KINETICS OF RECOVERY AND RECRYSTALLIZATION OF THE LARGE HEAT OF V-4Cr-4Ti — A. N. Gubbi , A. F. Rowcliffe, W. S. Eatherly and L. T. Gibson

(Oak Ridge National Laboratory)

OBJECTIVE

The purpose of this research is to evaluate the kinetics of recovery and recrystallization, and to develop a suitable model to explain the mechanistics of recrystallization of vanadium alloys.

SUMMARY

A series of slow cycle and rapid cycle anneals was carried out on the large heat of V-4Cr-4Ti alloy (heat 832665). Also, a differential scanning calorimetry (DSC) study was initiated on the samples of the same alloy. The recovery and recrystallization phenomena of V-4Cr-4Ti in slow cycle annealing were quite different from that observed in rapid cycle annealing. The large driving force for recrystallization due to rapid heating resulted in the first nuclei appearing after only 1 min at 1000°C. There was a two-stage hardness reduction; the first stage involved recovery due to cell formation and annihilation of dislocations, and second stage was associated with the growth of recrystallization nuclei. This is consistent with results obtained from the DSC in which there was a broad exothermic peak from ~200° to 800°C due to recovery followed by a sharp exotherm associated with recrystallization. The activation energy for recrystallization for V-4Cr-4Ti, which was determined as 576 ± 75, kJ/mole is significantly higher than that for pure V, and is thought to be related to Ti and Cr in solid solution.

INTRODUCTION

Vanadium alloys with Cr and Ti contents ranging from 3 to 6 wt. % have been proposed as possible candidate materials for the first wall/blanket structure in a demonstration reactor.[1-4] More recently, it was concluded by researchers in the U.S.[5] that a V-4Cr-4Ti alloy has an optimum combination of creep and fracture properties, and resistance to irradiation-induced swelling and embrittlement. Using plate material from a 500 kg heat of V-4Cr-4Ti prepared by Teledyne Wah Chang (TWCA), Albany, Oregon, the U.S. fusion materials program is engaged in a broad study of physical and mechanical properties, gaseous and liquid metal compatibility, insulating coatings, and irradiation performance. The work reported here was undertaken to provide an understanding of recovery, recrystallization, and precipitation behavior in support of efforts to further improve strength and creep properties and swelling resistance.

EXPERIMENTAL PROCEDURE

Specimens for TEM and optical metallography were prepared from the 500 kg heat of V-4Cr-4Ti using 1.02-mm-thick sheet supplied by TWCA in a ~40% cold-worked condition. Three types of annealing study were carried out to investigate recovery, recrystallization and precipitation kinetics.

(a) Slow cycle annealing: Conventional heat treatments were carried out in a tungsten element furnace with a vacuum better than 1 x 10^{-6} torr (<10^{-4} Pa). Temperatures ranged from 900° to 1100°C for times ranging from 1 to 4 hours. The time to reach temperature and the time for subsequent cool-down was approximately 120 minutes.

(b) Rapid cycle annealing: Specimens were encapsulated in quartz tubes under a vacuum of ~10^{-5} torr (10^{-3} Pa) and annealed in an induction heating system capable of reaching a temperature of 1200°C in 60 to 80 seconds with a temperature control of ± 5°C. A thermocouple was fixed in contact with the quartz tube. The rapid cycle annealing was carried out at 1000°C for times from 60 s to 3600 s. Following the anneal, the quartz capsule was quenched into ice-cold water to produce a cool-down time of 1 to 2 seconds.

(c) Differential scanning calorimetry: This was carried out in a Stanton-Redcroft apparatus using 5 mm diameter disks prepared from the ~1.0 mm thick sheet. Heat flow measurements were obtained with heating rates of 0.167 to 0.667°C/s for temperatures up to 1300°C. Three disks were used in each anneal cycle to increase the heat release rate. The same mass of fully annealed material was used as a reference. These anneals were carried out in an atmosphere of high purity flowing argon.

