RECOVERY AND RECRYSTALLIZATION STUDY ON VANADIUM ALLOYS –

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OBJECTIVE

The aim of this work is to determine the kinetics of recovery and recrystallization, and to develop a suitable model to explain mechanistics of recrystallization of vanadium alloys with Cr and Ti contents ranging from 3 to 6 wt %.

SUMMARY

A series of vacuum-anneals at temperatures from 900° to 1100°C for 1 to 4 h was carried out on vanadium alloys with Cr and Ti contents ranging from 3 to 6 wt.%. Compositional variants of vanadium alloys (~15-kg melt) and a large heat (~500-kg melt) of V-4Cr-4Ti alloy were studied in this work. Optical microscopy, TEM, and microhardness testing were carried out. The alloys tested followed the metallurgically well-established axiom that longer times at low temperatures and shorter times at high temperatures were needed for complete recrystallization. The recrystallization kinetics was faster in the alloys with higher amount of cold work compared to that exhibited by alloys with lower cold work. The large heat of V-4Cr-4Ti alloy with 40% CW showed recovery for anneals at 900°C, and began recrystallizing at 950°C. Complete recrystallization in this alloy occurred at 1000°C, with grain growth for temperatures of 1050°C and above. Recovery and recrystallization kinetics were faster for the small heats because of the higher level of cold work (49%) in the starting material. However, variations in Cr and Ti over the range 3 to 6 wt % had no discernible effect on recovery/recrystallization behavior. The hardness of both recovered and recrystallized structures increased with total (Cr + Ti) content.

INTRODUCTION

Vanadium alloys with Cr and Ti contents ranging from 3 to 6 wt.% were proposed earlier as possible candidate materials for first wall/blanket structure in fusion reactors.[1-4] More recently,[5] it was suggested that a V-4Cr-4Ti alloy could be a suitable candidate for the first wall and blanket structure for ITER. This was based on its thermal creep properties, low DBTT determined by Charpy (CVN) testing, resistance to helium- and irradiation-induced embrittlement, and swelling resistance. All these tests were conducted on a laboratory-scale heat of V-4Cr-4Ti alloy. Recently, a large heat (~500-kg melt) of V-4Cr-4Ti alloy (heat 832665) was fabricated by Teledyne Wah Chang (Albany, Oregon). No serious efforts have been made till now to determine the kinetics and mechanistics of recovery and recrystallization of vanadium alloys in general, and V-4Cr-4Ti alloy in particular. The present study has been undertaken to accomplish the fundamental understanding of the recrystallization phenomenon in vanadium alloys. Also included in this study were small heats (~15-kg melt) of compositional variants of vanadium alloys with Cr and Ti contents ranging from 3 to 6 wt.%. The objective of including the compositional variants is to obtain a window on the tolerable limits of Cr and Ti contents without significant change in the physical and mechanical properties.

EXPERIMENTAL PROCEDURE

A large heat (~500-kg melt) of V-4Cr-4Ti alloy (heat 832665) and a small heat of (~15-kg melt) V-5Cr-5Ti (T87) were produced by Teledyne Wah Change as per the specifications supplied by Argonne National Laboratory. Four small heats (each ~15-kg melt), V-3Cr-3Ti (heat T91), V-4Cr-4Ti-Si (heat T89), V-6Cr-3Ti (heat T92), and V-6Cr-6Ti (heat T90) were fabricated according to the specifications set by Oak Ridge National Laboratory. The heat T89 was intended to have a higher Si content than that in heat 832665, but ended up being almost the same composition as heat 832665. Therefore, this heat can be considered as a small heat of V-4Cr-4Ti with a different processing history. The samples for the present study were obtained from the rolled plates (~1.02-mm thick) of both the large and small heats. The V-4Cr-4Ti alloy (heat 832665) and the small heat of compositional variant V-5Cr-5Ti had a cold work level of approximately 40%[6] whereas the other small heats had a cold work of approximately 49%. The chemical composition of the large heat is given in Table 1; that of the small heats is given in Table 2. Heat treatments were carried out on samples (for both optical metallography and TEM analysis) from 900° to 1100°C for 1 to 4 h in a vacuum better than 1 x 10^{-6} torr (<10^{-4} Pa). Optical metallography, microhardness testing, and TEM analysis were carried out to understand the effect of temperature-time on the recovery and recrystallization of vanadium alloys.

Table1. Chemical Composition of the large heat of V-4Cr-4Ti

Element	Teledyne Analyses 3 Ingot Positions (wt. ppm)			Glow Discharge Mass Analysis (wt. ppm) (±10-30%)	Inductively coupled Plasma-emission (±5-10%)	Inert Fusion Analysis (wt. ppm)
Al	180	190	105	<200		
As				<3		
B	7	<5	<5	<6*		
C	64	80	94	<310		139
Ca	<10	<10	<10			
Cl	<2	<2	<2			
Cr	3.76%	3.72%	3.83%	3.0%	3.1%	
Fe	180	220	270	256		
Hf				10.8		
Mo	330	350	280	244		
N	82	80	93	<4		102
Nb	<60	60	<60	<80		
Ni				<12		
O	280	360	290	<190		383
P	<30	<30	<30	<61		
Ru				<7		
S	<10	<10	<10	40		8
Si	790	840	720	1000		
Sr				<60		
Ta				<3*		
Ti	4.16%	3.78%	3.80%	5.3%	4.1%	
V				91.6%		
W				22.8		
Zr				<65		

*Known contaminant

RESULTS AND DISCUSSION

LARGE HEAT OF V-4Cr-4Ti (Heat 832665)

The starting material was 1.02 mm thick sheet, which had been annealed by the manufacturer at 1050°C for 2 hours after cold rolling ~40% reduction in thickness. The microstructure contained an elongated grain structure and precipitate particles which had been aligned into stringers during the initial hot working operations. The initial hardness was 200 ± 5 DPH. Annealing at 900°C for 1 to 4 hours reduced the hardness to 165-168 DPH (Fig. 1); corresponding microstructures are shown in Fig. 2. After 1 hour at 950°C, sub-grains approximately 1 μm dia developed within the original elongated grain structure. With increasing annealing time the residual dislocation density within the sub-grains continued to decrease and

