HARDNESS RECOVERY OF 85% COLD-WORKED V-Ti AND V-Cr-Ti ALLOYS UPON ANNEALING AT 180°C TO 1200°C* - B. A. Loomis, L. J. Nowicki, and D. L. Smith (Argonne National Laboratory)

OBJECTIVE

The objective of this research is to determine the effect of heat treatment of cold-worked V-Ti and V-Cr-Ti alloys on their resulting microstructures and to correlate the results with the physical and mechanical properties of these alloys.

SUMMARY

Annealing of 85% cold-worked unalloyed V and V-(1-18)Ti alloys for 1 hr at 180°C to 1200°C results in hardness maxima at 180-250°C, 420-600°C, and 1050-1200°C and in hardness minima at 280-360°C and, depending on Ti concentration in the alloy, at 840-1050°C. Annealing of 85% cold-worked V-(4-15)Cr-(3-6)Ti alloys for 1 hr at 180°C to 1200°C results in hardness maxima at 180-250°C, 420-800°C, and 1050-1200°C, and in hardness minima at 280-360°C and 920-1050°C. Tentative interpretations are presented for the hardness maxima and minima. Annealing of specimens at 1200°C results in significant increase of VHNs upon removal of a 0.05-mm-thickness surface layer from the specimens.

INTRODUCTION

Vanadium-base alloys have been identified as leading candidates for fusion first-wall/blanket applications. The performance advantages of vanadium-base alloys, in addition to their excellent safety and environmental features, have been evaluated in several design studies [1-5]. The current focus of experimental effort on the mechanical and physical properties of vanadium-base alloys is on alloys with 3-5% Cr and 3-5% Ti [6-9]. However, most of the experimental data reported for these alloys have been obtained on materials in the fully recrystallized condition [6-16]. The purpose of the research presented in this report is to comprehensively evaluate the effect of heat treatment of cold-worked V-Ti and V-Cr-Ti alloys on their resulting microstructure and to correlate the results with the physical and mechanical properties of these alloys. Recovery of the microhardness of cold-worked alloys with annealing temperature is utilized for the initial definition of the principal thermodynamic processes that these cold-worked alloys undergo during heat treatment.

MATERIALS AND PROCEDURES

Specimens of unalloyed V, V-Ti alloys, and V-Cr-Ti alloys with the compositions listed in Table 1 were obtained from recrystallized stock containing <30 appm H (Charpy-impact specimens, 0.33-cm thickness, 20-40 μm average grain size) by rolling of this stock to 0.05-cm thickness (85% thickness reduction at 25°C) without an intermediate annealing. One surface of the rolled specimens was polished to a surface finish of 1 μm for hardness measurement. The unalloyed V and V-Ti binary alloy specimens were polished simultaneously. The V-Cr-Ti alloy specimens were also polished simultaneously, but separate from the V-Ti alloys. Hence, the concentration of hydrogen introduced into the V-Ti and V-Cr-Ti alloy specimens during polishing was nearly equivalent. Specimens were also obtained with no alteration of the rolled surface, in order to evaluate the effect on hardness measurement of hydrogen introduced during polishing of the specimens [11]. In addition, hardness measurements were made on specimens annealed at 1200°C after removal of a 0.05-mm-thickness layer for evaluation of the effects of environmental contamination of the specimens and/or thermal evaporation of alloy constituents.

The cold-worked (CW) specimens were annealed in an ion-pumped system capable of maintaining a pressure of $< 2 \times 10^{-5}$ torr during annealing of specimens at 1200°C. The specimens were wrapped in tantalum sheet with an enclosed thermocouple and were heated by a resistance furnace. The specimens were heated at a rate of 10

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-15°C/min to the annealing temperature, maintained at the selected temperature (±5°C) for 60 min, and subsequently cooled to <100°C at 50-100°C/min.

Microhardness measurements were conducted on the CW and annealed specimens at 25°C with a Leitz Durimet Hardness Tester equipped with a Vickers indenter. The Vickers Hardness Number (VHN) was obtained from the average of two dimensions of each of two or three indentations on a specimen resulting from application of a 50-g load to the indenter for 0.3 min.

