Microstructures of Pd_{47.5}Ag_{47.5}La₅ Alloy Studied by Transmission Electron Microscopy

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Microstructures of Pd_{47.5}Ag_{47.5}La₅ alloy produced by three types of procedure methods, i.e., casting, rapid quenching and rolling, were examined by transmission electron microscopy (TEM). The Pd-Ag-La alloy in as-quenched and subsequent cold-rolled states has a finely mixed non-equilibrium structure consisting of a face-centered cubic (fcc) and LaNi₃-type phases and the structural feature is independent of the two procedure methods. The grain size and the volume fraction of the fcc phase are measured to be about 100 nm and 72%, respectively. The two phases dispersed homogeneously over the whole specimen. The Pd-Ag-La alloy with such a finely mixed structure is attractive for a hydrogen permeative material. [doi:10.2320/matertrans.MRA2008045]

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1. Introduction

Palladium alloy membranes show very high performances in terms of hydrogen permeability because of high solubility and diffusivity of hydrogen isotopes in their lattices.¹⁻³⁾ Embrittlement and subsequent delamination of palladium atoms for palladium thin films are a current problem with palladium membranes.^{4,5)} Pure palladium membranes cannot be used below 298°C due to the lattice expansion caused by dissolved hydrogen. This problem can be remedied by the addition of silver or other group 1b metals,⁴⁻⁸⁾ and their addition increases hydrogen flux.

Nanostructured materials often have some peculiar properties that cannot be obtained for conventional bulk materials, and elucidation of these properties has already led to breakthrough in various fields of science and technology. In hydrogen permeation, the flux of hydrogen can be greatly increased without compromising selectively by using thin membranes of a Pd-Ag alloy. The decrease of Pd-Ag film thickness plays a key role in the cost reduction both for decreasing the amount of precious metals and increasing the permeation flux. However, it is difficult to achieve fine structures without heavy working in the Pd-Ag system, because the Pd-Ag alloy system has a complete continuous solid solution in an equilibrium state.⁹⁾ McCool and Lin studied the effect of grain size on gas permeation properties in Pd-Ag membranes.¹⁰⁾ They have concluded that hydrogen permeation properties are very sensitive to grain sizes of the thin nano-crystallites in Pd-Ag membranes.

It has been reported that the hydrogen permeability is enhanced by alloying Pd metal with rare earth elements.^{11,12)} Recently, Zhang has investigated a ternary Pd-Ag-La alloy (Pd_{47.5}Ag_{47.5}La₅),¹³⁾ because the addition of both Ag and La is expected to result in the cost reduction by decreasing the amount of Pd and the remedy for the embrittlement of membranes. In addition, in order to obtain exceedingly fine microstructure, three types of procedure methods, i.e., casting, rapid quenching and rolling, were employed. It is expected

that structural variations lead to changes of properties. It is important for further progress of such a high-performance material to clarify the relations between properties and microstructures. In this study, we have employed TEM observations to elucidate the microstructures of Pd_{47.5}Ag_{47.5}La₅ samples obtained by different preparation methods.

2. Experimental

An alloy ingot with composition of Pd_{47.5}Ag_{47.5}La₅ was prepared by arc melting the mixture of pure Pd, Ag and La metals in an argon atmosphere. Subsequently, the ingot was remelted and then quenched rapidly by the single roller melt-spinning process to fabricate ribbon samples of about 28 μm in thickness. The ribbon sample was cold-rolled finally to 18 μm in thickness.

Crystalline phases were identified by means of X-ray and electron diffractions. Thin specimens for TEM observations were prepared by a conventional ion-milling method. Electron diffraction patterns and bright-field electron microscopy images were obtained using a 200 kV electron microscope (JEM-2000EXII). High-resolution images were taken upon JEOL JEM-2010 with a resolution of 0.19 nm, using an accelerating voltage of 200 kV.

3. Results and Discussion

X-ray diffraction patterns of the Pd-Ag-La samples are shown in Fig. 1; as-cast (a), rapidly solidified (b) and as-rapidly solidified and subsequently cold-rolled (c) states. The X-ray diffraction patterns show that a main phase in these three samples is a face-centered cubic (fcc)-type structure (indicated by solid circles in Fig. 1(a)). In the as-cast alloy (Fig. 1(a)), however, an extra peak is recognized as marked with an asterisk, indicating that the as-cast alloy includes a secondary phase. In the as-rapidly solidified alloy (Fig. 1(b)), a LaPd₅-type phase is clearly observed as indicated with arrows. In the rolled ribbon sample (Fig. 1(c)), an extra peak is seen, as indicated with an arrow, and also broadening of diffraction peaks can be seen.

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Fig. 1 X-ray diffraction patterns of $\text{Pd}_{47.5}\text{Ag}_{47.5}\text{La}_5$ alloys; (a) as-cast, (b) the rapidly solidified and (c) the rapidly solidified and subsequently rolled alloys.