Table 2. Chemical Compositions of small heats of Compositional Variants

	V-3Cr-3Ti (T91) Wt.ppm		V-4Cr-4Ti-Si (T89) Wt.ppm		V-5Cr-5Ti (T87) Wt.ppm		V-6Cr-3Ti (T92) Wt.ppm		V-6Cr-6Ti (T90) Wt.ppm	
Element	Lab**	TWCA*	Lab**	TWCA*	Lab**	TWCA*	Lab**	TWCA*	Lab**	TWCA*
B	3.8		3.5		2.7	<6	3.4		3.9	
C	<140	120	<120	112	<110	111	<92	105	<120	104
N	<5.5	62	<1.8	79	<5.5	89	<1.8	95	<4.5	85
O	<270	230	<270	270	<370	380	<200	280	<260	250
Al	240	200	270	200	260	160	300	255	270	235
Si	1200	940	1100	1050	830	545	1000	950	1400	960
P	26	<50	24	<50	32	<30	22	<50	24	<50
S	27	12	23	10	20	<20	21	12	20	10
Ti	3.1%	3.02%	5.3%	4.14%	4.8%	5.07%	3.0%	2.94%	4.6%	5.98%
V	94%	bal.	90%	bal.	90%	bal.	91%	bal.	91%	bal.
Cr	3.0%	2.85%	4.9%	3.7%	4.7%	4.94%	6.2%	5.91%	4.3%	5.74%
Mn	1.1		1.9		3.2		1.7		1.7	
Fe	110	130	140	170	210	160	140	165	120	195
Ni	7.6		12		4.8	77	8.3		10	
Cu	79	83	50	83	62		130	140	48	55
Zn	5.3		4.7		5.8		4.5		4.0	
Ga	3.9		5.9		5.4		7.6		5.0	
As	1.7		2.4		0.31		1.4		2.0	
Sr	<76		<120		<150		<70		<110	
Y	<5.9		<9.3		<11		<6.1		<8.6	
Zr	<48		<63		<73		<56		<66	
Nb	≤55	<50	≤56	<50	≤75	<100	≤50	<50	≤54	<50
Mo	380		360		340	515	380		340	
Rh	0.024		0.016		<0.008		0.02		0.0083	
Ru	0.22		0.18		0.35		0.25		0.252	
Hf	0.45		01.2		0.35		0.45		0.82	
Ta	<9.7		<5.2		<430		<9.0		<98	
W	32		32		35		32		28	

*Teledyne Wah Chang analysis
**Analysis obtained by ORNL from a private lab

after 4 hours a few recrystallized grain nuclei could be detected. No additional precipitation at grain boundaries or within the sub-grains could be detected.

At 950°C the hardness dropped rapidly to ~155 DPH after only 1 hour at temperature (Fig. 1). From the metallography, it was estimated that the material was approximately 10% recrystallized at this point. After 4 hours, the hardness dropped to its minimum value of ~145 DPH, with recrystallization about 30-40% complete. The remaining un-recrystallized regions consisted of well developed sub-grains with a low dislocation density, see Fig. 3. There was some evidence that pre-existing grain boundaries were favored sites for the nucleation of new grains.

Recrystallization occurred rapidly at 1000°C and was complete after 2 hours (Fig. 4); all sub-grains were consumed, leaving a low density of individual dislocations. Particles of an unidentified phase formed on many of the new grain boundaries during cooling from 1000°C.

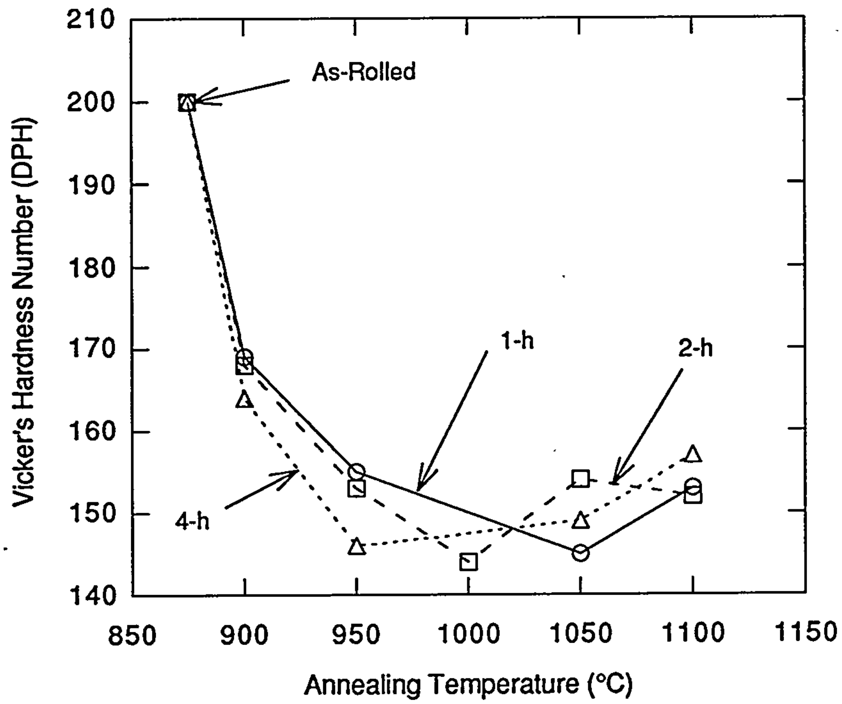

Figure 1. Microhardness as a function of Annealing Temperature for Heat 832665 V-4Cr-4Ti alloy

