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Microstructure control to improve mechanical properties of vanadium alloys for fusion applications

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Abstract

Powder metallurgy (P/M) methods including mechanical alloying (MA) treatment may be useful to improve both radiation resistance and high-temperature strength that are major concerns in the use of V–4Cr–4Ti for fusion reactor structural applications. For the P/M methods, however, there is a critical issue that solute oxygen and nitrogen contained in the starting powders and introduced through the fabrication processes cause a serious loss of ductility. In this paper, a process for microstructure control to solve the issue is proposed and applied to fabricate a vanadium alloy. The microstructures and mechanical properties of the fabricated alloy are also presented. It is shown that the proposed process is very effective in removing solute oxygen and nitrogen from the matrix resulting in a significant suppression of the ductility loss and that optimizing MA conditions will bring about further improvement in the ductility at low temperatures. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

A vanadium alloy, V–4Cr–4Ti, is a primary candidate material for fusion reactor structural applications because of its large thermal stress factor, high-fracture toughness before irradiation and inherently low-induced radioactivity. However, there are two major concerns with the alloy. One is that the alloy is severely embrittled by neutron irradiation to a displacement level of 0.5 dpa below 600 K [1–4]. The other is that the high-temperature yield strength of the alloy is significantly lowered with increasing the temperature above 1000 K [5,6]. It is thus necessary to improve both radiation resistance and high-temperature strength to the level acceptable for fusion applications.

Improvements in radiation resistance and high-temperature strength can be achieved by introducing a microstructure with fine grains and dispersed particles. The microstructure can be produced by powder metallurgy (P/M) methods including mechanical alloying (MA) [7–13]. However, vanadium powder, especially MA-treated powder, is very chemically active and thus easily subjected to contamination with gaseous interstitial impurities such as oxygen and nitrogen [8,11], which cause a serious degradation of mechanical properties, e.g., extreme loss of ductility. For this reason, to the authors' knowledge, no successful work on the development of vanadium and its alloys with the above microstructure and good mechanical properties has been reported so far.

In this paper, a process for microstructure control to overcome the loss of ductility in vanadium and its alloys with the target microstructure is proposed. The characteristics of the resulting microstructure and mechanical properties of a developed alloy are presented.

2. Principle for microstructure control

Preliminary studies [14] showed that an extreme loss of ductility in vanadium and its alloys fabricated by the P/M method including the MA treatment is caused by the embrittling effect of significant amounts of solute oxygen and nitrogen in the matrix. Therefore, in order to suppress the ductility loss, it is necessary to remove solute oxygen and nitrogen impurities from the matrix.

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The only solution for removal is that all of the solute oxygen and nitrogen are consumed to form finely dispersed oxide and nitride particles stable at high temperatures. For this, it is very effective to use powders of pure vanadium and yttrium as the starting materials because yttrium forms more stable oxides and nitrides than vanadium and yttrium oxide (Y_2O_3) and yttrium nitride (YN) has good high-temperature stability. A microstructure with fine grains and very finely dispersed yttrium particles is first produced by MA. Then solute oxygen and nitrogen, contained in the starting powders and introduced through the fabrication processes, are consumed as yttrium compounds formed during consolidation and subsequent heat treatments and thus are removed from the matrix. These oxide and nitride particles, in turn, can work to improve the high-temperature strength by impeding the movement of dislocations at high temperatures. They can also improve radiation resistance by suppressing radiation damage by providing a large number of sinks for vacancies and interstitials induced during irradiation. However, an excessive density of these particles may have the detrimental effect of decreasing ductility. Therefore, it is also necessary to control the content of oxygen and nitrogen to the level required to form a suitable amount of finely dispersed particles.