RESULTS

Slow cycle annealing

The microstructure of as-rolled plate consisted of elongated grains and precipitate particles, primarily titanium oxycarbonitrides, which were aligned into stringers during the initial hot working operations. The initial hardness was 200 ± 5 DPH. Hardness is plotted as a function of time for various temperatures in Fig. 1. After 1 hour at 900°C, sub-grains ~1 μm diameter developed within the original elongated grain structure. With increasing annealing time the residual dislocation density within the sub-grains continued to decrease and 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 for 1- and 4-h anneals at 900°C.

At 950°C the hardness dropped rapidly to ~155 DPH after only 1 hour at temperature (Fig. 1). New recrystallized grains appeared and it was estimated that at this point the material was approximately 10% recrystallized (Fig. 2). After 4 hours, the hardness dropped to its minimum value of ~145 DPH, with recrystallization about 30 to 40% complete. The remaining un-recrystallized regions consisted of well developed sub-grains with a low dislocation density; no additional precipitation could be detected following any of the treatments at 950°C.

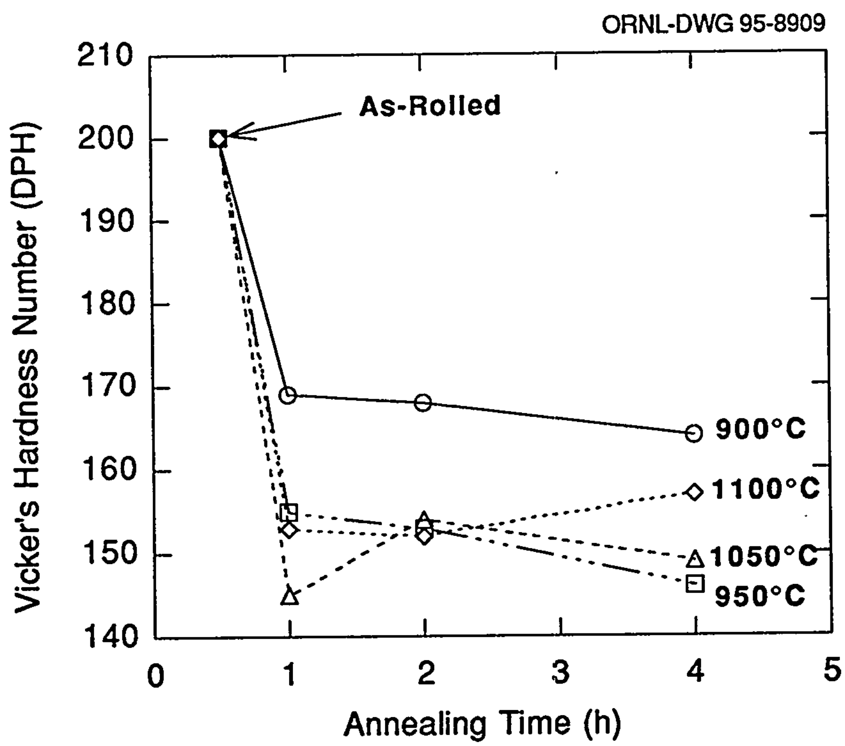

Figure 1. Microhardness as a function of annealing time for various temperatures for V-4Cr-4Ti

