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Recovery and recrystallization behavior of vanadium at various controlled nitrogen and oxygen levels

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Abstract

The effects of nitrogen and oxygen on recovery and recrystallization of vanadium were investigated using high-purity metal vanadium singly doped with nitrogen or oxygen. Nitrogen and oxygen contents ranged from 10 to 500 weight ppm (wppm) and 50 to 1000 wppm, respectively. The hardening coefficient, ($\Delta H/\Delta C$), for nitrogen is estimated to be almost twice that of oxygen. Additional hardening due to annealing at 200–400°C after rolling was observed. The anneal hardening was significantly decreased by restricting nitrogen contents below 100 wppm. On the other hand, oxygen up to 1000 wppm did not strongly affect the anneal hardening.

1. Introduction

It is known that interstitial impurities such as nitrogen and oxygen strongly affect various properties of vanadium and vanadium alloys for structural materials of fusion reactors [1]. It is widely recognized that reduction of these impurities is essential for maintaining workability [2,3] and weldability [4,5]. As to the post-irradiation properties, previous studies suggested that radiation hardening and embrittlement were attributed to fine precipitates composed of interstitial impurities [6,7]. A recent study on V–Cr–Ti–Y–Si–Al implied a relation between oxygen level and loss of elongation by irradiation below 400°C [8]. Nitrogen effects, on the other hand, remain to be studied further in spite of the fact that contamination with nitrogen to some extent is unavoidable during manufacturing of metal vanadium and alloying on a large-scale [9]. Some data on nitrogen effects on vanadium are available [1,10–12]. However, most of these studies failed to separate the nitrogen effects from those of oxygen.

Recently, a National Institute for Fusion Science (NIFS) program for a large-scale heat of a candidate vanadium alloy has been started [9]. In the program, high-purity large vanadium ingots were fabricated. The NIFS-grade vanadium contains only several tens weight ppm (wppm) oxygen. The NIFS-grade vanadium made it possible to systematically investigate the nitrogen effects at low oxygen levels.

The purpose of this study is to investigate the effects of nitrogen and oxygen on recovery and recrystallization of vanadium after work hardening using high-purity metal vanadium singly doped with nitrogen or oxygen. The data from this study will be applied to explain the effects of nitrogen and oxygen in candidate vanadium alloys, since intrinsic effects of the interstitial impurities can be more clearly extracted from the behavior of pure vanadium.

2. Experimental procedure

Table 1 shows the contents of interstitial impurities in the vanadium specimens used in this study. V-EB-1 was prepared by electro-refining and electron-beam-melting (EB-melting). V-EB-2 and -3 were EB-melted on a laboratory scale (60 g). Vanadium Large Ingot (V-LI) is the

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Table 1
Interstitial impurity content in the vanadium specimens used in the present study (wppm)

Code	N	O	C	Green materials	Final melting
V-EB-1	12	290	33	Electro-refined vanadium	EB-melting 300 g-scale
V-EB-2	75	52	46	Low-nitrogen V_2O_5 powder	EB-melting 60 g-scale
V-EB-3	100	50	60	Low-nitrogen V_2O_5 powder	EB-melting 60 g-scale
V-LI	91	43	93	Low-nitrogen V_2O_5 powder	EB-melting 25 g-scale
V-LI-R	94	55	70	V-LI	Arc-melting 30 g-scale
V–N-1	170	51	79	V-LI, N_2 gas	Arc-melting 30 g-scale
V–N-2	400	52	72	V-LI, N_2 gas	Arc-melting 30 g-scale
V–N-3	540	56	74	V-LI, N_2 gas	Arc-melting 30 g-scale
V–O-1	120	260	68	V-LI, Low-nitrogen V_2O_5 powder	Arc-melting, 60 g-scale
V–O-2	130	570	77	V-LI, Low-nitrogen V_2O_5 powder	Arc-melting 60 g-scale
V–O-3	140	920	64	V-LI, Low-nitrogen V_2O_5 powder	Arc-melting 60 g-scale

NIFS-grade vanadium produced by industrial scale (25 kg) EB-melting. The vanadium specimens with different nitrogen and oxygen levels were prepared by arc-melting of V-LI, a high-purity nitrogen gas and a high-purity V_2O_5 powder. V-LI-R was arc-remelted using V-LI as a reference material for comparison with the series of V–N and V–O specimens. Fig. 1 shows that nitrogen and oxygen contents of these specimens are systematically distributed from about 10 to 500 wppm and 50 to 1000 wppm, respectively. The arc-melted buttons were cut into cubes of 10 mm edge, which were then cold-rolled 90% or more. The resulting 1 mm thick sheets were wrapped in zirconium getter foil and annealed at 200–1100°C for 1 h in a vacuum. Vickers hardness tests and microstructural observations with an optical microscope (OM), a scanning electron microscope (SEM) and a transmission electron microscope (TEM) were carried out.