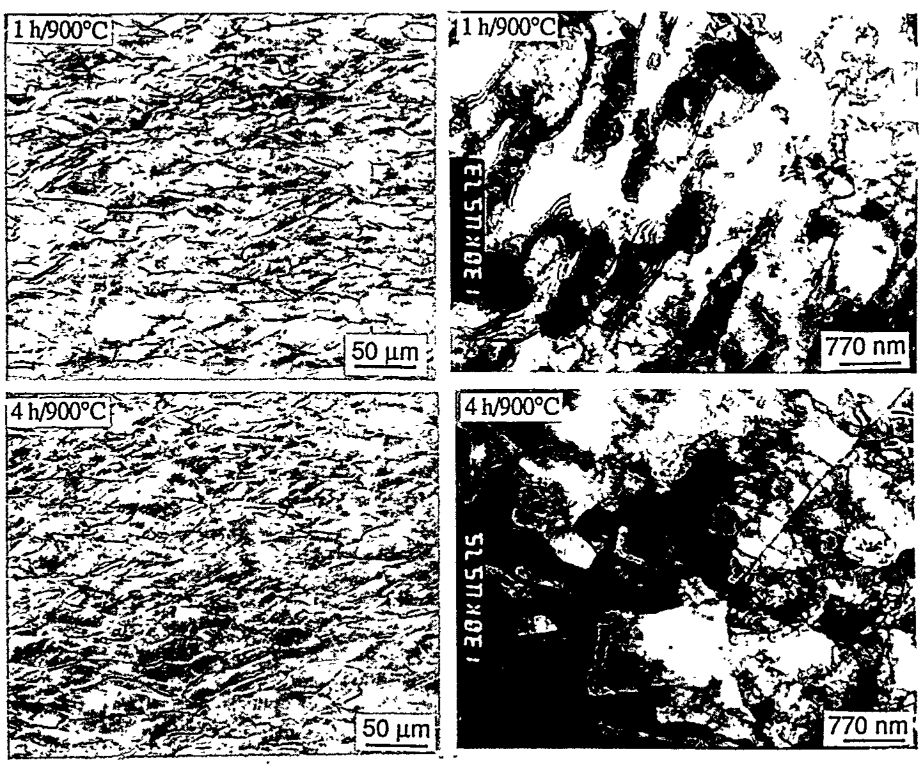

Figure 2. Optical and TEM microstructures at 900°C for the large heat of V-4Cr-4Ti

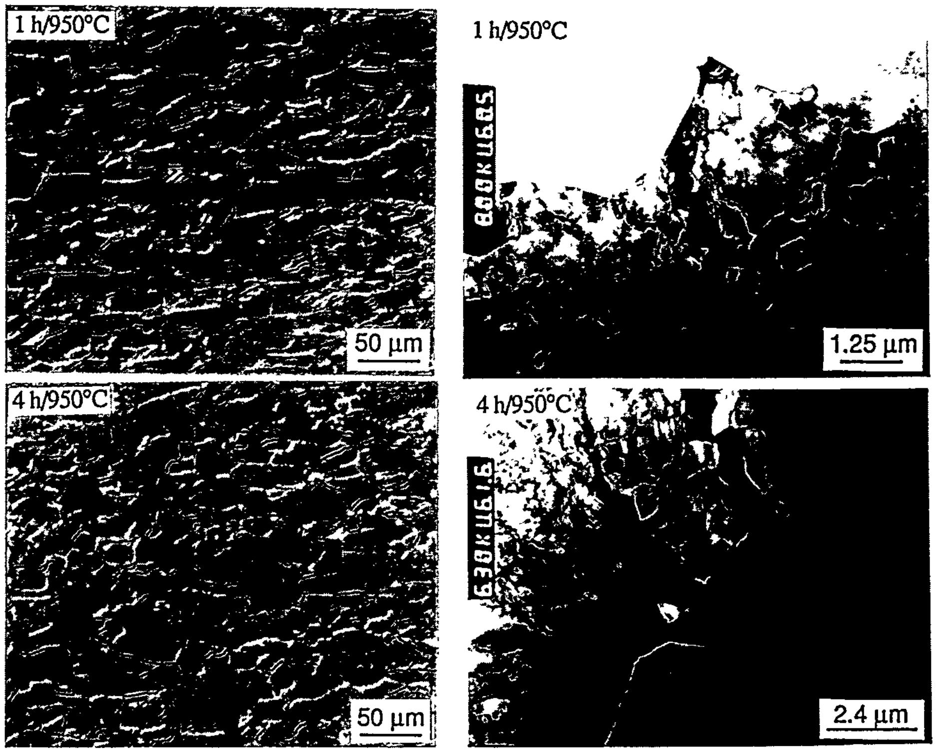

Figure 3. Optical and TEM microstructures at 950°C for the large heat of V-4Cr-4Ti

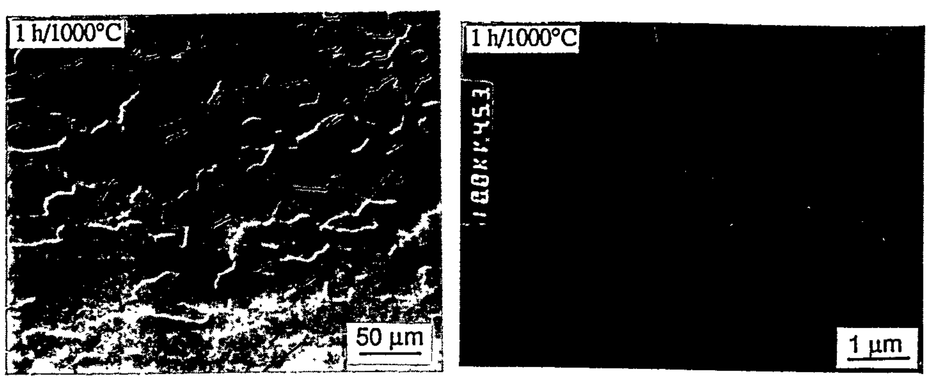

Figure 4. Optical and TEM microstructures at 1000°C for the large heat of V-4Cr-4Ti

At 1050°C after 1-h anneal, the microstructure (Fig. 5) exhibited a mixture of new fine-grains and some grains retaining the original texture (elongated in the rolling direction which is horizontal and parallel to the plane of the micrograph). The hardness decreased to around 145 DPH, see Fig. 1. With further increase in annealing time to 2 and 4 h, the hardness value increased, see Fig. 1. Grain growth occurred at this temperature and some grain boundaries were decorated with fine particles. The increase in hardness was possibly due to either precipitation of new phase or due to dissolution of existing precipitates which results in solution-hardening.

