



Effect of impurity levels on precipitation behavior in the low-activation V–4Cr–4Ti alloys

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Abstract

The precipitation behavior of the V–4Cr–4Ti model alloys with different oxygen and nitrogen levels has been investigated. Fine and large precipitates were observed. Large precipitates were formed during the initial fabrication process and were stable to 1373 K. Fine precipitates were formed at 973 K and disappeared at 1373 K. The dependence of the hardness and microstructure on oxygen and nitrogen levels at various annealing temperatures showed that most of nitrogen impurities are included into the large precipitates, and oxygen impurities are partitioned into the large, fine precipitates and the matrix.

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1. Introduction

Vanadium alloys have been identified as one of the promising candidate structural materials for fusion first wall/blanket applications, due to their low induced radioactivity, good resistance to neutron radiation damage and good elevated-temperature strength [1–3]. Based on the previous studies, V–4Cr–4Ti alloy is selected as a leading candidate [4].

Recently, a high-purity 30 kg V–4Cr–4Ti ingot (NIFS-HEAT-1) was fabricated by NIFS (National Institute for Fusion Science) [5,6]. The oxygen content of NIFS-HEAT-1 is almost half that of a large heat of V–4Cr–4Ti produced by a US-DOE (Department of Energy) program [7,8]. It is well known that solid solution and precipitation of interstitial impurities strongly affect the mechanical and irradiation properties in vanadium alloys [9–11]. Thus, various properties of NIFS-HEAT-1 are thought to be different from those of other V–4Cr–

4Ti alloys including the US-DOE heat because of the low impurity level.

For systematic understanding of the impurity effects, investigation of model alloys with a wide variation of the impurity levels is necessary as well as the comparative characterization of the large heat alloys. The purpose of this study is to clarify the precipitation behavior with heat treatment history and impurity levels for various large heats and model V–4Cr–4Ti alloys.

2. Experimental procedure

V–4Cr–4Ti model alloys doped with various levels of oxygen and nitrogen were fabricated by button arc melting. Each of them was about 60 g in weight. The chemical compositions of the V–4Cr–4Ti model alloys used are shown in Table 1. The major difference in the composition among HP, VA-O-1 and VA-O-2 is the level of oxygen. The other model alloys were made for examining the effect of nitrogen level. Table 1 also shows the impurity levels of NIFS-HEAT-1 and US 832665, a 500 kg heat fabricated by the US-DOE program [7]. The

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Table 1
Interstitial impurity content in the alloys used

Alloy designation	wt%		Mass ppm		
	Cr	Ti	C	N	O
HP	3.94	3.81	75	88	44
VA-O-1	3.98	4.11	56	115	244
VA-O-2	3.95	3.94	89	125	513
VA-N-1	3.94	4.09	75	362	49
VA-N-2	3.92	3.89	86	734	46
VA-N-3	3.99	4.08	99	1070	74
NIFS-HEAT-1	4.12	4.13	56	103	181
US 832665	3.8	3.9	80	85	310

thermomechanical treatments after melting for NIFS-HEAT-1 and US-DOE 832665 were hot forging and hot and cold rolling, and hot extrusion and warm rolling, respectively. The dimension of as-received NIFS-HEAT-1 and US 832665 were 10 and 4 mm thick plates, respectively.

Model alloys were machined into 10 mm thick slabs from the buttons. All the sheets were cold-rolled to a reduction of >50% in thickness. They were mechanically polished and electro-polished, followed by annealing at 1373 K for an hour in a vacuum ($<10^{-3}$ Pa) to redissolve the impurities and for removal of dislocations introduced by cold rolling. The specimens were then heat treated again from 873 to 1373 K for an hour. Vickers hardness testing and microstructure observation with optical microscope, scanning electron microscope (SEM)

and transmission electron microscope (TEM) were carried out after annealing.

3. Results

Fig. 1 shows the hardness of oxygen-doped V-4Cr-4Ti model alloys and two large heats, NIFS-HEAT-1 and US 832665, as a function of heat treatment temperature. For these alloys, the nitrogen and carbon

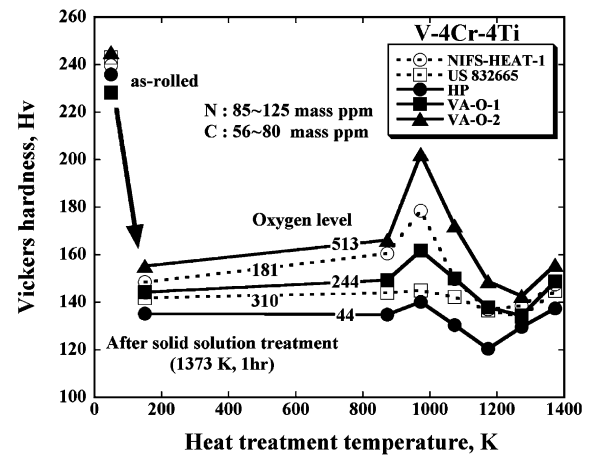


Fig. 1. Effect of heat treatment temperature on hardness for alloys with various oxygen levels.