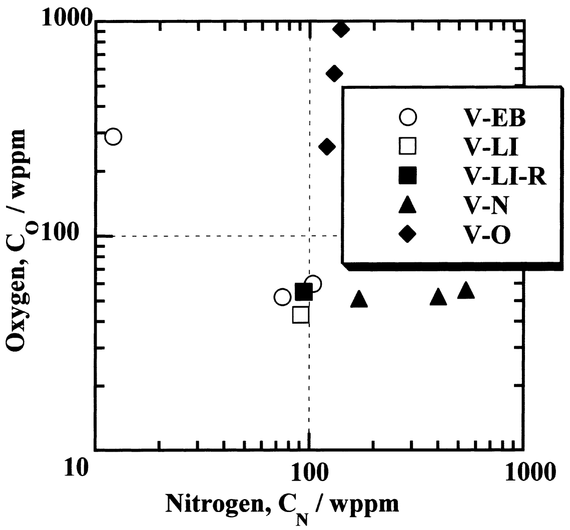

Fig. 1. Nitrogen and oxygen contents of the vanadium specimens used in the present study.

3. Results

Fig. 2 shows typical hardness recovery curves. For the other vanadium specimens, the curves ranged between those of V-EB-1 and V–O-3. The recovery curves were shifted upward with increasing nitrogen and oxygen contents. Additional hardening due to annealing at

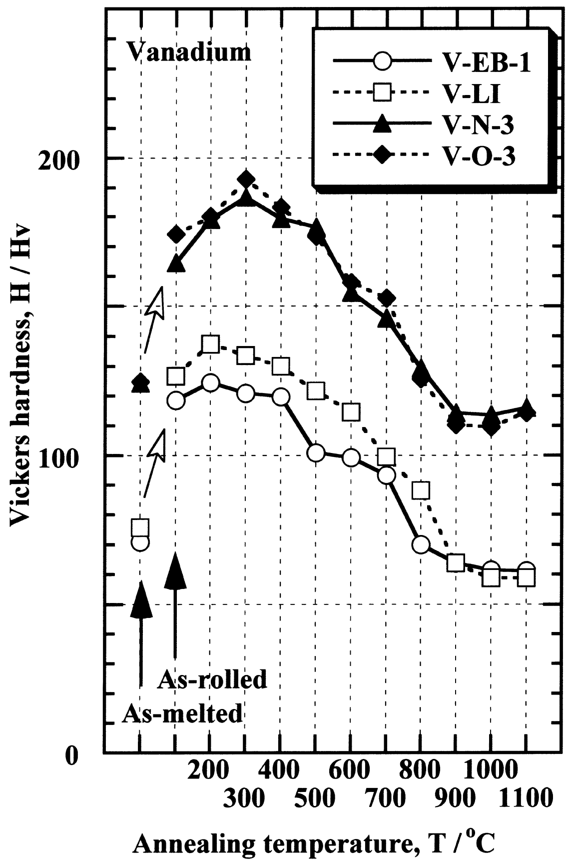

Fig. 2. Recovery behavior of hardness of the EB-melted, nitrogen-doped or oxygen-doped vanadium.