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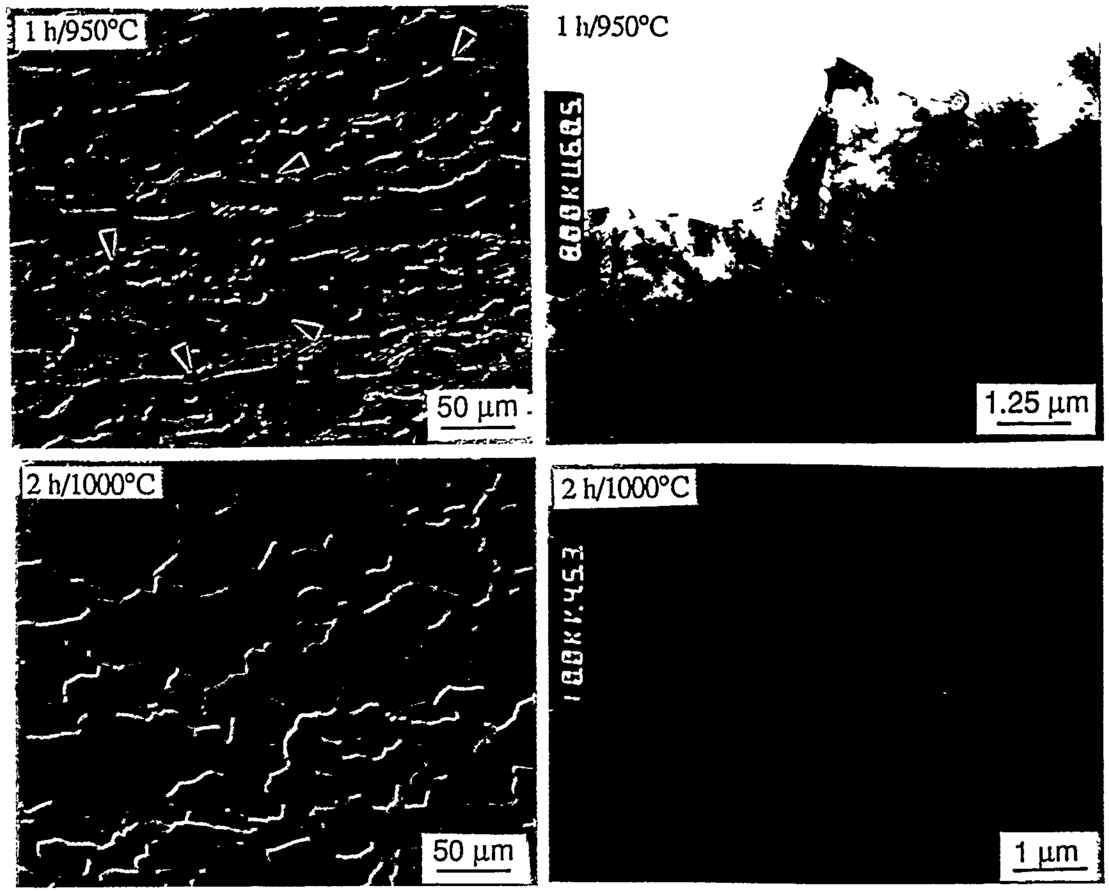

Figure 2. Optical and TEM microstructures at 950° and 1000°C for the large heat of V-4Cr-4Ti. The arrow heads indicate nuclei appearing at pre-existing grain boundaries.

Recrystallization occurred rapidly at 1000°C and was complete after 2 hours (Fig. 2); all sub-grains were consumed, leaving a low density of individual dislocations. After annealing, many of the new grain boundaries contained small titanium oxycarbonitride particles which had precipitated during the cool-down from 1000°C.

After a 1 h anneal at 1050°C, recrystallization was complete; the microstructure consisted primarily of new equiaxed grains interspersed with larger grains which retained their original elongated shape. The latter were probably old grains which had undergone complete recovery without being swept by new migrating grain boundaries. New grain boundaries contained a dispersion of fine (0.06 to 0.2 µ) titanium oxycarbonitride particles. At 1100°C, recrystallization occurred rapidly followed by development of a bi-modal grain structure. Grain growth was restricted in the vicinity of the bands of coarse oxycarbonitrides produced during the initial stages of processing. After annealing for 4 hours, the hardness was significantly higher than after annealing for 2 hours, probably due to some pick-up of interstitial elements from the furnace atmosphere.

Rapid cycle annealing

Figure 3 shows the variation in hardness with annealing times for samples rapidly heated to 1000°C and quenched after holding for the time shown. Hardness dropped rapidly in the first 2 minutes from 200 DPH to ~180 DPH. During the next 8 minutes at 1000°C, very little change in hardness occurred. This period was followed by further softening until, after 1 hour at temperature, the minimum hardness value of ~150 DPH was approached. Optical metallography and TEM examination showed that the initial rapid drop in

