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Letter

Effect of Hf/Ni ratio on microstructure and hydrogen permeation of Nb–Hf–Ni ternary alloys

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ABSTRACT

The effect of the Hf/Ni ratio on the microstructures and hydrogen permeabilities of the Nb–Hf–Ni ternary alloys is studied in particular. The results demonstrate that with the increase in the Hf/Ni ratio, (i) the quantity of the primary (Nb, Hf) phase increases; (ii) a new HfNi phase with more Hf content appears; (iii) the Φ value decreases except that of the alloys with the same Hf and Ni contents.

1. Introduction

As we all know, palladium is expensive and not suitable for large-scale industrial application as hydrogen permeation alloy for separation and purification of hydrogen gas; therefore, palladium-based alloys are not currently preferred for hydrogen purification [1–4], but niobium-based hydrogen permeation alloys are of the optimal choice [5]. Nb–Ti–Ni and Nb–Zr–Ni alloys have already been investigated [1,5] and Nb–Hf–Ni alloys are also studied [6]. Niobium plays an important role on the hydrogen permeability of Nb–Ti–Ni, Nb–Zr–Ni and Nb–Hf–Ni alloys [4–6]; however, the effect of Hf/Ni ratio on the microstructure and hydrogen permeation properties of the Nb–Hf–Ni ternary alloys was not studied. In this letter, Nb–Hf–Ni ternary alloys are particularly studied to analyze the influence of Hf/Ni ratio on the microstructures and hydrogen permeabilities of these new hydrogen permeation alloys as a progress report of the results in the other paper [6].

2. Experimental procedure

About 20 g ingots of $Nb_xHf_yNi_{(1-x-y)}$ alloys (mol%) were prepared by arc-melting in a purified argon atmosphere using Nb (99.9% purity), Hf (99.99% purity) and Ni (99.9% purity) as raw materials. Disk samples of 12 mm diameter and 0.5–0.7 mm thickness were cut from the ingots by the spark erosion method. The surface of the disks was polished using buff and alumina particle (0.5 μm). Microstructure observation and measurement of chemical composition of the samples were carried out with a scanning electron microscope (SEM) and an energy dispersion X-ray spectroscopy (EDS). Structures of the samples were identified by an X-ray diffractometer (XRD) using Cu Kα-radiation monochromated by graphite. Both sides of the disks were coated with pure Pd of 190 nm thickness by the magnetron sputtering machine. The disk sample sealed with copper gaskets was set into the hydrogen permeation measuring apparatus, i.e., a conventional gas-permeation technique, and then hydrogen permeability (Φ) of these alloys was measured in the temperature range of 623–673 K at a hydrogen pressure up to 0.5 MPa. The experimental procedure has been described in the previous papers [1,7].

3. Results and discussion

Figs. 1 and 2 show the XRD patterns of the $Nb_xHf_yNi_{(1-x-y)}$ alloys. As shown in Figs. 1 and 2, the Bragg peaks are indexed to the B_f-HfNi intermetallic compounds [8] and the bcc- (Nb, Hf) solid solutions, including some other compounds of $HfNi_3$, Hf_3Ni_7, Hf_2Ni_7, $HfNi_5$, and Hf_8Ni_{21}, as compared with JCPDS files of Nos. 32-0475, 71-0477, 26-1129, 17-0027, and 32-0476 (International Center for Diffraction Data, 2002; marked with arrow and 1–11, as shown in Figs. 1 and 2). The main phase is the B_f-HfNi intermetallic compound; and as for the bcc- (Nb, Hf) solid solution, its quantity is less than that of the B_f-HfNi compound. As for the $Nb_{16}Hf_{41}Ni_{43}$ alloy, the intensity of the B_f-HfNi diffraction peaks is stronger than those of the other two alloys, whereas the intensity of the bcc- (Nb, Hf) peaks is weaker than those of the other two alloys. In the $Nb_{16}Hf_{43}Ni_{41}$ alloy, the quantity of the bcc- (Nb, Hf) phase is more than those in the other two alloys because the (1 1 0) peak appears and the intensity of the (2 0 0) peak increases. As for the alloys of