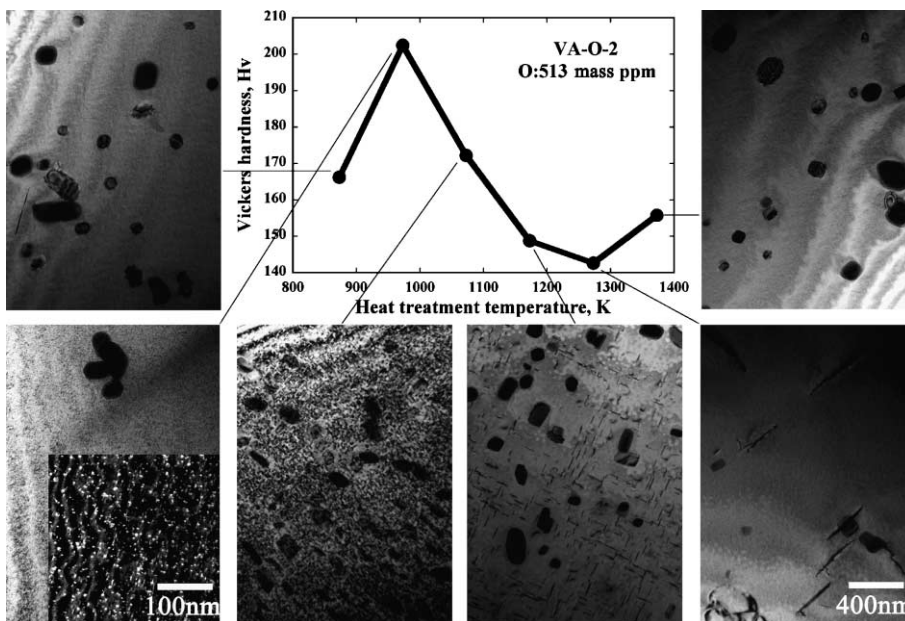


Fig. 2. Hardness and microstructure with heat treatment temperature in VA-O-2. The peak of hardness was identified at 973 K, where fine precipitates appeared.

levels ranged from 85 to 125 mass ppm and from 56 to 80 mass ppm, respectively. As shown in Fig. 1, the hardness has its peak at 973 K for all alloys. In model alloys, hardness increased with increasing the oxygen level. On the other hand, the peak hardness of the two large heats has an opposite dependence on the oxygen level.

Fig. 2 indicates the relation between hardness change and microstructure development with the heat treatment temperature for VA-O-2. Two kinds of precipitates, large and fine ones, were observed, as shown in Fig. 2. The hardness was highest at 973 K where a high density of fine precipitates was observed. The hardness decreased with annealing temperature above 973 K, which corresponds to the coarsening and the decrease in the precipitate density. Heat treatment at 1373 K resulted in disappearance of the fine precipitates and an increase in hardness.

Fig. 3 shows the hardness of nitrogen-doped V-4Cr-4Ti alloys as a function of heat treatment temperature. Hardness did not change significantly with annealing.

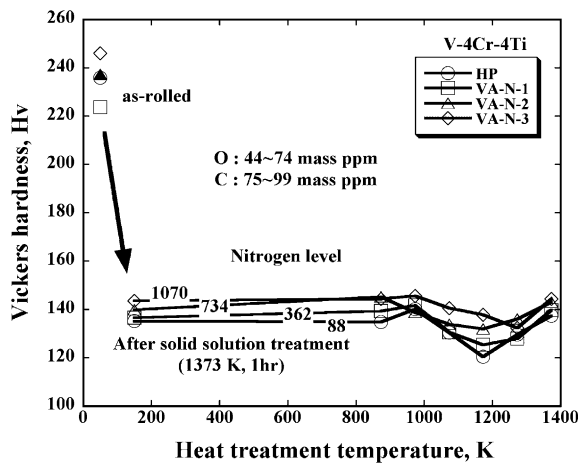


Fig. 3. Effect of the heat treatment temperature on hardness for alloys with various nitrogen levels.

Fig. 4 shows the dark field TEM images of the V-4Cr-4Ti alloys annealed at 973 K. Fine precipitates were formed by annealing at 973 K in VA-O-1, VA-O-2 and NIFS-HEAT-1.