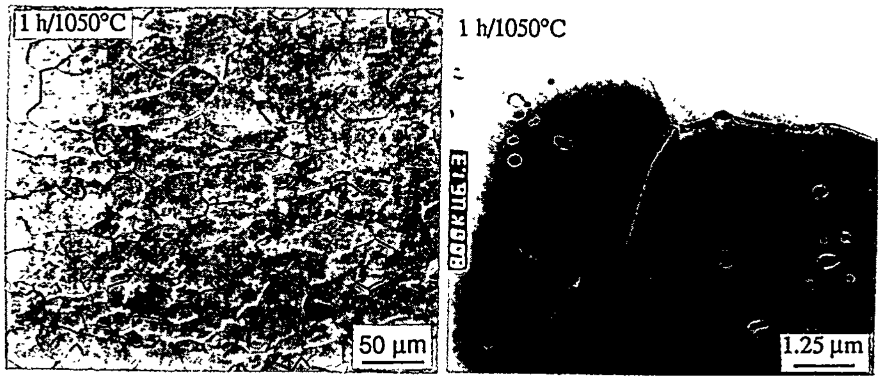

Figure 5. Optical and TEM microstructures at 1050°C for the large heat of V-4Cr-4Ti

At 1100°C there was an appreciable amount of grain growth and a bimodal grain distribution developed (see Fig. 6). This can be related to the non-uniform distribution of precipitates which are present in the form of stringers. The grain growth is significant where stringers are absent due to the lack of pinning of grain boundaries. On the other hand, the grains in the vicinity of stringers show little grain growth due strong pinning effect of precipitates on the grain boundaries. Hardness is higher than the minimum (~145 DPH), in the range of 150-155 DPH at 1100°C (see Fig. 1).

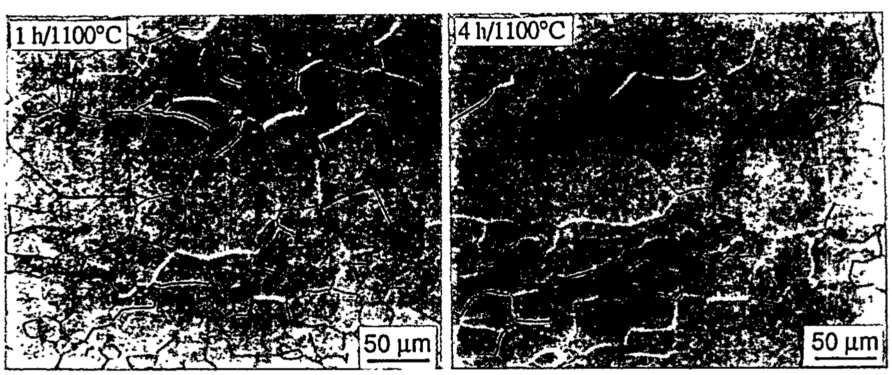

Figure 6. Optical microstructures at 1100°C for the large heat of V-4Cr-4Ti

Figure 7 shows the microhardness as a function of annealing time at various temperatures. The data fall into two groups. At 900°C, softening is primarily due to recovery with little recrystallization; the microhardness value drops from ~200 DPH in the cold-rolled state to a range of 165-168 DPH. The other group is for temperatures from 950° to 1100°C where recrystallization takes place partially at 950°C and completely at 1000°C. Grain-coarsening and precipitation at the grain boundaries occurs with further increase in temperature (1050-1100°C). After the 4 hour anneals there is a tendency for final hardness to increase with temperature, possibly related to impurity pick-up from the furnace atmosphere.

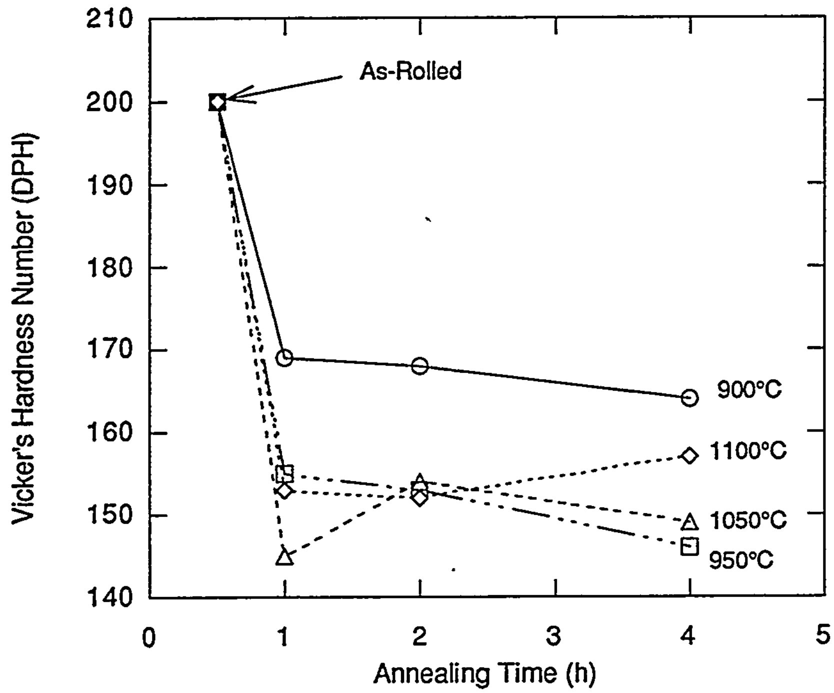

Figure 7. Hardness as a function of Annealing Time for different temperatures for the large heat of V-4Cr-4Ti

Figure 8 shows the comparison of variation in microhardness with annealing temperature for the large and small heats of V-4Cr-4Ti. The difference in the kinetics of recrystallization is clearly evident in the two heats. The small heat (T89) which has a higher cold work of ~49% recrystallizes faster than the large heat (heat 832665) with ~40% cold work. Due to the similar compositions, both heats had almost the same maximum and minimum hardness values of ~200 and 140 DPH, respectively. Microstructural examination revealed that the small heat is 80-90% recrystallized at 950°C after 2 h as compared to 20-30% recrystallization in the large heat for the same anneal. The large heat is fully recrystallized at 1000°C. It was reported by Chung, et al. that the 0.250 in. thick plate of the large heat of V-4Cr-4Ti was not fully recrystallized after 1 h at 1000°C.[8] This thicker sheet was warm-rolled at ~400°C from the extruded bar in contrast to the thin sheet which was cold-rolled at room temperature. Even though the thicker sheet had a warm work of around ~40%, because of the higher temperature of rolling the dislocation density is probably lower than that of the .040 in. sheet, leading to the slower recrystallization kinetics of the thicker sheet.[9]