Table 1. Compositions of V, V-Ti alloys, and V-Cr-Ti Alloys. *,**

Material	ANL No.	Cr	Ti	Other	O	N	C	Si
V	BL 51	<100	130	0.03% Mo	570	49	56	370
V-1Ti	BL 50	<100	1.0%	0.08% Al	230	130	235	1050
V-3Ti	BL 62	<100	3.1%	0.07% Al	320	86	109	660
V-5Ti	BL 46	<100	4.6%	0.04% Al	305	53	85	160
V-10Ti	BL 12	<100	9.8%	0.63% Fe	1670	390	450	245
V-18Ti	BL 15	150	17.7%	0.04% Fe	830	160	380	480
V-5Cr-3Ti	BL 54	5.1%	3.0%	0.07% Al	480	82	133	655
V-4Cr-4Ti	BL 47	4.1%	4.3%	0.03% Al	350	220	200	870
V-5Cr-5Ti	BL 63	4.6%	5.1%	0.02% Al	440	28	73	310
V-8Cr-6Ti	BL 49	7.9%	5.7%	0.02% Al	400	150	127	36
V-9Cr-5Ti	BL 43	9.2%	4.9%	0.02% Fe	230	31	100	340
V-14Cr-5Ti	BL 24	13.5%	5.2%	0.05% Fe	1190	360	500	390
V-15Cr-5Ti	BL 41	14.5%	5.0%	0.02% Fe	330	96	120	400

* All compositions in wt. ppm or wt. percent (%).

** Analyses performed by the Analytical Laboratory, Teledyne Wah Chang Albany, Albany, Oregon.

EXPERIMENTAL RESULTS

V and V - (1-18)Ti Alloys

The VHNs for unalloyed V and several V-Ti alloys after annealing of the 85% CW specimens for 1 hr at temperatures ranging from 180°C to 1200°C are shown in Fig. 1. Annealing of 85% CW specimens at 180°C to 1200°C results in hardness maxima at 180-250°C, 420-600°C, and 1050-1200°C and in hardness minima at 280-360°C and 840-1050°C. It can be noted in Fig. 1 that the 840-1050°C hardness minima are strongly dependent on the Ti concentration, with the temperature of the VHN minimum increasing with decreasing Ti concentration in the material. The VHN data (Fig. 1) for unalloyed V and V-Ti alloys after heat treatments at >900°C show that the maxima are ≈1130°C. The VHNs of specimens with polished surfaces were not significantly different from the VHNs of specimens without polished surfaces (data not shown in Fig. 1 for clarity). These results show that the amount of hydrogen (<50 appm) introduced into the specimens during polishing had no significant effect on the recovery behavior of these V and V-Ti alloys.

The dependence of the VHNs for V-Ti alloys on Ti concentration is shown in Fig. 2. The VHNs for V-Ti alloys increase significantly with addition of 1% Ti to vanadium. The VHNs of these V-Ti alloys can increase or decrease when the Ti concentration is increased from 3% up to 5%. Otherwise, the VHNs for the specimens are nearly linearly

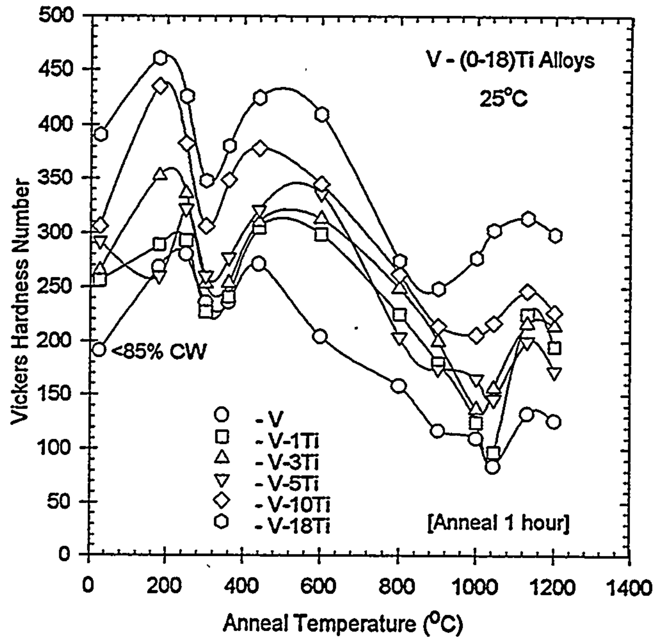

Fig. 1. Recovery of VHN of unalloyed V and V-Ti alloys with 85% CW upon annealing at 180°C to 1200°C.

