr–4Ti alloy and weld near 700–800°C, which overlaps the recovery stage and early recrystallization stage. With the onset of recrystalliztion, the hardness decreased further but the resistivity increased with increasing temperature in each material. The latter result was attributed to interstitials entering back into solution as the dislocation density decreased.

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