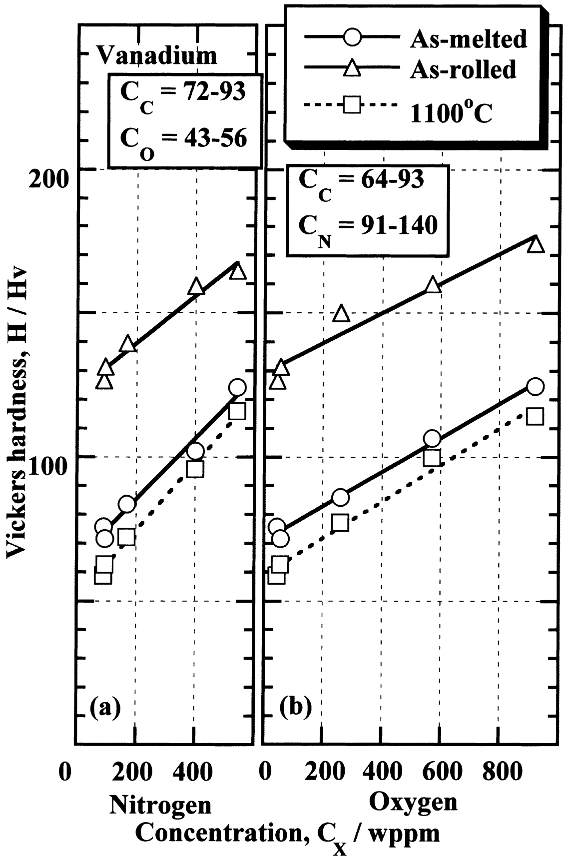

Fig. 3. Effect of: (a) nitrogen; (b) oxygen on the hardness of vanadium.

200–400°C was observed in most of the curves. In the series of V-EB and V-LI, however, the additional hardening was much smaller than that in the other specimens. Recovery stages were observed at two temperature ranges; i.e., 400–600°C and 600–900°C. More recoveries were observed in the latter range. Above 900°C, the hardness was almost constant.

Fig. 3 shows the effects of nitrogen and oxygen on hardness in the as-melted, as-rolled and full-annealed (1100°C) conditions. To estimate the single effect of nitrogen and oxygen, only the data from V-LI, V-LI-R, V–N and V–O specimens, which were made from the same vanadium ingot, are plotted in Fig. 3. Throughout these specimens, the carbon content was only 64–93 wppm. In this range of interstitial impurities, hardness linearly increased with increasing nitrogen and oxygen contents.

In all the as-melted specimens, the grain size was larger than 5 mm. Typical recrystallization behavior is shown in Fig. 4. In the specimens as-rolled and annealed at 200–700°C, only elongated patterns that aligned near the rolling direction were observed by OM, while few grains were observed at high magnification by SEM at 600°C and 700°C. In TEM observation, dislocation cell structures were observed at 600°C, but recrystallized grains were not detected. In OM observations, the specimens showed partial and complete recrystallizations at 800°C and 900°C, respectively. Grain growth was observed above 900°C. No significant effects of nitrogen or oxygen on grain size were found in the present range of nitrogen and oxygen contents.

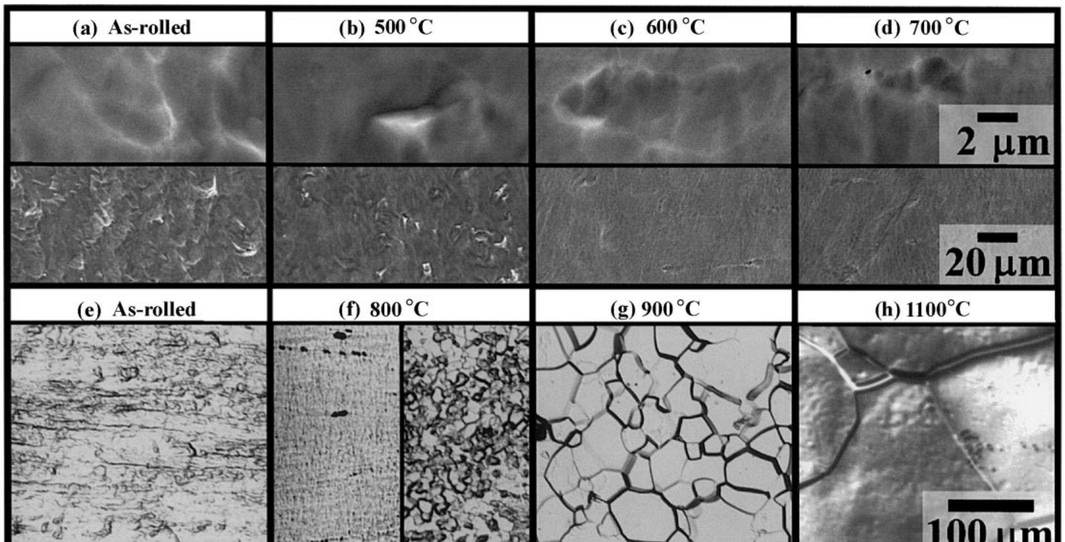

Fig. 4. Recrystallization behavior of EB-melted and 90%-cold-rolled vanadium (V-LI) after annealing for 1 h: (a)–(d) SEM; (e)–(h) OM photographs are shown.