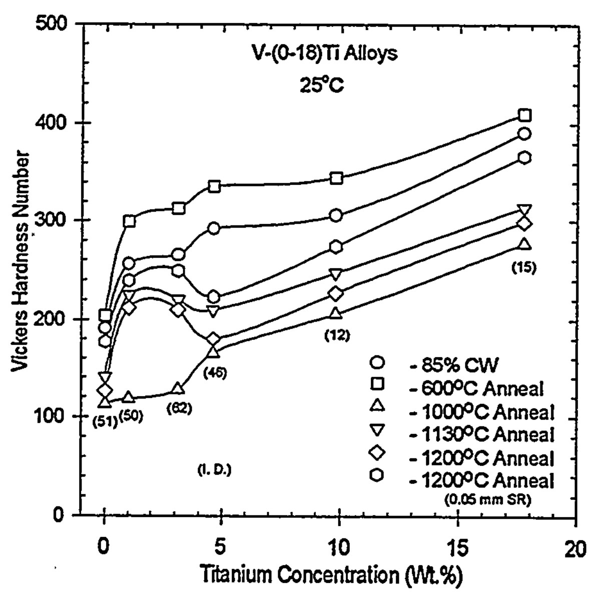

Fig. 2. Dependence of recovery of VHN of V and V-Ti alloys with 85% CW on Ti concentration.

dependent on Ti concentration in the range of 5 to 18% Ti. It can be observed in Fig. 2 that the VHNs of specimens after annealing at 1200°C and removal of a 0.05-mm-thickness surface layer (SR) from the specimens are significantly higher than the VHNs of specimens in the as-annealed condition (1200°C). The difference in VHNs for the specimens with/without SR increased with increasing Ti concentration in the alloy. The surfaces of specimens annealed at 1200°C exhibited significant thermal-induced relief of precipitates and grain boundaries.

V - Cr - (3-6)Ti Alloys

The VHNs of V-Cr-(3-5)Ti alloys after annealing of the 85% CW specimens for 1 hr at temperatures ranging from 180°C to 1200°C are shown in Fig. 3. Annealing of 85% CW specimens at 180°C to 1200°C results in hardness maxima at 180-250°C, 420-800°C, and 1050-1200°C, and in hardness minima at 280-360°C and 920-1050°C. Examination of the data in Fig. 3 for heat treatments of alloys at < 800°C shows that the maxima and minima for the V-4Cr-4Ti alloy (BL 47) are much higher and lower, respectively, than for the V-5Cr-3Ti (BL 54) and V-5Cr-5Ti (BL 63) alloys. In addition, the VHNs for the V-5Cr-3Ti (BL54), V-4Cr-4Ti (BL 47), V-5Cr-5Ti (BL 63), V-9Cr-5Ti (BL 43), and V-14Cr-5Ti (BL 24) alloys heat treated at >1000°C suggest that the VHN maxima are ≈1130°C. As in the case of the V-Ti alloys, the amount of hydrogen (<50 appm) introduced into the V-Cr-Ti specimens during polishing was not sufficient to affect the recovery behavior of these alloys.

The dependence of VHNs for V-Cr-(3-6)Ti alloys on Cr concentration is shown in Fig. 4. These data generally show minimum VHNs for alloys containing 5-8% Cr. It can also be observed in Fig. 4 that the VHNs for the V-14Cr-5Ti alloy (BL 24) are comparable to the VHNs for the V-15Cr-5Ti alloy (BL 41), even though the V-14Cr-5Ti alloy contains substantially higher oxygen, nitrogen, and carbon concentration. The VHNs of specimens annealed at 1200°C (Fig. 4) after removal of a 0.05-mm-thickness surface layer (SR) from the specimens were significantly higher than the VHNs of specimens in the as-annealed condition (1200°C). The difference in VHNs for the specimens with/without SR increased significantly for alloys with increasing Cr concentration in the alloy. The surfaces of specimens annealed at 1200°C exhibited significant thermal-induced relief of precipitates and grain boundaries.