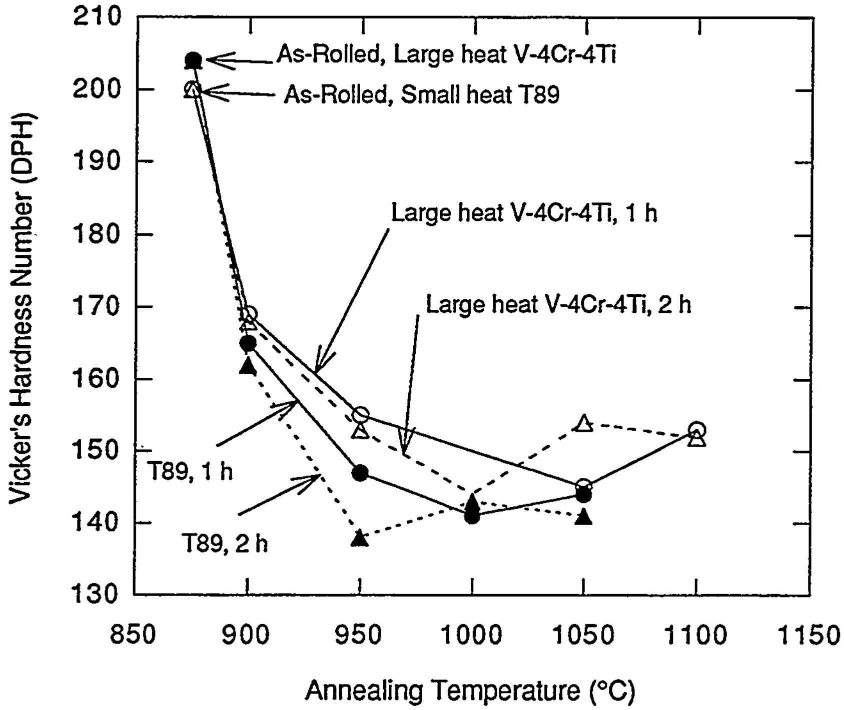

Figure 8. Comparison of variation in Hardness with Annealing Temperature for Large and Small heats of V-4Cr-4Ti

SMALL HEATS OF COMPOSITIONAL VARIANTS

There are five alloys with varying amounts of Cr and Ti; Fig. 9 (a) to (e) shows the variation of hardness with temperature for each alloy and these data will be discussed individually as follows.

V-3Cr-3Ti (Heat T91)

Figure 10 shows the microstructures corresponding to the data in Fig. 9 (a). New grains start nucleating at 900°C after 1 h. The hardness drops from ~190 to ~158 DPH, see Fig. 9 (a). After 2 h at 900°C, the hardness drops further to ~148 DPH with more or less the same amount of nucleated grains. At 950°C after 1 h, more new grains nucleate with 20-30% recrystallization, and the hardness is reduced to ~145 DPH. After 2 h at 950°C, recrystallization is 70 to 80% complete, and the hardness is at its minimum of ~125 DPH, see Fig. 9 (a). At 1000°C for 1 to 2 h, a fully equi-axed grain structure develops, and at 1050°C, the material is clearly in the grain growth regime.

V-4Cr-4Ti-Si (Heat T89)

The microstructures resulting from annealing for 1 to 2 h from 900° to 1050°C are shown in Fig. 11. The nucleation and recrystallization phenomenon is similar to that observed for V-3Cr-3Ti with ~80% recrystallization occurring after 2h at 950°C. The grain structure becomes more equi-axed at 1000°C and grain growth occurs at 1050°C. The only difference between V-3Cr-3Ti and V-4Cr-4Ti-Si is in the hardness values with the latter having consistently higher hardness from the as-rolled condition to the fully recrystallized state. The minimum hardness for V-4Cr-4Ti-Si is ~138 DPH, see Fig. 9 (b).