Fig. 5 indicates the number density of the fine precipitates with oxygen levels for the V-4Cr-4Ti model alloys annealed at 973 K. In model alloys, the density of the fine precipitates, which were shown in Fig. 4, increased with increasing the oxygen level. However, the fine precipitates were not observed for the nitrogen-doped V-4Cr-4Ti model alloys annealed at 973 K, as shown in Fig. 4.

Fig. 6 indicates the change of the areal number density of the large precipitates, shown in Fig. 2, with oxygen and nitrogen levels for V-4Cr-4Ti alloys annealed at 1373 K. The areal number density of the precipitates increased linearly with increasing the impurity levels. The change in the areal number density of precipitate for nitrogen-doped V-4Cr-4Ti alloys was larger than that of the oxygen-doped V-4Cr-4Ti alloys.

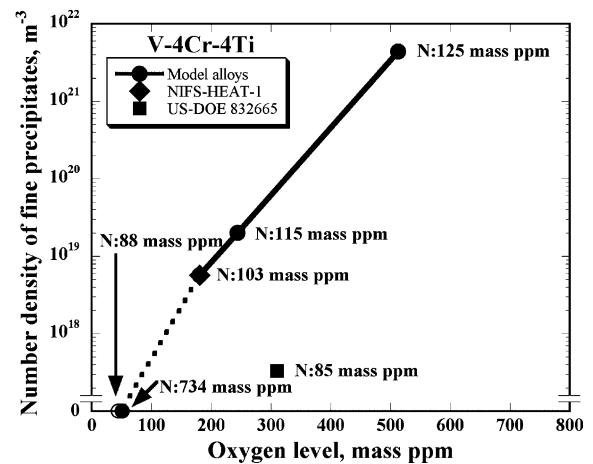


Fig. 5. Number density of the fine precipitates with oxygen and nitrogen levels for V-4Cr-4Ti annealed at 973 K.

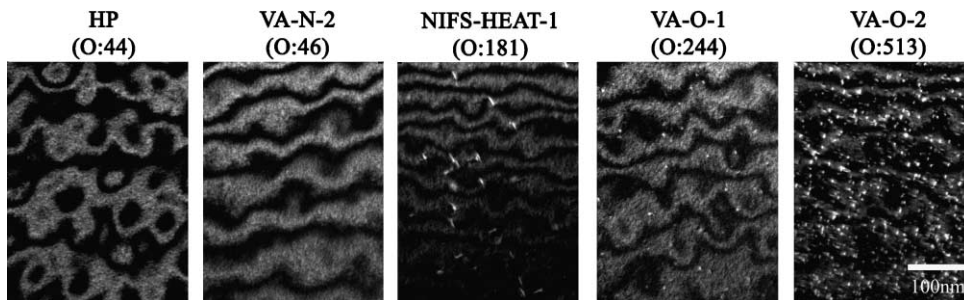


Fig. 4. Dark field image of the specimens annealed at 973 K. Fine precipitates (white spots) were identified, the density of which increased with increasing the oxygen level.

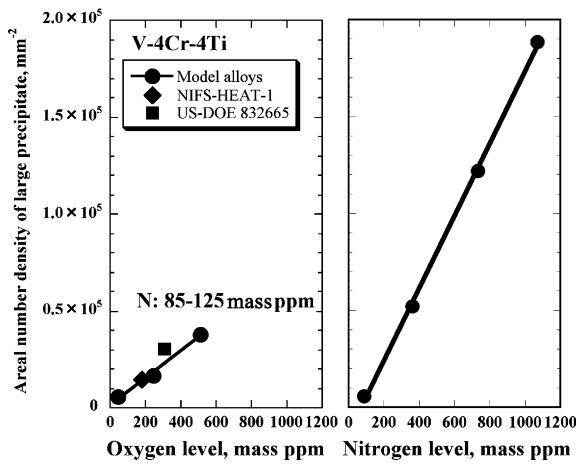


Fig. 6. Change of large precipitates with oxygen and nitrogen levels for model V-4Cr-4Ti alloys annealed at 1373 K.

4. Discussions

Fig. 7 compares the effect of oxygen and nitrogen level on hardness in model V-4Cr-Ti alloys as melted and as annealed at 1373 K. The data for unalloyed vanadium were also plotted for comparison [12]. Fig. 7 shows that the increase in hardness with the oxygen level after annealing at 1373 K is smaller than that for as-melted condition in the case of V-4Cr-4Ti, although the hardness for the two heat treatment conditions is almost the same in the case of unalloyed vanadium. For V-4Cr-4Ti, the increase in hardness with the nitrogen level after annealing at 1373 K is even smaller. The reason for the reduction of the effect of the oxygen and nitrogen level on the hardness in the case of annealing at 1373 K is that the large precipitates, in which oxygen or nitrogen was contained, were formed during initial process of its fabrication and stabilized by annealing at 1373 K. The difference in the dependence of the hardness on oxygen and nitrogen levels is considered to imply a difference in the impurity level in the matrix. The positive dependence of the hardness on oxygen level suggests that some fraction of oxygen should be in solid solution in the matrix after annealing at 1373 K. Note that the small precipitates are dissolved at 1373 K as shown in Fig. 2. The small precipitates are thus thought to be the source of the oxygen at 1373 K.