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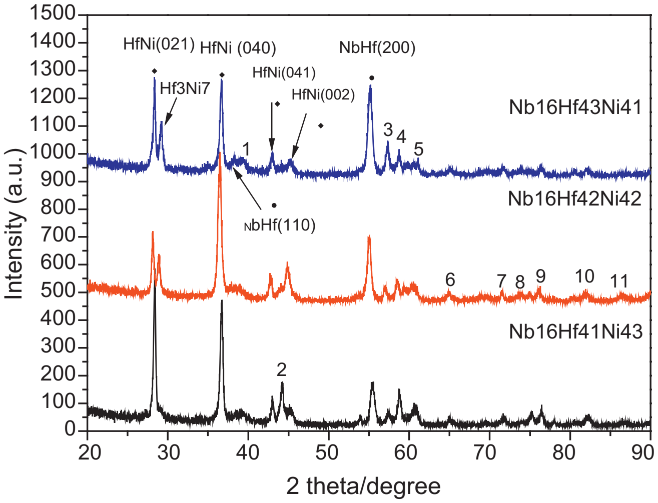

Fig. 1. The XRD patterns of the $Nb_{16}Hf_{41}Ni_{43}$, $Nb_{16}Hf_{42}Ni_{42}$, and $Nb_{16}Hf_{43}Ni_{41}$ alloys.

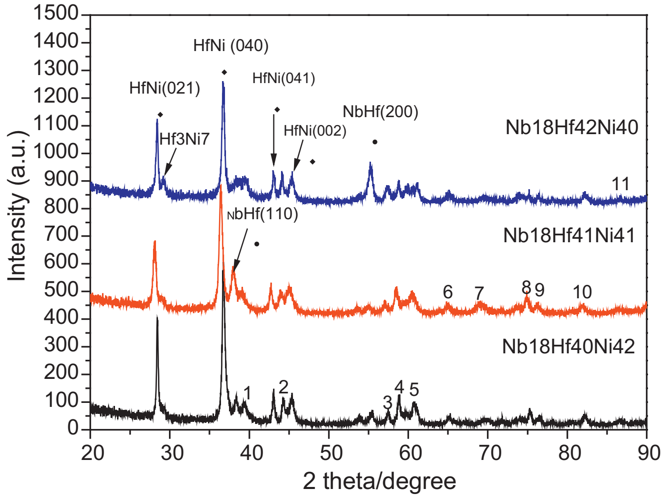

Fig. 2. The XRD patterns of the $Nb_{18}Hf_{40}Ni_{42}$, $Nb_{18}Hf_{41}Ni_{41}$, and $Nb_{18}Hf_{42}Ni_{40}$ alloys.

$Nb_{18}Hf_{40}Ni_{42}$, $Nb_{18}Hf_{41}Ni_{41}$, and $Nb_{18}Hf_{42}Ni_{40}$, the variation trend for the intensity of the diffraction peaks is similar to those alloys with Nb content of 16 mol%. In short, with the increase of the Hf/Ni ratio from 41/43 to 43/41 or from 40/42 to 42/40, the quantity of the primary (Nb, Hf) phase increases.

