Precipitation Softening and Precipitate Free Zones of $V_{55}Ti_{30}Ni_{15}$ Alloys During Heat Treatment

Peng Jiang · Yan-Dong Yu · Guang-Sheng Song · Daniel Liang · Michael Kellam · Michael Dolan

Received: 31 March 2014 / Revised: 25 May 2014 / Published online: 28 September 2014
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2014

Abstract The microstructure, hardness, and precipitate free zones (PFZ) of $V_{55}Ti_{30}Ni_{15}$ alloys during heat treatment have been investigated in this study. The microstructure resulting from different heat treatment conditions has a great influence on hardness. The microstructure resulting from different heat treatment conditions has a great influence on hardness. Fine NiTi particles precipitate from the supersaturated V-matrix solid solution at 750 °C, increase in quantity until 800 °C, and then dissolve back into the V-matrix at 850 °C. The resultant hardness decreases with temperature until 800 °C, and then increases from 800 to 850 °C. The microstructure containing small NiTi precipitates resulting from the treatment of 18 h at 800 °C has a good soft condition for workability. PFZ formed at the grain boundary of V-matrix during heat treatment was observed. Vacancies depletion in V-matrix maybe led to the formation of PFZ.

KEY WORDS: V–Ti–Ni; Heat treatment; Hardness; Precipitation softening; Precipitate free zones

1 Introduction

Pd-based alloy membranes are used for hydrogen separation because of their reasonable permeability, good durability, and good tolerance to impurities [1, 2]. However, Pd and its alloys are very expensive, thus limiting their applications in hydrogen production [3]. Non-Pd metals with the body-centered cubic (BCC) structure such as V, Nb, and Ta have intrinsically greater hydrogen

permeability and are significantly cheaper than Pd. Therefore, these types of membrane materials are being explored quite extensively as alternatives to Pd membranes for hydrogen separation [3–7].

Recent efforts have been put into the development of V-based alloy membranes in a ternary V–Ni–Ti system [3, 7, 8]. Some V-based alloys in this system have shown permeation of an order equal to pure Pd while maintaining reasonable mechanical stability in hydrogen. These alloys have a multiphase microstructure consisting of a primary BCC V-solid solution (V_{ss}) and a eutectic phase containing NiTi intermetallic compounds. The primary V-solid solution and eutectic phase are presumed to contribute to hydrogen permeation and resistance to hydrogen embrittlement, respectively. Recent work on a series of $V_{85-x}Ti_xNi_{15}$ ($x = 0–30$ at%) alloys has shown that the permeability of $V_{55}Ti_{30}Ni_{15}$ (1.05×10^{-7} mol/(m s Pa^{0.5}) at 400 °C) approaches that of pure V [7, 9] and its microstructure is similar to the aforementioned structure. This seems to be a promising alloy which may reach a good combination of hydrogen permeability and mechanical stability in hydrogen. Metal rolling processes are most

Available online at <http://link.springer.com/journal/40195>

P. Jiang · Y.-D. Yu (✉)
School of Materials Science and Engineering, Harbin University
of Science and Technology, Harbin 150040, China
e-mail: yyd@hrbust.edu.cn

P. Jiang · G.-S. Song · D. Liang · M. Kellam
CSIRO, Process Science and Engineering, Clayton, VIC 3168,
Australia

M. Dolan
CSIRO, Energy Technology, 1 Technology Court, Pullenvale,
QLD 4069, Australia

widely used for sheet fabrication and may be used to make multiphase V–Ti–Ni metallic membranes thinner for increased hydrogen transport flux [10]. Currently, there is little information on the rolling workability of this type of alloy membranes.

Precipitate free zones (PFZ) form during the heat treatment of metallic alloys [11], especially Al-based alloys. The role of PFZ on mechanical properties is clearly attested in the literature. The presence of PFZ was found to be harmful to the mechanical properties of Al–Li alloys [12], Al–Mg alloys [13] and Al–Mg–Zn alloys [14]. Similarly, the yield strength, the ultimate tensile strength, and the plastic strain to fracture of a γ' -strengthened nickel-base superalloy have been linked to the width of the PFZ [15]. However, some researchers thought that slip bands and stress concentration had a priority to be released in the PFZs, resulting in the increase of strength and ductility of the selected alloys [16, 17].

In the present work, the mechanical hardness and microstructural response to the heat treatments at different conditions for a selected $V_{55}Ti_{30}Ni_{15}$ alloy have been evaluated. Moreover, in this paper, the formation mechanism of the PFZ in the alloys during heat treatment was also explored.