3. Experimental

Powders of pure vanadium (particle size: <150 μm, oxygen: 0.08 wt%, nitrogen: 0.07 wt%) and pure yttrium (750 μm, 1.56 wt%, 0.05 wt%) were used as the starting materials. These powders were mixed to provide several compositions up to 1.6 wt% yttrium and then subjected to MA in a purified Ar atmosphere (purity 99.9999%). Details of the MA treatment are described elsewhere [9]. Hot isostatic pressing (HIP), which permitted consolidation of the MA-treated powder without exposure to air and at relatively low temperatures where the grain growth may not occur, was conducted in an Ar atmosphere at 1273 K and 200 MPa for 3 h. As a result, it was found that the highest concentrations of oxygen and nitrogen in the fabricated alloys after all treatments were 0.20 and 0.08 wt%, respectively. These oxygen and nitrogen contents require 1.25 wt% yttrium to form Y_2O_3 and YN. Thus, 1.60 wt% yttrium was added by considering the contamination which might occur during machining and neutron irradiation experiments. The density of the as-HIPped sample was 6.05 g/cm^3, 99.3% theoretical density.

From the as-HIPped body, bend bar specimens with the dimensions of $1\ \mathrm{mm} \times 1\ \mathrm{mm} \times 20\ \mathrm{mm}$ were machined. The surfaces of the specimens were mechanically polished with emery paper of #220 to #1500. The specimens were wrapped with Zr foil and heat treated at 1273 K for 1 h in a vacuum of 10^{-5} Pa for dehydrogenation as well as for further formation of yttrium compounds. Table 1 shows the chemical composition of the specimens. The impurity content of tungsten came from the milling vessel and balls made of WC/Co used during MA.

The low-temperature ductility was examined by 3-point bend impact tests at temperatures from 77 to 298 K by using a specially designed electrically controlled hydraulic machine [15] with a span of 12.5 mm and an impact velocity of approximately 5 m/s. X-ray analysis was performed to identify the dispersed compound particles with a voltage of 30 kV and an amperage of 250 mA. Vickers microhardness measurements were conducted with loads of 0.098 and 1.96 N for 20 s. Microstructure examinations were performed by optical microscopy, scanning electron microscopy (SEM) with a JSM-5400 equipped with an energy dispersive X-ray (EDX) spectrometer operating at 15 kV and transmission electron microscopy (TEM) with a JEM-2000FXII equipped with an EDX spectrometer operating at 200 kV in the Oarai Branch of IMR at Tohoku University.

4. Results and discussion

Fig. 1 shows an optical micrograph of the etched surface of the specimen. Most of grains are fine, though a fraction of the grains remain coarse. Crack-like pores are observed mainly around the interfaces between fine- and coarse-grained regions. Fig. 2 shows a TEM image from fine- and coarse-grained regions. In the fine-grained region, the average size of the grains is approximately 250 nm and there are a large number of dispersed particles with an average diameter of approximately 25 nm. In the coarse-grained region, on the other hand, there are only a few particles. In order to identify the nature of the coarse-grained regions, SEM/EDX and TEM/EDX analyses were made on one of the typical coarse grains in the specimen. The result by SEM/EDX analysis is shown in Fig. 3. TEM/EDX analysis also gives essentially the same result. As seen

Table 1
Chemical composition of the specimen used (wt%)

V	Y	O	N	C	H	Ar	W
Bal.	1.56	0.141	0.075	0.022	0.0004	0.0012	0.09

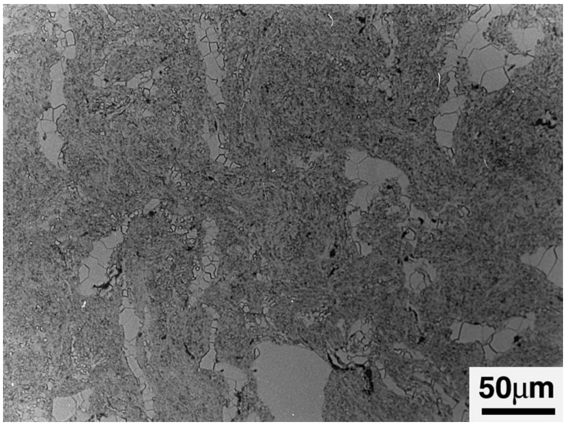

Fig. 1. An optical micrograph showing the grain appearance.