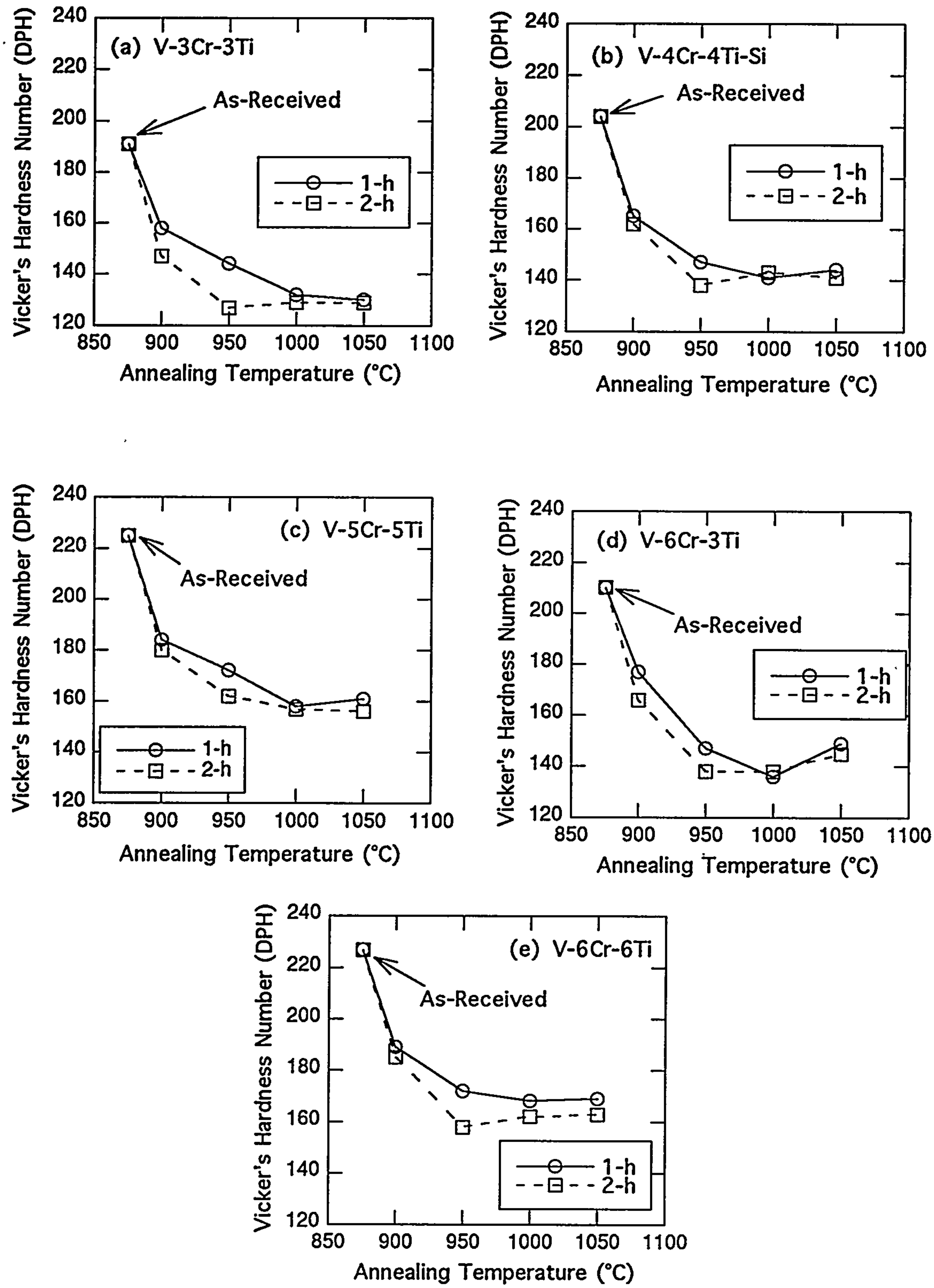

Figure 9. Microhardness as a function of annealing temperature for small heats of compositional variants

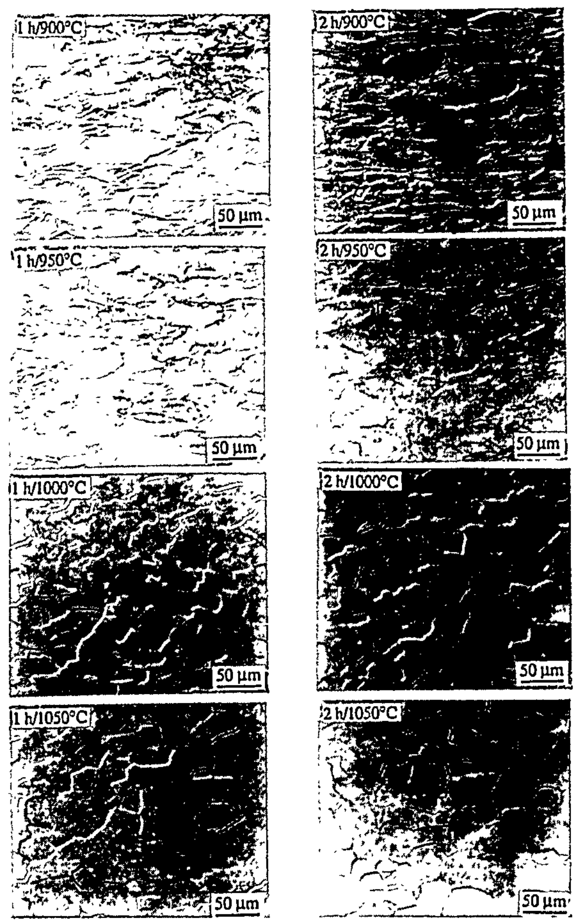

Figure 10. Microstructures of V-3Cr-3Ti as a function of annealing temperature and time

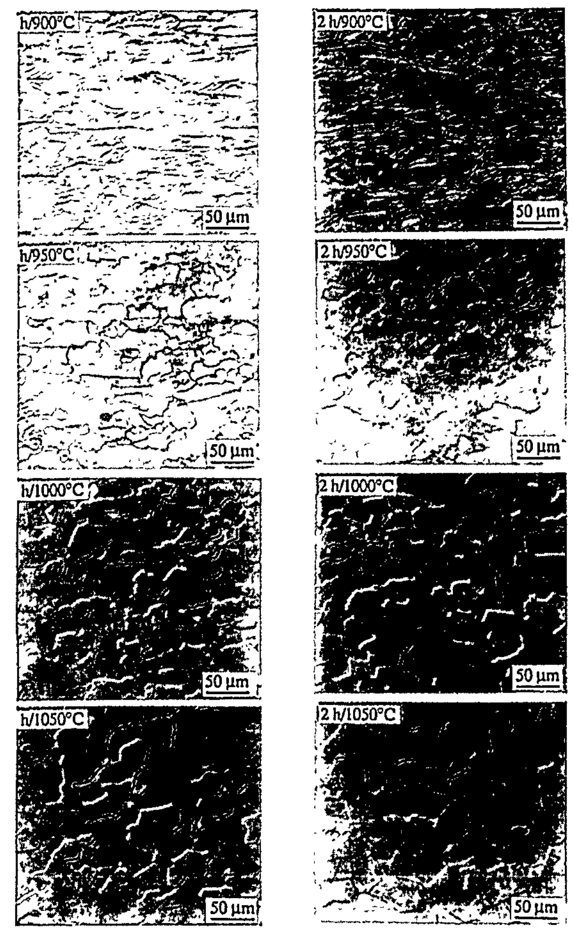

Figure 11. Microstructures of V-4Cr-4Ti-Si as a function of annealing temperature and time

V-6Cr-3Ti (Heat T92)

This alloy exhibits microstructural changes (Figure 12) as a function annealing temperature in an identical manner to that shown by the preceding 2 alloys. In this alloy also, the recrystallization is practically complete after 2 h at 950°C, with grains becoming more equi-axed after 2 h at 1000°C and at 1050°C grain growth occurs. The hardness also changes in a similar fashion with a minimum hardness of around 140 DPH, see Fig. 9 (d).