2 Experimental

2.1 Sample Preparation

High-purity (99.9%) vanadium, titanium, and nickel pellets were mixed and melted on a water-cooled copper hearth using a vacuum/argon arc melter to make a nominal composition of $V_{55}Ti_{30}Ni_{15}$ (at%). The arc-melted ingot (total weight 100 g) was turned over and re-melted several times to ensure compositional homogeneity. During melting, the chamber was evacuated to $<0.7 \times 10^{-3}$ Pa and then backfilled with high-purity argon gas up to a pressure of 100 kPa.

2.2 Heat Treatment

According to the Ni–Ti binary phase diagram [18] and the constituent phases reported in the microstructure of as-cast $V_{55}Ti_{30}Ni_{15}$ alloy [7], the $NiTi_2$ phase has the lowest decomposition temperature of 984 °C compared to the other phases present in this cast alloy. Therefore, the maximum treatment temperature of the as-cast $V_{55}Ti_{30}Ni_{15}$ alloy should be lower than the melting point of $NiTi_2$. An arc-melted ingot was sectioned to produce several small samples using electrical discharge machining (EDM). These samples were sealed in quartz tubes which were evacuated and backfilled with high-purity argon gas in

Fig. 1 $V_{55}Ti_{30}Ni_{15}$ alloy microhardness as a function of time at various temperatures

order to avoid oxidation. The sealed samples were heated at different temperatures ranging from 750 to 850 °C and held for different times between 3 and 24 h, and then rapidly removed and quenched into water at room temperature.

2.3 Sample Characterization

Vickers hardness measurements of as-cast and heat-treated samples were carried out at 500 and 100 g loads for a dwell time of 15 s using a digital microhardness tester. The applied loads of 500 and 100 g were able to make large indent to cover multiple phases and small indent to cover Vss phase on these samples, respectively.

An Olympus optical microscope (OM) was used to observe the microstructures of the polished and etched samples. Precipitates formed in the heat-treated samples were examined using scanning electron microscopy (Quanta 200 FEG-SEM, FEI Company) equipped with X-ray energy-dispersive spectroscopy (EDS). A back-scattered electron (BSE) mode in the SEM was used to acquire images from the polished samples without etching. X-ray diffraction (XRD) data were collected using a Bruker D8 advance X-ray diffractometer employing CuK_{α} radiation with a tube voltage of 40 kV and current of 40 mA. The 2θ range was 20° – 100° with a step size of 0.02° and a count time of 4 s per step. Fine precipitates were identified by a transmission electron microscope (TEM, JEM-2100, JEOL, Japan) equipped with EDS operating at an accelerating voltage of 200 kV. Approximately 0.1-mm thick slices were obtained from heat-treated samples by wire cutting, and ground to 50 μ m using different grit sandpapers. These were then placed in an ion milling machine for thinning TEM samples at a voltage of 4.4 kV and an incidence angle of 6° – 8° .

Fig. 2 $V_{55}Ti_{30}Ni_{15}$ alloy microhardness as a function of temperature showing the trend between bulk and phase hardness conditions and the indentations of bulk and phase hardness in the set

3 Results and Discussion

3.1 Vickers Hardness

Figure 1 shows hardness-time curves at temperatures ranging from 750 to 850 °C. At $t = 0$, the hardness value denotes the initial arc-cast state of $V_{55}Ti_{30}Ni_{15}$ alloy. At this, the temperatures ranging the hardness decreases gradually with time. Of interest is that the hardness values at 18 h are similar to those at 24 h for the temperatures investigated in the paper. This suggests that the heat-affected microstructure becomes relatively stable in the 18–24 h range. Therefore, a holding time of at least 18 h at different temperatures is required to produce a near equilibrium microstructure in these $V_{55}Ti_{30}Ni_{15}$ alloy heat-treated samples.

Figure 2 compares the hardness from bulk (4.9 N load) and V-based solid solution phase (1.0 N load) in the heat-treated samples at different holding temperatures for a period of 18 h, and shows the indentations of bulk and phase hardness. Of particular interest is the fact that a very similar trend was observed with an initial decrease in hardness before 800 °C followed by an increase at 850 °C. This suggests that the V-based solid solution phase is a predominant microstructural factor controlling the change in hardness.

3.2 Initial Microstructure

In the as-cast alloy, the microstructure consists of primary dendrites of Vanadium solid solution surrounded by interdendritic metallic compounds, as shown in the OM image of Fig. 3. These metallic compounds can be seen clearly in the SEM image (inset of Fig. 3), and were

Fig. 3 Optical micrograph of the initial microstructure from the arc-melted cast ingot showing primary V_{ss} dendrites and intermetallic compounds distributed in the interdendritic region detailed features in the SEM inset

identified as $NiTi$ (light phase) and $NiTi_2$ (light-gray phase) using a combination of EDS/SEM and XRD techniques, which are in agreement with the previously reported multiphase microstructure [7].