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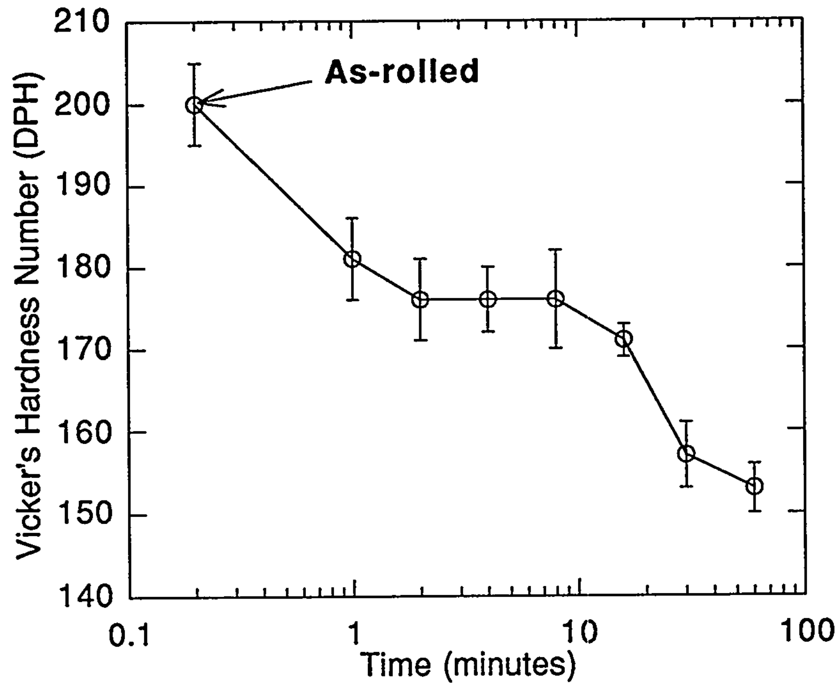

Figure 3. Microhardness as a function of annealing time for V-4Cr-4Ti

hardness during the first minute was entirely due to recovery of the cold worked dislocation structure into a system of cells which still contained a fairly high dislocation density. However, a small number of randomly occurring subrains (1 to 2 µm diameter) were almost completely free of dislocations and it is believed that these are the nuclei for recrystallization. During the 480 to 600-s period where the hardness remains fairly constant, the sub-grain structure became better developed and the number of recrystallization nuclei increased. The subsequent period of decreasing hardness with annealing time was associated with the rapid growth of the recrystallization nuclei, which expanded to consume the remaining sub-structure.

Differential scanning calorimetry

Differential scanning calorimetry has been widely used to provide kinetic information on solid state reactions such as recovery, recrystallization, precipitation and dissolution, and radiation damage annealing[6-14]. The technique measures the difference between the heat flow required to heat the material under investigation and a thermally inert reference material. Both materials are heated at a constant rate and the changes in heat flow due to endothermic or exothermic reactions are recorded until the reaction is complete. Kinetic parameters are obtained by plotting the peak temperature as a function of heating rate. The relationship between the heating rate β and the peak temperature T_p is given by

$$\beta = A \exp\left(-\frac{Q}{RT_p}\right)$$

where A is a transformation function and Q is the activation energy[13] which can be determined from a plot of Ln (β) as a function of reciprocal of T_p [9].

In the present study, calorimetric measurements were carried out on the 40% cold-worked material using fully annealed samples as a reference. Heating rates ranged from 10 to 40°C per min. A typical thermogram determined for a heating rate of 20°C/min is shown in Fig. 4. A broad region of exothermic behavior with several subsidiary peaks occurs over the approximate range from 200 to 800°C. A second, more sharply defined exotherm, that is associated with recrystallization, begins at around 900°C. Gaussian curves were fitted to the recrystallization exotherms and first derivatives were obtained to determine the peak temperatures for a series of heating rates. A plot of Ln (β) versus the reciprocal of the peak temperature is shown in Fig. 5.