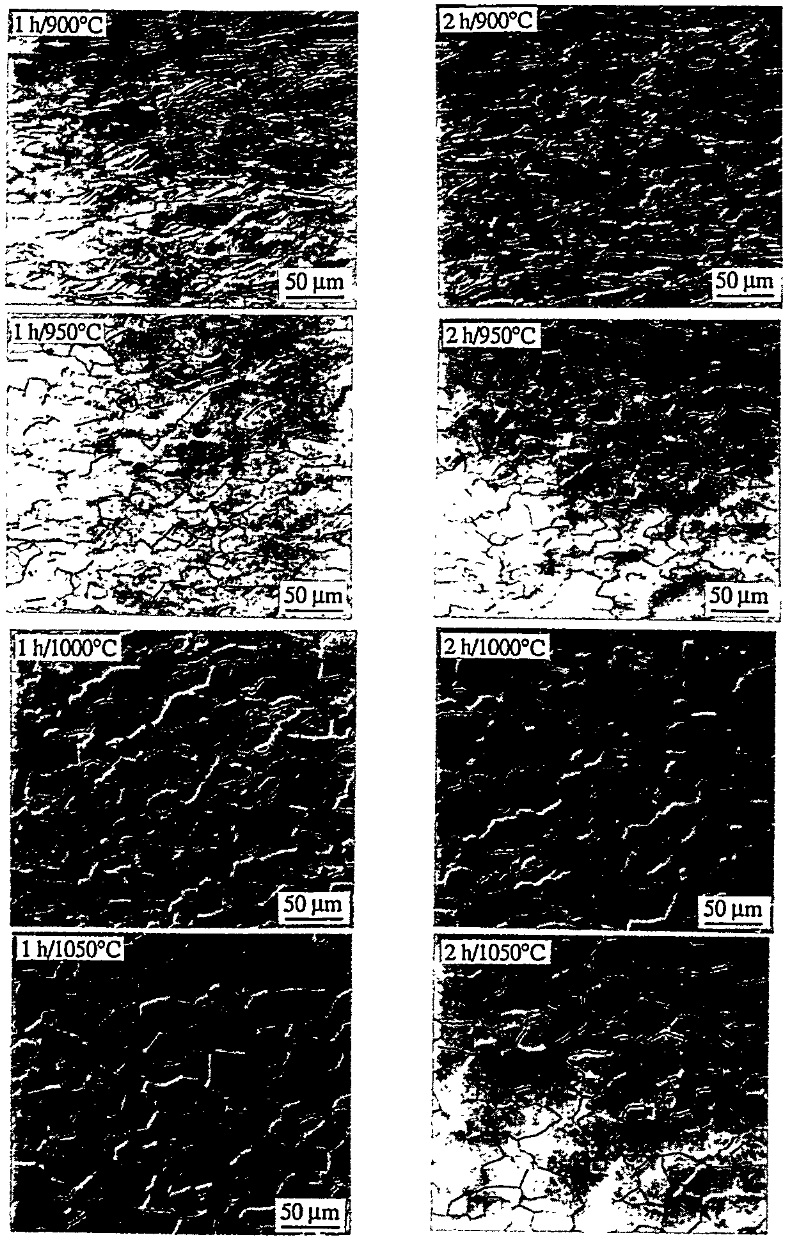

Figure 12. Microstructures of V-6Cr-3Ti as a function of annealing temperature and time

V-6Cr-6Ti (Heat T90)

The hardness and microstructural changes are again similar to the other alloys. The microstructure shows some new grains nucleating at 900°C, see Fig. 13. After 1 h at 950°C, recrystallization is 20 to 30% complete, and after 2 h recrystallization is near completion, with the hardness reaching a minimum of around 160 DPH. For temperatures of 1000°C and above, grain growth occurs.

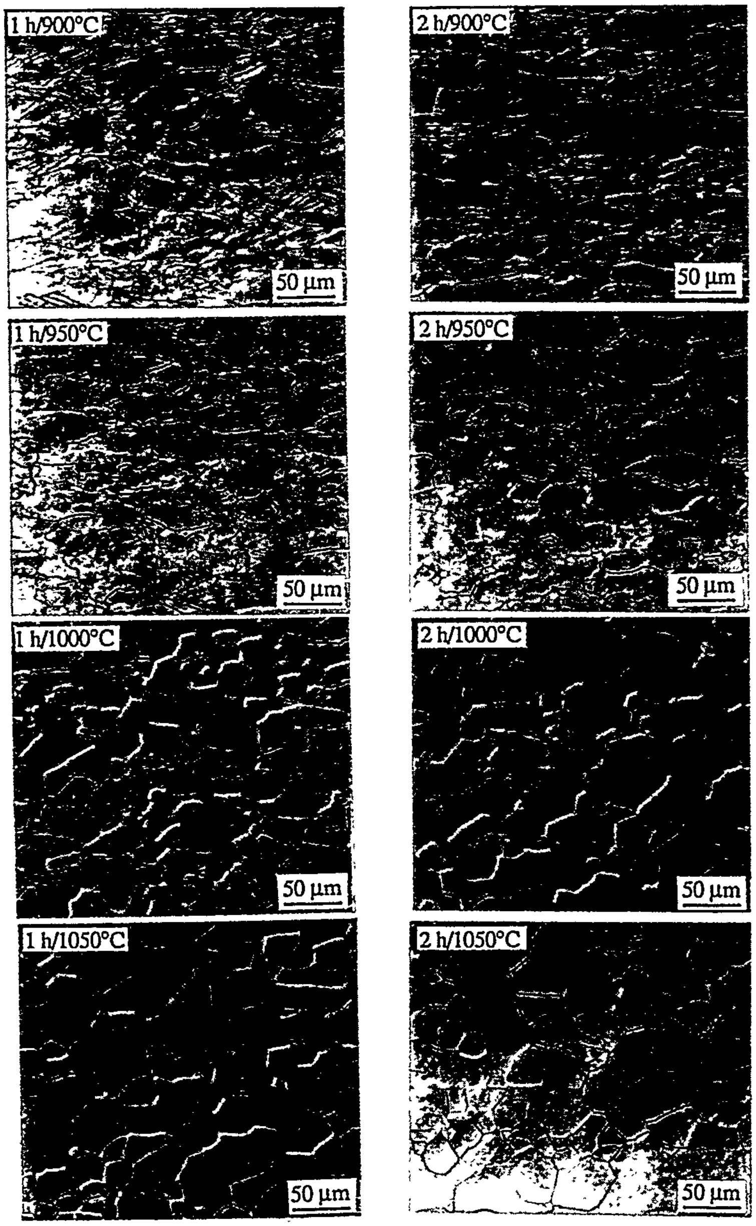

Figure 13. Microstructures of V-6Cr-6Ti as a function of annealing temperature and time

V-5Cr-5Ti (Heat T87)

Figure 14 shows the microstructural evolution of V-5Cr-5Ti with change in annealing temperature and time. The microhardness drops initially from ~225 DPH (as-rolled) to ~180 DPH for 900°C anneals for 1 and 2 h, see Fig. 9 (c). In contrast to the other alloys, this is just a recovery process with very little or no recrystallization. New grains start appearing at 950°C after 1 h indicating the onset of recrystallization. After 2 h at 950°C, the recrystallization is 30 to 40% complete. At 1000°C, the recrystallization is complete and the hardness drops to a minimum of around 158 DPH, see Fig. 9 (c). There is a slight grain growth at 1050°C. The observed difference in the recrystallization temperature (of 1000°C) of this alloy and that of the other four compositional variants (of 950°C) can be attributed to the difference in the amount of cold work between them. It can be recalled that V-5Cr-5Ti had less cold work (~40%) compared to that of the other four compositional variants (V-3Cr-3Ti, V-4Cr-4Ti-Si, V-6Cr-3Ti, and V-6Cr-6Ti have ~49% cold work). Due to the higher amount of cold work in latter group of alloys, they exhibit faster kinetics of recrystallization as compared to that shown by V-5Cr-5Ti, in accordance with the well-established law of recrystallization.[9]