Owing to the high thermal conductivity of copper and rapid heat extraction, this molten alloy solidifies rapidly as it comes into contact with the water-cooled copper hearth. In this case, rapid dendritic solidification of primary V produces a supersaturated solid solution with much higher solute concentration than the limit of equilibrium solid solubility at room temperature [19, 20]. With respect to pure V as a reference, the supersaturated V-matrix causes the V_{ss} (211) peak to shift to lower diffraction angles, as shown in Fig. 4 and Table 1. This result suggests that lattice expansion in the V-matrix was due to the combined presence of Ni and Ti. In addition, a large atomic size difference between the solutes Ni (0.1246 nm)/Ti (0.1462 nm) and solvent V (0.1316 nm) [21] generates more distortion of the V-matrix lattice thereby impeding the movement of dislocations which results in a higher alloy strength. Therefore, the initial hardening (see Fig. 2) is attributed to the formation of supersaturated solid solution of these alloying elements Ni and Ti in V, i.e. solid solution strengthening mechanism.

3.3 Precipitation and Dissolution During Heat Treatment

The shifting of XRD peaks was observed to occur in the V_{ss} phase during heat treatment, as seen in Fig. 4. At 750

Fig. 4 X-ray diffraction patterns for $V_{55}Ti_{30}Ni_{15}$ alloy in the as-cast and heat treated (various temperatures for 18 h) conditions

Table 1 XRD 2θ peak values, d -spacing and lattice constant corresponding to crystal plane (211) of the V_{SS} phase

Heat treatment temperature T (°C)	2θ (°)	d -spacing (nm)	Lattice constant a (nm)
Pure V	77.08	0.12363	0.30274
As-cast	75.61	0.12566	0.30781
750	76.35	0.12463	0.30527
800	76.83	0.12397	0.30365
850	76.25	0.12476	0.30561

and 800 °C, the XRD peaks shifted to higher 2θ values compared to the initial as-cast state, but at 850 °C, moved back to lower diffraction angle values. Such a change can be exemplified using a peak position of (211) reflection from as-cast and heat-treated ingots (see Table 1). One possible explanation for this peak shift is that the solute concentration of Ni and Ti in the V-matrix changes during heat treatment. In other words, initially in the as-cast, the saturated solute concentration trapped in the lattice decreases with increasing temperature, leading to a decrease in the lattice constant and thus causing the peak to shift to high angles. As the temperature increases further, the peaks shift back to lower 2θ values, indicating that the lattice constant returns almost to the initial as-cast state. It can be inferred that the concentration of Ni and Ti solutes entering the lattice increases back toward the saturated concentration. In order to verify why the change in solute concentration occurred in the V-matrix, a combination of SEM and TEM analysis was carried out.

Figure 5a–c shows SEM micrographs of the as-cast alloy treated at temperatures between 750 and 850 °C for 18 h. Initially, the supersaturated V_{SS} formed by liquid quenching is thermodynamically unstable and decomposes with precipitation of new particles upon heating at temperatures above 750 °C. In the treated sample at 750 °C for 18 h, it was observed that small particles preferentially formed near the boundaries between V_{SS} and $NiTi_2/NiTi$. This indicates that the Ni and Ti distribution in the V-matrix were not homogeneous, i.e. getting richer toward the boundaries. The heat-treated sample at 800 °C showed more precipitates, extending toward the center of V-matrix, as shown in Fig. 5b. However, further increases in temperature resulted in dissolution of these precipitates. Smaller precipitates seemed to dissolve easily in the center region, while larger ones still remained in the boundary regions and displayed partial dissolution occurring at 850 °C after 18 h.

In order to identify the precipitated phase formed within the V-matrix, the use of analytical TEM is appropriate for fine precipitate characterization. The TEM images in Fig. 5d show the fine precipitates within the V-matrix in the sample treated at 800 °C for 18 h. These precipitates are nanoscale (about 100 nm) in size and spherical in morphology. To determine the structure and crystallography of fine precipitates, structural analysis of fine precipitates was carried out using selected area electron diffraction (SAED) patterns taken from a particle denoted by ‘A’ in Fig. 5d. In the SAED pattern of Fig. 5d inset, the particle was identified as $NiTi$. In addition, the small/faint spots of $(100)_{NiTi}$ and $(111)_{NiTi}$ are observed in the $[0\bar{1}1]_{NiTi}$ zone diffraction pattern, showing the existence of a superlattice structure.

