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Effect of oxygen and nitrogen on microstructure and mechanical properties of vanadium

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ABSTRACT

The effect of oxygen and nitrogen content on the microstructure and mechanical behavior of vanadium was investigated. Vanadium specimens containing 40–4536 ppm nitrogen and 624–9092 ppm oxygen, respectively were prepared using diffusion heat treatments. The specimens were characterized with respect to chemical composition, microstructure and mechanical properties. Both V-O specimens and V-N specimens had single phase microstructure with no precipitates. Increase in oxygen and nitrogen content increased hardness and tensile strength and decreased ductility. The specimens were characterized for grain boundary segregation using scanning transmission electron microscopy (STEM) equipped with super-X EDS and high resolution ion microprobe (NanoSIMS). The mechanical properties were discussed in view of the measurements of composition and microstructure.

1. Introduction

Vanadium based alloys have been identified as potential candidates as membrane materials in hydrogen separation and purification technologies [1,2], hydrogen storage applications [3] besides fusion reactor structural applications [4]. However, vanadium has a high affinity for oxygen and nitrogen and can absorb considerable amounts from the environment during fabrication, heat treatment processing and while in use. Both oxygen and nitrogen interstitials strengthen vanadium through solid solution strengthening but can adversely affect ductility leading to failure at high concentrations [5–8]. It is therefore important to understand the influence of high concentration of interstitials on mechanical properties of vanadium.

Typically both oxygen and nitrogen are present in vanadium specimens making it difficult to determine their individual effects. Nevertheless the increase in hardness independently due to oxygen and nitrogen (Hv/wppm) has been reported [6,7,9]. Typically, nitrogen interstitials increases the hardness of vanadium much more than oxygen. Effect of nitrogen and oxygen on the tensile properties of vanadium has also been reported [5,6,8]. Loria [8] reported that at the same impurity level nitrogen produced a two fold increase in strength when compared with oxygen. Kainuma et al. [6] reported that the yield strength increased as the oxygen or nitrogen content increased, with nitrogen being more effective. The elongation correspondingly decreased with increasing oxygen or nitrogen content. At concentrations above ~0.48 wt% O and ~0.24 wt% N in V-O and V-N alloys the specimens fractured without plastic deformation.

Interstitials can promote brittle behavior by segregating to grain boundaries or forming precipitates. They can also stay in solid solution and inhibit dislocation movement and reduce resistance to crack propagation [10]. Most research (for e.g. Ref. [11,12]) points to the drop in ductility with increasing nitrogen and oxygen content but few investigations examine their role in embrittling vanadium. In V-Cr-Ti alloys the intergranular failure of the specimens is speculated to be due to segregation of oxygen to the grain boundary [13–15]. In V-N alloys the loss in ductility was reported [11] to be due to cracking initiated at grain boundaries. In Nb [16] and Ta [17], which along with vanadium are group Va elements, first principles calculations showed that oxygen and nitrogen interstitials segregate to grain boundary. However, there are no reports, to the authors' knowledge, experimental or theoretical on the segregation of interstitials in vanadium.

In the present study, microstructure and tensile behavior of vanadium specimens containing 40–4536 ppm nitrogen and 624–9092 ppm oxygen, respectively were investigated. These solute concentrations are higher than those reported in published literature. The change in hardness with oxygen and nitrogen (Hv/wppm) was contrasted with those reported in published literature.

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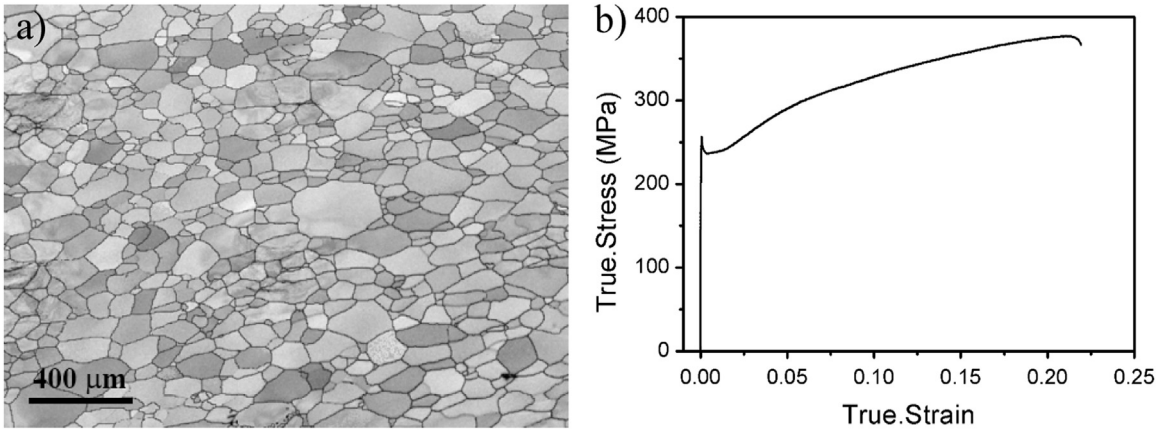

Fig. 1. Microstructure and tensile stress-strain behavior of annealed vanadium.