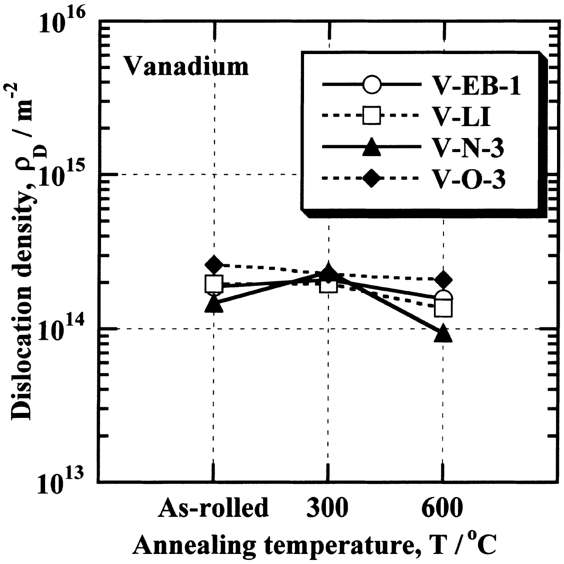

Fig. 5. Dislocation density after annealing at 300°C and 600°C.

Fig. 5 shows the dislocation density as estimated by the TEM observations. No significant change in dislocation structure was found due to annealing at 300°C. Precipitates were not observed in the specimens examined.

4. Discussion

4.1. Single effects of nitrogen and oxygen on hardness of vanadium

In this study, several hundred wppm of nitrogen and oxygen linearly hardened V-LI as shown in Fig. 3. Assuming independent contributions of nitrogen and oxygen to the hardness, the hardness, H, varies with nitrogen and oxygen contents, C_N and C_O, as follows:

$$H = H_0 + \frac{\Delta H}{\Delta C_N} C_N + \frac{\Delta H}{\Delta C_O} C_O, \quad (1)$$

where H_0 is a constant, and $\Delta H/\Delta C_N$ and $\Delta H/\Delta C_O$ the hardening coefficients of nitrogen and oxygen, respectively. As the carbon content varies only from 64 to 93 wppm, the effect of carbon on the hardness is assumed to be constant and included in H_0. Since the oxygen contents vary only within 13 wppm, single nitrogen effects, $\Delta H/\Delta C_N$, can be extracted from Fig. 3(a) by assuming the last term of Eq. (1) to be constant. Then the constant, H_0, and $\Delta H/\Delta C_O$ can be acquired from Fig. 3(b) by using Eq. (1) and the value of $\Delta H/\Delta C_N$ derived from Fig. 3(a).

In the as-melted, as-rolled and full-annealed specimens, the indentation depths of the hardness tests were less than 150 μm which will contain only one or several grains. Thus, the values of $\Delta H/\Delta C_N$ and $\Delta H/\Delta C_O$ should not be affected by grain boundaries and represent solid solution effects of nitrogen and oxygen, respectively. Table 2 shows the hardening coefficients of nitrogen and oxygen, $\Delta H/\Delta C_N$ and $\Delta H/\Delta C_O$, at the three states. The hardening coefficient of nitrogen is almost twice that of oxygen.

Fromm and Horz [11] reported that the hardening coefficients of nitrogen and oxygen were 0.064 and 0.056 Hv wppm^{-1}, respectively. From a part of the data up to 1000 wppm in another study by Kainuma et al. [12], the hardening coefficients of nitrogen and oxygen are estimated to be 0.093 and 0.065 Hv wppm^{-1}, respectively, in the material annealed at 950°C for 0.5 h. These data on oxygen seem to agree with that for the full-annealed specimens of the present study. The effect of nitrogen, on the other hand, is generally lesser than that in the present study. One possible explanation is that the nitrogen effect on the hardness is different in the case of low and high oxygen levels. Since the oxygen level is low, the hardening coefficient in the present study is expected to indicate more intrinsic effects of nitrogen.

4.2. Additional hardening after annealing at 200–400°C

In this study, the dislocation structure was not changed by annealing at 300°C. No precipitates and additional defects were observed. Therefore, the hardening due to annealing at 200–400°C may be induced by the interaction of interstitial impurities either with dislocations or with submicroscopic vacancy clusters. Single vacancies produced during cold working are not likely to be the responsible defects, because they should migrate below 300°C and anneal out below 400°C, according to their migration energies ranging from 0.5 to 1.2 eV [13,14]. The interaction of the impurities with vacancy clusters is being investigated by heavy ion irradiation on the same set of specimens as the present study [15].