In the temperature range of 750–800 °C, the supersaturated V_{SS} decomposes with the precipitation of $NiTi$ nanoparticles according to the reaction $V_{SS}^{supers} \rightarrow V_{SS}^{equilibrium} + NiTi^{nano}$. As precipitation proceeds, the saturated solution (V_{SS}^{supers}) loses more Ni and Ti solutes required for the formation of $NiTi$ nanoparticles, and moves toward equilibrium. In other words, the amount of Ni and Ti in solid solution is reduced by precipitation of $NiTi$ phase. On the other hand, with increasing temperature, the precipitated $NiTi$ particles start to dissolve and diffuse back into the V-matrix solution according to the reaction $V_{SS}^{equilibrium} + NiTi^{nano} \rightarrow V_{SS}^{supers}$.

The changes in hardness of $V_{55}Ti_{30}Ni_{15}$ alloy occurring when subjected to isochronic heat treatment at different temperatures (see Fig. 2) are due to the internal structural changes that occur in the V-matrix during heat treatment. The drop in the initial hardness is presumed to be associated with the formation of $NiTi$ precipitates, whereas the subsequent hardness increasing at 850 °C is attributed to the dissolution of precipitated $NiTi$ particles into the

Fig. 5 SEM images of $V_{55}Ti_{30}Ni_{15}$ alloy heat treated for 18 h at temperatures: **a** 750 °C, **b** 800 °C, **c** 850 °C, **d** TEM image of the V-matrix heat treated at 800 °C for 18 h and SAED pattern taken from area A in the TEM inset

V-matrix solution. After a heat treatment of 18 h at 800 °C, there was approximately 30% reduction in hardness compared to the hardness maximums. This phenomenon is called a softening process, which is caused by the precipitation of NiTi or solid solution decomposition in the V-matrix. This finding is not consistent with conventional understanding of the precipitation hardening mechanism dominant in many precipitation-strengthened materials such as Al-based, Ni-based, and Ti alloys [22–26]. More investigation is needed to understand the softening mechanism occurring in this alloy system. The as-cast alloy can be softened by precipitation of NiTi occurring during heat treatment. The softest condition was found to be a heat treatment of 18 h at 800 °C in the present work (see Fig. 2). In order to optimize the formability/rollability of the as-cast alloy, it undergoes a softening process under such conditions.

3.4 Formation of the PFZs After Heat Treatment

The PFZs formed at the boundary of the V-matrix can be seen obviously in Fig. 5. The relation curve of the PFZs

Fig. 6 Relation curve of PFZs widths and temperature for $V_{55}Ti_{30}Ni_{15}$ alloys heat treated for 18 h

widths and heat treatment temperature is shown in Fig. 6. The PFZs widths were measured by Image Pro-Plus software 6.0 (IPP 6.0). It can be seen that the PFZs widths

Fig. 7 EDS composition profiles along *white line* for the V-matrix of the as-cast alloy. (Color figure online)

monotonically increases with temperature until 800 °C, and the value increases from 224 nm at 750 °C to 291 nm at 800 °C. When the temperature increases to 850 °C, the PFZs widths decrease slightly.

The possible reason of the PFZs formed at the boundary of V-matrix was analyzed in the following discussion. Supersaturate solid solution is a metastable phase with higher energy, not only solute atoms but also vacancies are in supersaturate state. Vacancies can provide the driving force of nucleation to stimulate nucleation by accelerating the diffusion process or unleashing their own energy [11]. Figure 7 shows the distribution of elements Ti and Ni in the V-matrix. It can be seen that the distribution of elements Ti and Ni in the V-matrix is not homogeneous, and the concentrations of Ti and Ni are higher at the boundary of V-matrix. The concentrations of Ti and Ni gradiently distribute between the boundary and the center of the V-matrix.

Supersaturate vacancies with high concentration were formed in V-matrix when $V_{55}Ti_{30}Ni_{15}$ alloy solidified with high cooling rate. During heat treatment, vacancies near the boundary of V-matrix were privileged to diffuse toward the boundary and were absorbed because the grain boundary is vacancy trap. Vacancies near the boundary of V-matrix dissipated and the concentration was decreased and gradiently distributed from the boundary to the center of V-matrix. Although the solutes concentration near the boundary of the V-matrix is higher, vacancies concentration near the grain boundary is lower than the critical

concentration for new phases nucleation [11]. Therefore, NiTi particles firstly nucleated and precipitated at the positions where the concentrations of the solute atoms and vacancies contributed to the precipitation of new phases, and local precipitation occurred in the V-matrix. Meanwhile, the PFZs formed at the boundary of V-matrix due to lower vacancies concentration in the PFZs. When the temperature increased, the solute atoms and the vacancies diffused rapidly, the precipitation of NiTi particles started to extend to the center of V-matrix grain gradually and vacancies which are far from the grain boundary of the V-matrix also diffused to the grain boundary, leading to the increase of the width of the PFZs.