Table 1
Composition of vanadium specimens (ppm by weight).

	Notation	Nitrogen	Oxygen	Vanadium
Vacuum annealed*	Annealed	1	463	Balance
V-N specimens	V-N1	40	1132	
	V-N2	412	889	
	V-N3	727	1157	
	V-N4	1028	735	
	V-N5	4536	1038	
V-O specimens	V-O1	29	624	
	V-O2	2	1538	
	V-O3	1	2080	
	V-O4	6	3008	
	V-O5	1	9092	

* The results of carbon and sulfur analysis were: 270 wppm carbon, 37 wppm sulfur

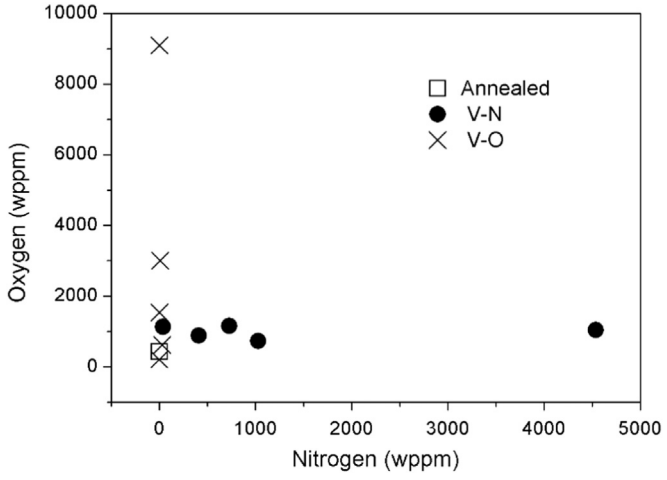

Fig. 2. Oxygen and nitrogen content of the vanadium specimens.

The high resolution ion-microprobe (NanoSIMS) and STEM-EDS were used to determine segregation at grain boundaries. The mechanical properties were discussed in view of the measurements of composition and microstructure.

2. Experimental procedure

Granules of electro-refined grade of vanadium were arc-melted and suction cast into ingots of dimension $10 \times 40 \times 4$ mm. These were then cold rolled (90% reduction) into 0.3 mm thick strips. Sub-size tensile specimens with a gage length of 8 mm were wire cut from these strips. The specimens were then annealed for 1h at 1200 °C in high purity argon (99.999%) gas, which was further purified with a gas purifier that reduced the oxygen content to $\sim 10^{-10}$ wppm. Additionally the specimens were surrounded by titanium pieces to getter argon gas.

The vanadium specimens with different nitrogen and oxygen content were prepared using diffusion heat treatment as follows.

Quartz tube containing the annealed specimen was evacuated and purged with argon repeatedly and then filled with nitrogen at pressures between 0.02–0.05 MPa and sealed. The sealed quartz tubes were held at 700 °C for 264 h and quenched. Similarly, the vanadium specimens containing different amounts of oxygen were prepared using evacuated and purged quartz tubes filled with oxygen at pressures between 0.005–0.07 MPa, held at 650 °C for 144 h and quenched. Another set of specimens were prepared by heat treating them in evacuated quartz tubes at the same temperature-time conditions that were used for nitrogen and oxygen treatments but without oxygen or nitrogen. These specimens were used to compare the effect of oxygen and nitrogen on grain size. All quartz tubes were sealed when the pressure was ≤ 0.013 Pa. The specimens' heat treated in nitrogen and oxygen will henceforth be referred to as V-N and V-O specimens, respectively.

Eltra ON-900 was used to determine the oxygen and nitrogen contents of the specimens. LECO CS600 was used to determine carbon and sulfur contents in the annealed specimen. Gatan MicroTest300N was used to conduct tensile tests at the crosshead speed of 1.0 mm/min (strain rate $\sim 2.1 \times 10^{-3}\ s^{-1}$). Hardness was measured using 100 g load on Mitutoyo HM-122 vickers hardness testing machine. X-ray diffraction (Bruker D8 ADVANCE, Cu target 40 kV, 40 mA) was used to monitor alloying and phase formation in V-N and V-O specimens using the step size: $2\theta = 0.02°$ and time per step of 2 s. The microstructure was characterized using scanning electron microscopy (FEI SEM, Inspect F50) and high resolution scanning transmission electron microscopy (STEM, Talos F200X) equipped with advanced energy dispersive spectrometer (Super-X EDS). The specimens for STEM were prepared using the focused ion beam technique (FIB Nova 600). High resolution ion-microprobe (Cameca NanoSIMS 50) was used to determine element composition maps and line scans across grain boundaries. A focused 16 keV Cs^+ ion beam with beam current 0.4pA was used for all experiments and the following ion species were collected simultaneously: $^{16}O^-$, $^{12}C^-$, $^{12}C\ ^{14}N^-$, $^{32}S^-$ and $^{51}V^{16}O^-$. The $^{12}C^{14}N^-$ signal was chosen in preference to the $^{14}N^-$ signal because it gives the highest signal intensity. Prior to each measurement the specimen surface was cleaned with a high current primary ion beam.