Table 2
Hardening coefficients of nitrogen and oxygen in as-melted, 90%-cold-rolled and full-anneled vanadium

State	H_0 (Hv)	$\frac{\Delta H}{\Delta C_N}$ (Hv wppm^{-1})	$\frac{\Delta H}{\Delta C_O}$ (Hv wppm^{-1})	$\frac{\Delta H}{\Delta C_N} / \frac{\Delta H}{\Delta C_O}$
As-melted	61	0.11	0.054	2.0
As-rolled	123	0.083	0.047	1.8
Full-annealed (1100°C)	48	0.12	0.057	2.1

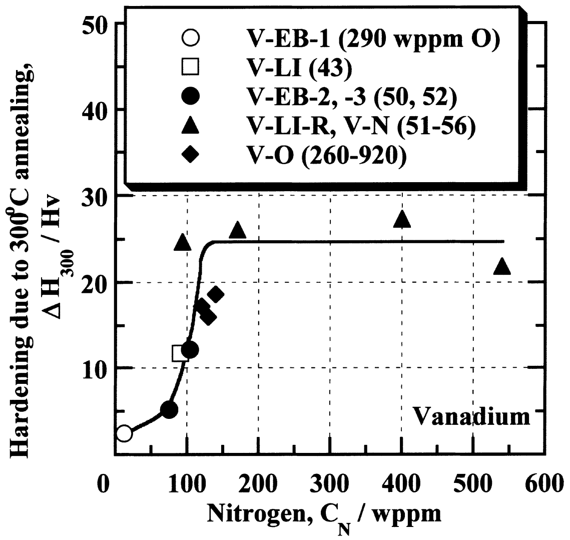

Fig. 6. Effect of nitrogen on the hardening due to annealing at 300°C. Oxygen contents are also indicated in parentheses after the material codes.

Vanadium exhibits post-irradiation anneal hardening at 200–450°C [16,17]. It was suggested that the anneal hardening would be caused by the migration of interstitial impurities to dislocation loops produced by irradiation [16,17]. Electrical resistivity and internal friction studies [17] indicated that post-irradiation annealing resulted in a decrease in oxygen and carbon contents in the solid solution state, and that the magnitude of the resistivity change was increased with increasing oxygen and carbon contents.

In this study, a correlation between hardening due to annealing at 200–400°C and nitrogen content is found. Fig. 6 shows the nitrogen effect on the hardening due to annealing at 300°C, ΔH_{300}, which is defined as the difference between the hardness of 300°C-annealed and as-rolled specimens. ΔH_{300} is almost constant at 25 Hv above 100 wppm, whereas it is drastically decreased with decreasing nitrogen contents below 100 wppm. Considering that ΔH_{300} of V-EB-1 is nearly zero, and that ΔH_{300} for the series of V–O specimens is similar in spite of the large variation of oxygen contents, it is suggested that, in the present region of impurity level, oxygen does not affect ΔH_{300} strongly.

4.3. Recovery and recrystallization behavior above 500°C

In Fig. 2, the profile of the recovery curves after annealing at above 500°C were similar for all specimens. The previous studies reported that strengthening by dynamic strain aging, which was also attributable to the aggregation of interstitial impurities to dislocations, was observed in vanadium with the peak at about 400°C. The effect decreases continuously up to 600°C and disappears above 600°C [1]. Thus, a slight decrease in hardness from 400°C to 600°C in Fig. 2 could be induced by both loss of dislocation–impurity interactions and recovery of dislocations.

Since recrystallized grains were already observed after annealing at 600°C, the relatively large recovery at 600–900°C should be caused not only by recovery of dislocations, but also by recrystallization and grain growth. At 900°C, the grain size becomes too large to contribute to the hardness. This should be the reason for the constant hardness above 900°C.

The present study showed that recrystallization of unalloyed vanadium was not affected by nitrogen and oxygen. This may not be the case with alloys. For a large heat of V–4Cr–4Ti alloy, it was reported that a bimodal grain size distribution was observed even in the fully recrystallized condition [18]. This was related to the non-uniform distribution of precipitates, which were already present before annealing. Thus, in alloys the interstitial impurities could produce precipitates with alloying elements affecting the recrystallization behavior.

5. Conclusions

1. Hardness of vanadium as-melted, as-rolled and annealed at 1100°C linearly increased with increasing nitrogen and oxygen contents. The hardening coefficient of nitrogen was almost twice that of oxygen.
2. Additional hardening was observed due to annealing at 200–400°C after cold rolling. This was attributed to the decoration of dislocations with interstitial impurities. The anneal hardening is very small when the nitrogen content is below 100 wppm. The effect of oxygen on the anneal hardening was weak relative to that of nitrogen.
3. The effects of nitrogen and oxygen on recrystallization and grain growth were small.

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