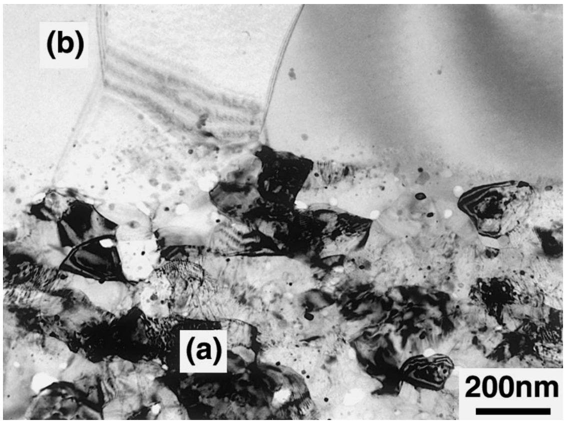

Fig. 2. TEM image showing the microstructure with: (a) fine grains; (b) coarse grains.

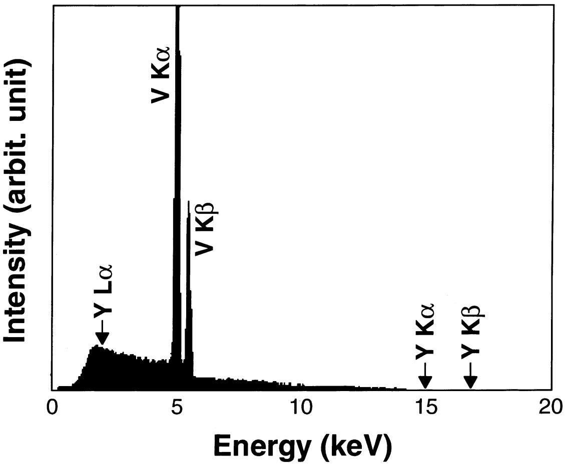

Fig. 3. SEM/EDX spectrum obtained from a coarse grain.

from Fig. 3, only the vanadium peaks appear, no yttrium peaks, showing that the coarse grain consists of vanadium. This may indicate that a part of the starting vanadium powder was not sufficiently MA treated and is responsible for the coarse-grained regions, whereas the starting yttrium powder was sufficiently MA treated and was finely dispersed in the fine-grained regions. Therefore, we can say that the process for microstructure control proposed and performed in this study leads to the target microstructure. Improvement in MA conditions will produce the microstructure without insufficiently MA-treated regions in the specimen, and this is now in progress.

Fig. 4 shows an X-ray diffraction pattern showing the peaks of Y_2O_3 and YN which were formed by reaction of very finely dispersed yttrium particles in the fine-grained regions with solute oxygen and nitrogen contained in the starting powders and introduced through the fabrication processes. Since oxygen and nitrogen in vanadium cause a significant solution hardening, the degree of removal of solute oxygen and nitrogen from the matrix is estimated by the hardness of matrix regions free from dispersed particles. As shown in Fig. 1, several coarse grains that were large enough to measure Vickers microhardness were observed. We noted that such coarse grains contained only a few particles. Therefore, Vickers microhardness for coarse-grained regions was measured and the result is shown in Fig. 5. In the figure, the hardnesses for the fine-grained region, electron-beam-melted pure vanadium containing 214 wt ppm oxygen and 4 wt ppm nitrogen [16] and V–4Cr–4Ti [17] and the calculated hardness for solution-hardened vanadium containing oxygen and nitrogen of the same concentrations with those of the present specimens are also shown. For the calculation, the experimental data on specific hardening by oxygen and nitrogen [18,19] were used. The hardness of the fine-grained region is 183 HV, which is considerably higher than that of V–4Cr–4Ti (~155 HV [17]). This high value is attributable to both dispersion and grain boundary strengthening. On the other hand, the hardness for coarse-grained regions

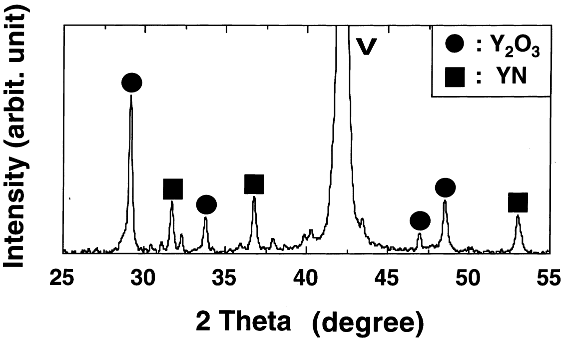

Fig. 4. X-ray diffraction pattern.