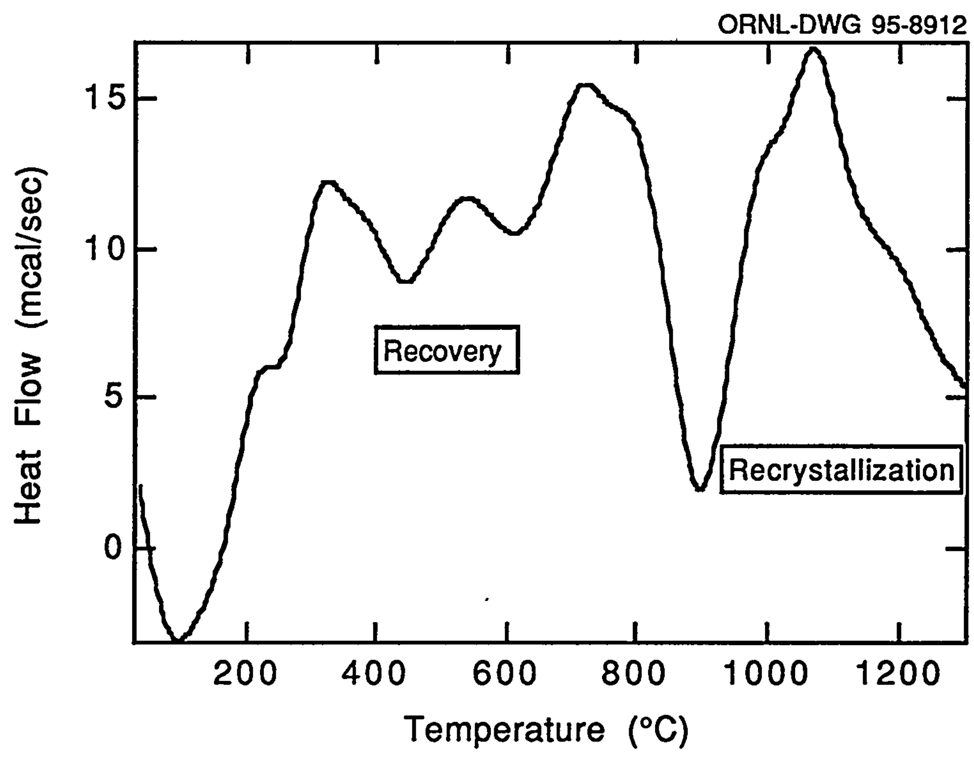

Figure 4. DSC thermogram obtained for a heating rate of 20°C/min for V-4Cr-4Ti

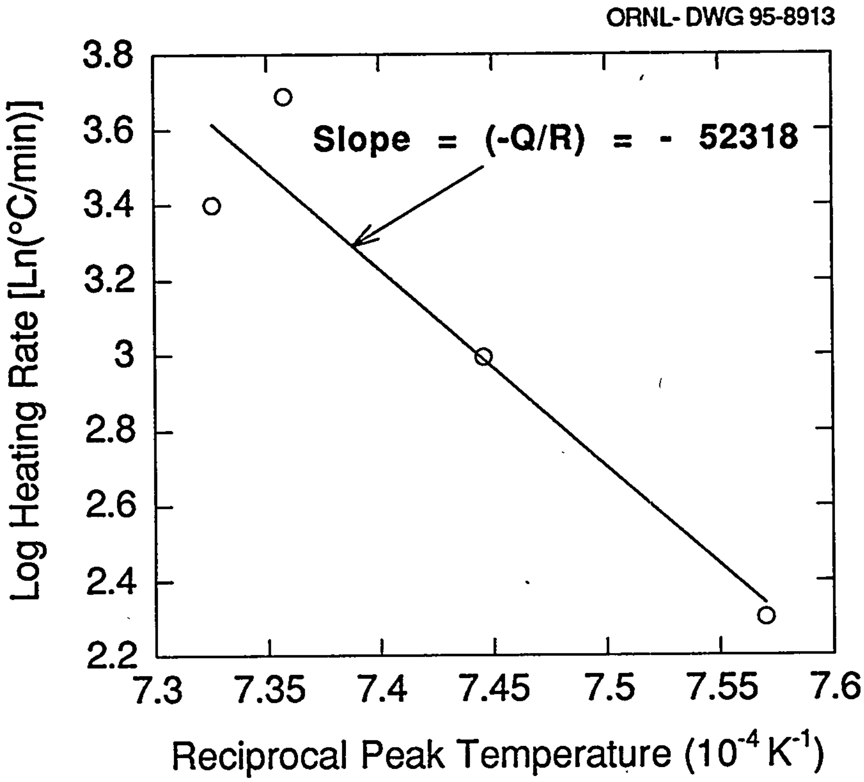

Figure 5. Log heating rate as a function of reciprocal peak temperature of recrystallization