Fig. 3 shows the SEM photographs of the $Nb_xHf_yNi_{(1-x-y)}$ alloys. As shown in Fig. 3, there are four phases included in these images: the eutectic phase (marked as A, as shown in Fig. 3(c) and (f)), the primary bcc- (Nb, Hf) solid solution (the black phase, marked as B, as shown in Fig. 3(c) and (f)), the B_f-HfNi intermetallic compound (the grey phase, marked as C, as shown in Fig. 3(c)

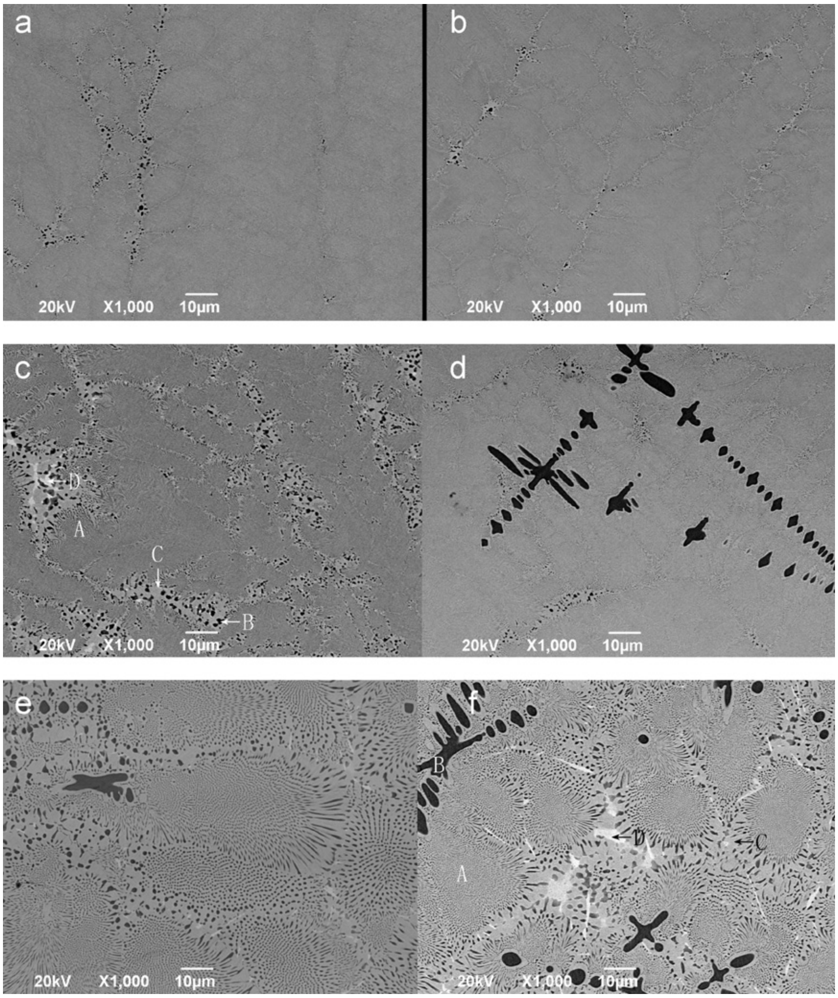

Fig. 3. The SEM photographs of the $Nb_xHf_yNi_{(1-x-y)2}$ alloys; (a) $Nb_{16}Hf_{41}Ni_{43}$ alloy; (b) $Nb_{16}Hf_{42}Ni_{42}$ alloy; (c) $Nb_{16}Hf_{43}Ni_{41}$ alloy; (d) $Nb_{18}Hf_{40}Ni_{42}$ alloy; (e) $Nb_{18}Hf_{41}Ni_{4}$; and (f) $Nb_{18}Hf_{42}Ni_{40}$ alloy.