Very weak dependence of the hardness on nitrogen level suggests that almost all nitrogen should be contained in the large precipitates. This idea of the impurity partitioning into large and fine precipitates is consistent with the experimental results shown in Figs. 1–6.

For the two large heats, NIFS-HEAT-1 and US 832665, oxygen level of US 832665 is higher than that of

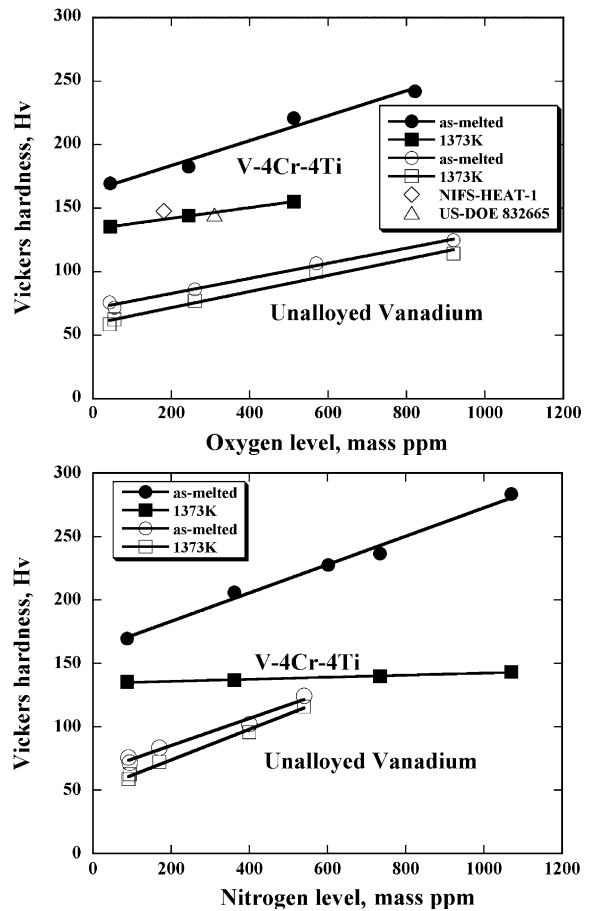


Fig. 7. Effect of oxygen and nitrogen level on the hardness.

the NIFS-HEAT-1. However, the density of fine precipitates of US 832665 formed by annealing at 973 K was lower than that of the NIFS-HEAT-1, as shown in Fig. 5, which resulted in a decrease in the degree of hardening, as shown in Fig. 1. The reason seems that compared with NIFS-HEAT-1, US 832665 was more repeatedly annealed at 1323–1343 K for 2 h during the rolling procedures. It is known that the large precipitates were formed during these procedures [9–11]. Repeated annealing may have resulted in an increase in the density of large precipitates, in which impurities (C, N, O) are contained, as shown in Fig. 6. As the result, the impurity level in the matrix of US 832665 may become lower than that of the NIFS-HEAT-1.

5. Conclusions

The effect of impurity levels on hardness and precipitation behavior by heat treatment after solid solution treatment at 1373 K was investigated for some model

and large heat V–4Cr–4Ti alloys with different oxygen and nitrogen levels.

1. Large and fine precipitates were observed in the matrix. The large precipitates are stable in all heat treatments to 1373 K, but the fine precipitates appeared at 973 K and vanished at 1373 K.
2. The density of the large precipitates increased with nitrogen level more than oxygen level.
3. The hardness after annealing at 1373 K is a positive and a very weak function of oxygen and nitrogen level, respectively, implying that some fraction of the oxygen is in solid solution and most of the nitrogen is in precipitates.
4. These data show that, in V–4Cr–4Ti alloys, most of the nitrogen impurities are included into the large precipitates by annealing at 1373 K and are stable during the following heat treatments. Some fraction of the oxygen impurities will be in large and fine precipitates. The oxygen in the fine precipitates will be released into matrix by annealing at 1373 K, resulting in the increase in hardness.
5. The two large heat alloys are different from the model alloys in the dependence of precipitation and hardness on the impurity levels. The history of the thermomechanical treatment may be responsible for the difference.

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