DISCUSSION

The slow heating and cooling cycles are typically used during heat treatment of specimens for mechanical property testing and irradiation experiments, or during fabrication of components. It is not possible to define a unique recrystallization temperature. The extent of recrystallization in any given heat treatment is strongly dependent upon the initial level of deformation and upon the temperature at which that deformation was carried out. It also depends upon the heating and cooling rate and upon the time at temperature. The slow cycle annealing study of the V-4Cr-4Ti alloy in 40% cold-worked condition showed that annealing for 1 hour produces recovery and subgrain formation at 900°C, partial recrystallization at 1000°C, full recrystallization at 1050°C, and significant grain growth at 1100°C. It is critically important to specify heat treatments in terms of the microstructures produced rather than simply quoting the time at temperature. It has been shown in companion studies[15] that Charpy impact properties depend upon microstructure, as well as upon the distribution and concentration of interstitial elements; the resistance to transgranular cleavage at low temperatures is greater when the microstructure contains a high proportion of recovered subgrains.

The rapid cycle annealing (in which the annealing temperature is reached in ~30 to 40 s gives a better definition of the kinetics of recovery and recrystallization. Because of the rapid heating rate there is a large driving force for the formation of recrystallization nuclei, and the first nuclei are detected after only 1 minute at 1000°C. Following the initial hardness reduction due to dislocation recovery, there is a period during which further nuclei develop, unaccompanied by any significant change in hardness. This is followed by a second stage of hardness reduction associated with the rapid growth of recrystallization nuclei.

The differential scanning calorimetry measurements show an exothermic recovery process beginning in the vicinity of 200°C. A hardness recovery process at ~200°C in 85% CW V-4Cr-4Ti was reported by Loomis, et al[16], followed by several minima and maxima in hardness with increasing annealing temperature. The low temperature maxima was tentatively ascribed to the diffusion of carbon, oxygen, hydrogen, and nitrogen to dislocations and the low temperature recovery was ascribed to evolution of hydrogen, and/or removal of oxygen, nitrogen and carbon from solid solution. The interstitial species are highly mobile at these temperatures[17] and the strong interaction between interstitials and dislocations is evidenced by the strain-aging phenomena at ~100°C described by Edington, et al.[18]. Thus, the broad exothermic recovery region between 200 and 800°C (Fig. 4) probably encompasses contributions from several processes, including segregation of interstitial elements to dislocations, annihilation of vacancies, and the climb and annihilation of dislocations. The second, more well defined exothermic peak is ascribed to recrystallization. This is consistent with the observation from the rapid cycle anneal of two fairly distinct stages of hardness recovery separated by a recrystallization incubation period where very little hardness recovery occurs.

From the plot of Fig. 5, the activation energy for recrystallization is determined to be 576 ± 75 kJ/mole. This value is significantly greater than the value of 397 kJ/mole reported by Loria et al[19] for recrystallization in pure V, and the activation energy of 309 kJ/mole for self-diffusion in V single crystals reported by Pelleg[20]. The higher value determined here is thought to be related to the presence of Ti and Cr in solid solution, although some influence of un-dissolved titanium oxycarbonitrides is possible.

CONCLUSIONS

The recovery and recrystallization phenomena of V-4Cr-4Ti in slow cycle annealing are quite different from that observed in rapid cycle annealing. The large driving force for recrystallization due to rapid heating results in first nuclei appearing after only 1 min at 1000°C. There is a two-stage hardness reduction; the first stage involves recovery due to cell formation and annihilation of dislocations, and second stage is associated with the growth of recrystallization nuclei. This is consistent with results obtained from the differential scanning calorimetry in which there is a broad exothermic peak from ~200° to 800°C due to recovery followed by a sharp exotherm associated with recrystallization. The activation energy for recrystallization for V-4Cr-4Ti, which is determined as 576 ± 75, kJ/mole is significantly higher than that for pure V, and is thought to be related to Ti and Cr in solid solution.

ACKNOWLEDGMENT

This research is sponsored by the Office of Fusion Energy, U. S. Department of Energy, under contract DE-AC05-84OR21400 with Lockheed Martin. We thank W. D. Porter for doing DSC analysis. This research was supported in part by an appointment (ANG) to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute for Science and Education.

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