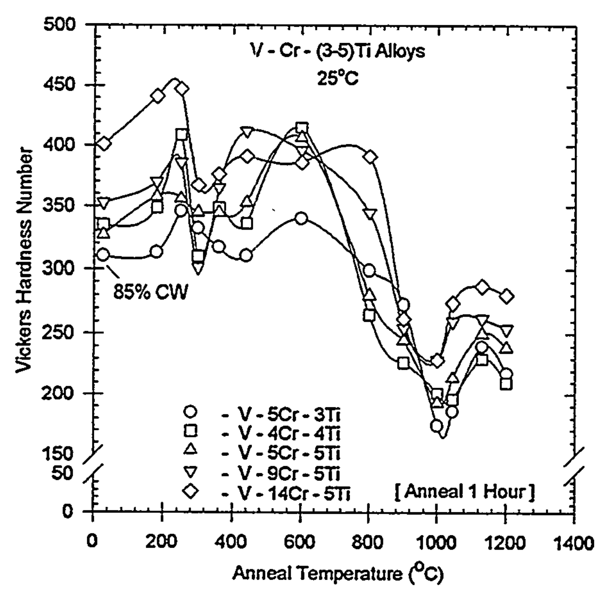

Fig. 3. Recovery of VHN of V-Cr-(3-5)Ti alloys with 85% CW upon annealing at 180°C to 1200°C.

Comparison of Recovery for V-(4-5)Cr-(3-5)Ti Alloys

The dependence of recovery of 85% CW specimens of V-5Cr-3Ti (BL 54), V-4Cr-4Ti (BL 47), and V-5Cr-5Ti (BL 63) alloys upon annealing temperature is shown in Fig. 5. The VHNs for the V-5Cr-3Ti alloy for annealing temperatures < 800°C are, in general, significantly less than the VHNs for the V-4Cr-4Ti and V-5Cr-5Ti alloys. The

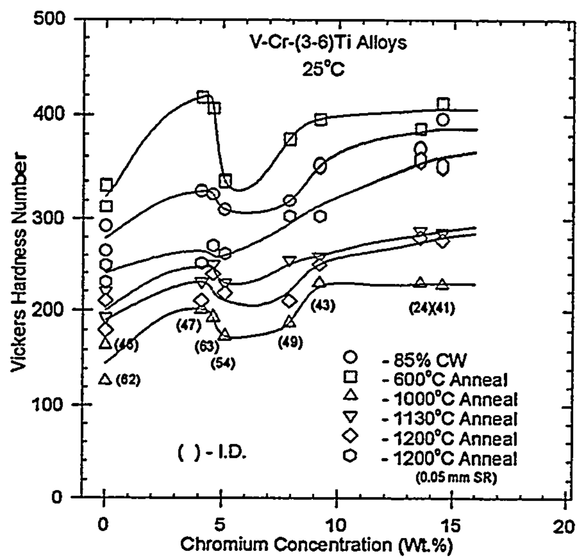

Fig. 4. Dependence of recovery of V-Cr-(3-6)Ti alloys with 85% CW on Cr concentration.

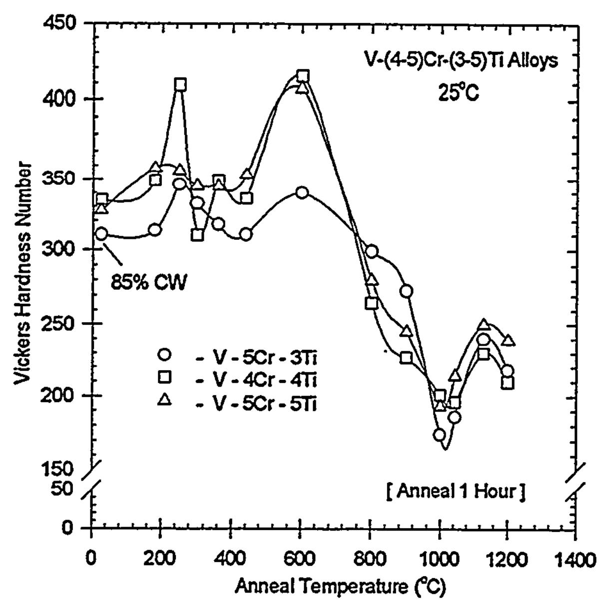

Fig. 5. Recovery of V-5Cr-3Ti, V-4Cr-4Ti, and V-5Cr-5Ti alloys with 85% CW upon annealing.