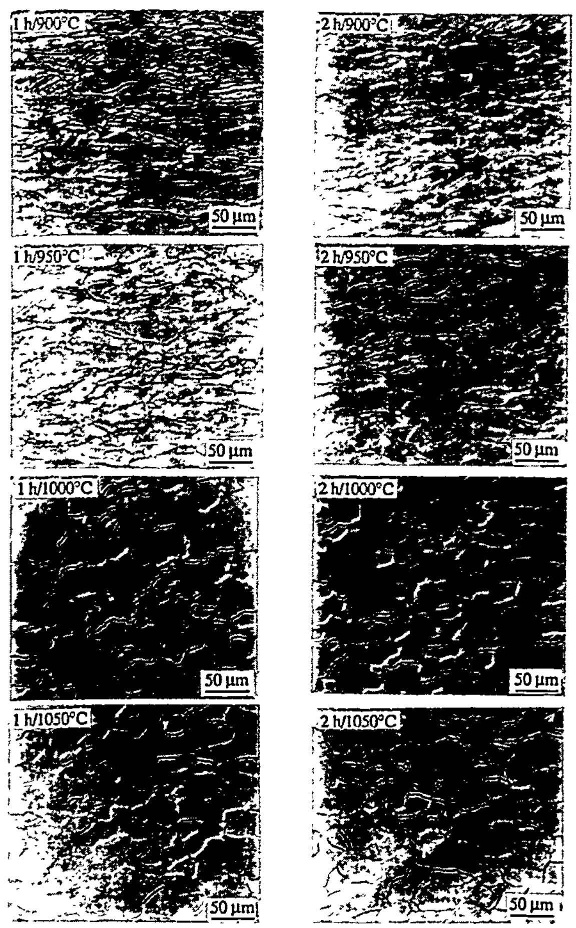

Figure 14. Microstructures of V-5Cr-5Ti as a function of annealing temperature and time

EFFECT OF Cr AND Ti ADDITIONS ON HARDNESS

Figure 15 shows a plot of microhardness as a function of (Cr + Ti) content for alloys in a recovered (900°C) condition and in a fully recrystallized (1050°C) condition. The increasing dependence of hardness of V alloys on Cr and Ti concentration has been reported by Loomis et al.[10] and the data reported here follow the same trend. In the present work, however, there does seem to be a significant incremental step in hardness values when the combined Cr + Ti concentration exceeds ~9 wt%. This can also be seen in Fig. 9; the 3Cr-3Ti, 4Cr-4Ti, and 6Cr-3Ti alloys have a minimum hardness in the range 130 to 142 DPH, whereas minimum hardness for the 5Cr-5Ti and 6Cr-6Ti alloys fall in the range 160 to 165 DPH.

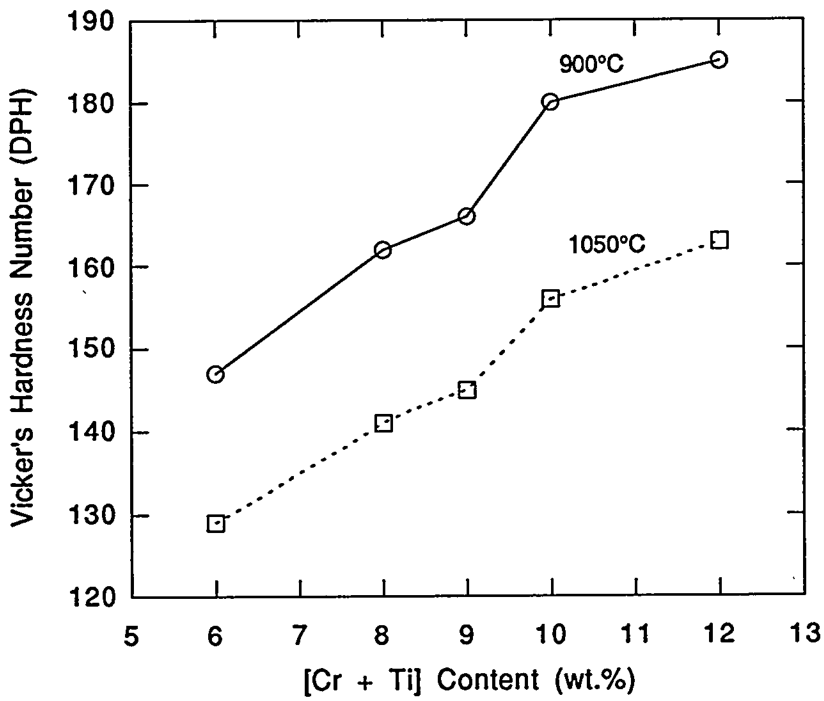

Figure 15. Variation of Hardness with (Cr + Ti) content (All 2-h anneals)

CONCLUSIONS

The recovery and recrystallization behavior of the 500 kg heat of V-4Cr-4Ti in the 40% CW condition has been studied using hardness and TEM. For 1 hour vacuum heat treatments, recovery and subgrain formation occurs at 900°C, partial recrystallization at 950°C, nearly complete recrystallization at 1000°C, full recrystallization at 1050°C, and significant grain growth at 1100°C.

The 15 kg heat of V-4Cr-4Ti exhibits faster recovery and recrystallization kinetics than the large heat because of the higher cold work level of the initial sheet material.

Variations in Cr and Ti over the range 3 to 6 wt % have no discernible effects on recovery and recrystallization kinetics; the hardness of both recovered and recrystallized structures increases with total (Cr + Ti) content.

WORK IN PROGRESS

Differential Scanning Calorimetry analysis has been initiated for quantitative determination of activation energy for recrystallization in the large heat of V-4Cr-4Ti (heat 832665) alloy. TEM analysis is underway for completing microstructural characterization of small heats. Modeling work is being thought of to depict the mechanistics of recrystallization phenomenon.

ACKNOWLEDGMENT

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