4 Conclusions

The changes in microhardness of $V_{55}Ti_{30}Ni_{15}$ alloy after heat treatment were found to be associated with NiTi precipitation and dissolution of precipitated NiTi nanoparticles in the V-matrix during heat treatment. The microstructure containing small NiTi precipitates resulting from the treatment of 18 h at 800 °C has a good soft condition for workability. This is an anomalous case where the precipitation strengthening is less effective than solid solution strengthening. The PFZs formation at the boundary of V-matrix may be caused by the vacancies depletion.

Acknowledgments The authors would like to thank China Scholarship Council for the financial support for Peng Jiang's study at CSIRO.

References

- [1] J.E. Philpott, *Platinum Met. Rev.* **29**, 12 (1985)
- [2] Y. Shirasaki, Y. Ohta, K. Kobayashi, K. Kuroda, *Membrane Reformer Technical Bulletin* (Mitsubishi Heavy Industries Ltd., Yokohama, 1996)
- [3] T.M. Adams, J. Mickalonis, *Mater. Lett.* **61**, 817 (2007)
- [4] M.D. Dolan, *J. Membr. Sci.* **362**, 12 (2010)
- [5] J.W. Phair, R. Donelson, *Ind. Eng. Chem. Res.* **45**, 5657 (2006)
- [6] K. Hashi, K. Ishikawa, T. Matsuda, A. Aoki, *J. Alloys Compd.* **404–406**, 273 (2005)
- [7] G. Song, M.D. Dolan, M.E. Kellam, D. Liang, S. Zambelli, *J. Alloys Compd.* **509**, 9322 (2011)
- [8] S.I. Jeon, E. Magnone, J.H. Park, Y. Lee, *Mater. Lett.* **65**, 2495 (2011)
- [9] S.A. Steward, *Review of Hydrogen Isotope Permeability Through Metals*, US National Laboratory Report, 1983, UCRL-53441
- [10] K. Ishikawa, S. Tokui, K. Aoki, *Intermetallics* **17**, 109 (2009)
- [11] D. Porter, K. Easterling, *Phase Transformations in Metals and Alloys*, 2nd edn. (Chapman & Hall, New York, 1992)
- [12] G. Itoh, M. Kanno, T. Hagiwara, T. Sakamoto, *Acta Mater.* **47**, 3799 (1999)
- [13] S. Lee, A. Utsunomiya, H. Akamatsu, K. Neishi, M. Furukawa, Z. Horita, T.G. Langdon, *Acta Mater.* **50**, 553 (2002)

- [14] D. Dumont, A. Deschamps, Y. Bréchet, *Acta Mater.* **51**, 2529 (2004)
- [15] R. Maldonado, E. Nembach, *Acta Mater.* **45**, 213 (1997)
- [16] T. Krol, D. Baither, E. Nembach, *Acta Mater.* **52**, 2095 (2004)
- [17] T. Kawabata, O. Izumi, *Acta Metall.* **24**, 817 (1976)
- [18] P. Villars, L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd edn. (American Society for Metals, Metals Park, 1991)
- [19] L.A. Jacobson, J. McKittrick, *Mater. Sci. Eng. R* **11**, 355 (1994)
- [20] C. Nishimura, M. Komaki, S. Hwang, M. Amano, *J. Alloys Compd.* **330–332**, 902 (2002)
- [21] O.N. Senkov, D.B. Miracle, *Mater. Res. Bull.* **36**, 2183 (2001)
- [22] S. Esmaeili, X. Wang, D.J. Lloyd, W.J. Poole, *Metall. Mater. Trans. A* **34**, 751 (2003)
- [23] V. Munjal, A.J. Ardell, *Acta Metall.* **23**, 513 (1975)
- [24] Z. Wang, S. Xie, J. Lu, L. Wang, H. Yang, *Acta Metall. Sin. (Engl. Lett.)* **8**, 102 (1995)
- [25] W.H. Tian, *Acta Metall. Sin. (Engl. Lett.)* **14**, 313 (2001)
- [26] S. Shimizu, Y. Xu, E. Okunishi, S. Tanaka, K. Otsuka, K. Mitose, *Mater. Lett.* **34**, 23 (1998)