VHN maximum for the V-4Cr-4Ti alloy after annealing at 250°C is substantially higher than the maximum for the V-5Cr-3Ti and V-5Cr-5Ti alloys; and the VHN minimum for the V-4Cr-4Ti alloy after annealing at 300°C is substantially lower than the minimum for the V-5Cr-3Ti and V-5Cr-5Ti alloys.

DISCUSSION OF RESULTS

The recovery behavior of 85% CW unalloyed V, V-Ti alloys, and V-Cr-Ti alloys upon annealing at temperatures from 180°C to 1200°C (which is evidenced by the VHNs) suggests that similar thermodynamic processes occur in these materials upon heat treatment. However, critical examination of the data in Figs. 1-5 shows that processes are occurring in these materials that require further investigation, e.g., (1) VHN maxima at 840-1050°C in V-Ti alloys that increase with decrease of Ti concentration in the alloys; (2) heat treatment of V-Cr-Ti alloys at < 800°C resulting in VHN maxima and minima for the V-4Cr-4Ti alloy that are significantly higher and lower, respectively, than for the V-5Cr-3Ti and V-5Cr-5Ti alloys; (3) the significant increase of VHN for the materials upon heat treatment at >1050°C; and (4) the increase of VHN of the specimens at 0.05-mm-depth below the surface of specimens after annealing.

Interpretation of the recovery and the maxima and minima of VHNs for the unalloyed V, V-Ti alloys, and V-Cr-Ti alloys upon heat treatment would be supposititious in the absence of a comprehensive series of microstructural observations by optical and transmission electron microscopy. However, it is tentatively suggested that the following processes may be involved in the recovery of the 85% CW microstructure upon annealing of these unalloyed V and V alloys. The maxima at 180-250°C may be due to the diffusion of H, O, N, and C to the CW dislocation structure [11, 17]. The relative contributions to the 180-250°C maxima would seem to favor an effect due to the O, N, and C impurities, since the hydrogen concentration in the specimens was < 50 appm. Moreover, the VHNs for theV-10Ti and V-18Ti alloys (Fig. 1) and V-4Cr-4Ti and V-14Cr-5Ti alloys (Fig. 3) after annealing at 180-250°C are the highest of the alloys, which is in agreement with the highest O, N, and C concentration in the alloys (Table 1). The minima at 300-360°C may be attributed to the evolution of H from the specimens and/or removal of O, N, and C from solid solution by interaction with V atoms (unalloyed V) and Ti solute in the alloys. The maxima at 420-800°C may be attributed to the formation of precipitates, e.g., Ti(C, N, O), $Ti(C_{1-x-y}N_xO_Y)$, V_6O_{13}, VS_4 and V_4C_3[15]. The minima at 840-1050°C may be attributed to a combination of annihilation and rearrangement of CW dislocation structure, recrystallization, grain growth, formation of additional precipitates, e.g., Ti_5Si_3, [8,9] and redistribution of impurities, e.g., S and P. The maxima at 1050-1200°C may be attributed to formation of additional precipitates, e.g., Ti_5Si_3, redistribution of impurities, and thermal evaporation of alloy constituents.

The significant increase of VHNs of 1200°C-annealed specimens upon removal of a 0.05-mm-thickness surface layer (Figs. 2 and 4) is not understood, since it is expected that O, N, and C impurities should equilibrate rapidly throughout the specimen thickness upon annealing at temperatures of >700°C [18]. It may be that evaporation of alloy constituents contributed to the lower VHNs in the near-surface region.

FUTURE EFFORT

(1). The microstructures of the unalloyed V, V-Ti alloys, and V-Cr-Ti alloys will be observed by optical and transmission electron microscopy (TEM) for determination of the significance of the maxima and minima VHNs after heat treatment of the 85% CW material.
(2). The number density and average diameter of precipitates in the 85% CW and heat-treated materials will be determined, and these results will be compared with previously reported data on these parameters for 50% CW and heat-treated material [15].
(3). The dependence of the dislocation density and average grain size in the materials on heat treatment will be determined from optical and TEM observations.
(4). These effects of heat treatment on the recovery and microstructure will be correlated with previously reported experimental data on the physical and mechanical properties of vanadium alloys with different heat treatments [6-16].
(5). The viability of utilizing the temperature-dependent recovery of VHN of CW vanadium alloys for selection of

an alloy with the optimum physical and mechanical properties for use in fusion first-wall/blanket applications will be evaluated.

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