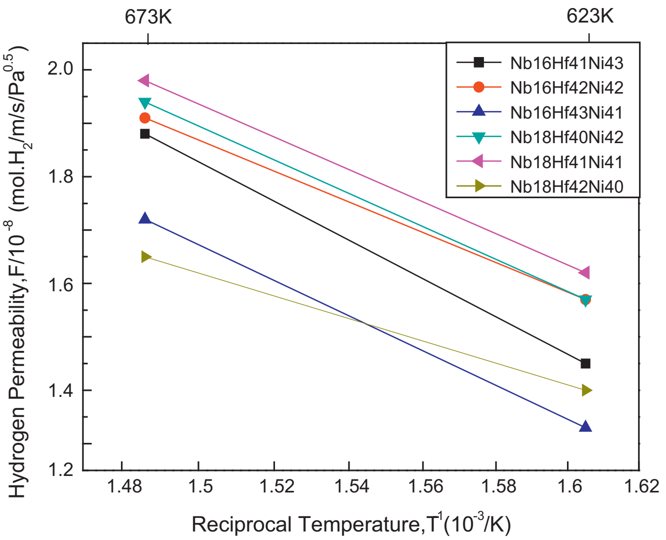

Fig. 4. Plots of hydrogen permeabilities (Φ) for the $Nb_xHf_yNi_{(1-x-y)}$ alloys in the form of the Arrhenius plot.

and (f)) with the composition of (c) $Nb_5Hf_{64}Ni_{31}$, (f) $Nb_5Hf_{61}Ni_{34}$, and a new HfNi phase (the white phase, marked as D, as shown in Fig. 3(c) and (f)) with the composition of $Nb_{2.5}Hf_{79}Ni_{18.5}$ (c), and $Nb_2Hf_{70}Ni_{28}$ (f), which can be observed clearly from Fig. 3. With the increase of Hf/Ni ratio from 41/43 to 43/41 or from 40/42 to 42/40 in the alloys with the same Nb content, the new HfNi phase appears in white color, whose Hf content is about 10–15 mol% more than that of the B_f-HfNi phase appearing with grey color.

Fig. 4 shows the plots of hydrogen permeabilities (Φ) for the $Nb_xHf_yNi_{(1-x-y)}$ alloys in the form of the Arrhenius plot.

For the alloys of $Nb_{16}Hf_{41}Ni_{43}$, $Nb_{16}Hf_{43}Ni_{41}$, $Nb_{18}Hf_{40}Ni_{42}$, and $Nb_{18}Hf_{42}Ni_{40}$, the Hf/Ni ratio significantly affects the hydrogen permeability (Φ), which decreases when the ratio of Hf/Ni increases. That is, the higher the value of Hf/Ni ratio, the lower the Φ value. But as for the alloys of $Nb_{16}Hf_{42}Ni_{42}$ and $Nb_{18}Hf_{41}Ni_{41}$, they have the highest Φ values in the alloys with the same Nb content because they have the least B_f-HfNi phases, which do harm to the hydrogen permeability. Although with the increasing Hf/Ni ratio, the primary (Nb, Hf) phase increases in the quantity, the Φ value decreases accordingly rather than increases [6] because of the appearance of the new HfNi phase, which has more Hf content and plays a worse role on the hydrogen permeability, i.e., it impedes the hydrogen flux passing through the alloys of $Nb_{16}Hf_{43}Ni_{41}$ and $Nb_{18}Hf_{42}Ni_{40}$. In short, the primary (Nb, Hf) phase does good to the hydrogen permeability, while the B_f-HfNi phase and the new HfNi phase do harm to the hydrogen permeability, especially the latter one. The new HfNi phase plays a worse role on the hydrogen permeability than that of the B_f-HfNi phase even with more primary (Nb, Hf) phase existing.

4. Conclusion

The influence of Hf/Ni ratio on the microstructures and hydrogen permeabilities of the Nb–Hf–Ni ternary alloys is studied in particular. With the increase in the Hf/Ni ratio from 41/43 to 43/41 or from 40/42 to 42/40, the quantity of the primary (Nb, Hf) phase increases and the new HfNi phase appears with white color, which has more Hf content of about 10–15 mol% than that of the B_f-HfNi phase. The Hf/Ni ratio can significantly affect the hydrogen permeability (Φ) and with the increase in the Hf/Ni ratio, the Φ value decreases except that of the alloys with the same content of Hf and Ni, i.e., the ratio of Hf/Ni equals 1. The new HfNi phase with more Hf content goes against the hydrogen permeability of the Nb–Hf–Ni ternary alloys.

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