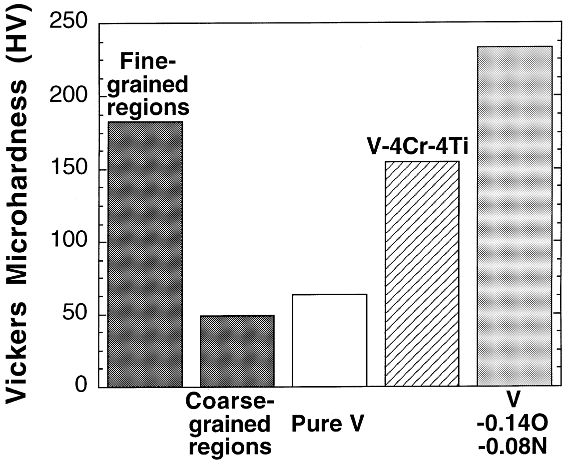

Fig. 5. Vickers microhardnesses for fine- and coarse-grained regions in the present specimen. The hardness for pure vanadium [16] and V–4Cr–4Ti [17] and the calculated hardness for solution-hardened vanadium (V–0.14O–0.08N) [18,19] are also shown.

is 55–58 HV with the average of 56 HV for seven grains (seven data points) examined, which indicates less grain orientation dependence of hardness. This value of 56 HV is much lower than the calculated value for the solution-hardened vanadium and is slightly lower than that of the pure vanadium (~63 HV [16]). From this result, it appears that solute oxygen and nitrogen were effectively removed from the matrix.

Fig. 6 shows the test temperature dependence of total deflection for the specimens measured by 3-point bend impact tests. It should be noted that the alloy exhibits full bend without break at temperatures down to 130 K and shows a relatively large amount of deflection prior to fracture even at 77 K. This result seems significant in that vanadium and its alloys fabricated by P/M methods have long been believed to be too brittle to exhibit an appreciable ductility even at room temperature. The good ductility of the specimen is believed to be attributable to the successful removal of solute oxygen and nitrogen from the matrix and a suitable amount of finely dispersed oxide and nitride particles. The occurrence of fracture at 77 K would be attributed to a detrimental effect of non-uniform microstructure with fine- and coarse-grained regions and crack-like pores. The detrimental effect may be overcome by producing more uniform microstructures consisting of fine grains. It is therefore considered that vanadium and its alloys with the target microstructure will exhibit much improved ductility.

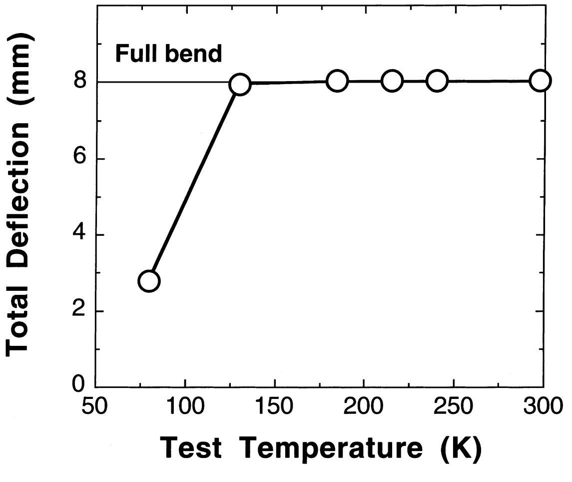

Fig. 6. Test temperature dependence of total deflection measured by 3-point bend impact tests.

5. Conclusion

The process for microstructure control to overcome the loss of ductility in vanadium and its alloys produced by P/M methods including MA treatment was proposed and applied to fabricate a vanadium alloy. The essential point of the process was that most of the solute oxygen and nitrogen was consumed to form yttrium compounds as finely dispersed particles (Y_2O_3 and YN). The fabricated alloy had a microstructure with fine grains and dispersed particles, although some coarse-grained regions remained and crack-like pores existed. Vickers microhardness of the matrix almost free from dispersed particles in the alloy was lower than that of electron-beam-melted pure vanadium indicating that solute oxygen and nitrogen were effectively removed from matrix. Three-point bend impact tests showed that the alloy exhibited a good ductility even at 77 K. Optimizing MA conditions to achieve microstructures without coarse grains and crack-like pores should further improve the low-temperature ductility.

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