Fig. 2 A bright-field TEM image from a part of the as-cast alloy and an electron diffraction pattern (inset) from a dark region indicated by a circle.

A bright-field (BF) TEM image of the as-cast alloy in Fig. 2 exhibits a heterogeneous microstructure showing the existence of the fcc-type primary phase and the second phase. The electron diffraction pattern of an inset in Fig. 2, taken from the second phase region with dark contrast shows long periodicity along one direction. The fcc-type phase regions with bright contrast have curved surfaces and no special habit plane is recognized. The sizes along the short and long directions are about 200 and 500 nm, respectively. In the TEM image, bright and dark contrast regions were deter-

Fig. 3 (a) electron diffraction pattern of the as-cast alloy, taken with the incident beam parallel to the $[110]$ direction of the LPS- LaPd_5 -type phase, and (b) schematic illustration of (a). Open and close squares in (b) present diffraction spots of twin-related variants, respectively. Shade circles in (b) indicate the reflection positions that reflections of the both variants are overlapped.

mined to have $\text{Pd}_{39.0}\text{Ag}_{60.6}\text{La}_{0.3}$ and $\text{Pd}_{57.8}\text{Ag}_{32.1}\text{La}_{10.0}$ compositions, respectively, by TEM-energy dispersive spectrometry (EDS). From the chemical compositions and X-ray/electron diffraction measurements, the bright and dark contrast regions correspond to fcc- and La-Pd polytype (e.g., LaPd_5 , hexagonal symmetry, space group: $P6/mmm$ (No. 191), lattice parameters: $a = 0.5300$ nm and $c = 0.4431$ nm¹⁴) phases, respectively, and La atoms are mostly dissolved in the La-Pd polytype phase.

The electron diffraction pattern (Fig. 3(a)), taken from the La-Pd polytype domain, does not indicate that the La-Pd polytype phase has a simple LaPd_5 -type one. For relatively strong reflection spots, which are indicated by arrowheads and indexed as 001 and $3\bar{3}0$ of the LaPd_5 structure, one can observe additional reflection spots with $00\frac{1}{2}$ and $1\bar{1}\frac{1}{6}$ indexes, indicated by large and small white arrows in Fig. 3(a). It is reasonably considered that the $1\bar{1}\frac{1}{6}$ type reflection spots result from twin-related two domains, as shown by parallelograms in Fig. 3(b).

It is well known that many polytype phases exist in La-Ni (-Mg) alloy system, as reported by Komura,¹⁵ Yamamoto *et al.*¹⁶ and Hayakawa *et al.*¹⁷ Figure 4 shows a schematic illustration of atomic arrangements of LaNi_3 (PuNi_3)¹⁸-type structure (a) together with a calculated electron diffraction pattern (b) of the phase. The LaNi_3 -type structure is formed by stacking of blocks, consisting of Laves (LaNi_2)- and LaNi_5 -type substructures, along the one direction, as can be

Fig. 4 (a) crystal structure of LaNi₃-type structure, which consists of stacked Laves- and LaNi₅-type substructures, and (b) calculated electron diffraction pattern. A shaded rectangle in (a) indicates unit cell of LaNi₃-type structure. Reflections in (b) are indexed by LaNi₅-type structure.

seen in Fig. 4(a). The calculated diffraction pattern of Fig. 4(b) shows that the observed pattern of Fig. 3 can be understood by twin-related two domains with different stacking directions of the Laves (LaNi₂)- and LaNi₅-type substructures for the LaNi₃-type structure. The long periodic stacking (LPS)-LaNi₃-type phase is different from a LaPd₃ phase with a cubic Cu₃Au-type structure¹⁹⁾ in the La-Pd phase diagram.⁹⁾ It may be therefore concluded that the

LPS-LaNi₃-type phase observed in the present study is a new one in a non-equilibrium state obtained through the rapid solidification process.

Figure 5 shows a TEM lattice image taken from an LPS-LaNi₃-type domain in the as-cast alloy, and an enlarged image in an inset. From an arrangement of bright dots in Fig. 5, one can see the stacking of the Laves (LaNi₂)- and LaNi₅-type substructures, as indicated with black lines, and a fine and disordered mixture of two stacking directions. Figures 6 show a BF TEM image and corresponding electron diffraction pattern of the rapidly solidified alloy. Fine mixture of randomly oriented fcc-type grains with an average size of about 100 nm and LPS grains along boundaries of the fcc-type grains is observed. The volume fraction of the fcc-type phase is estimated as about 72% on the basis of the BF image. Fine contrasts in the fcc-type grains, which can be seen in Fig. 6, are La precipitates with a size of about 5 nm. It is thus characterized that the rapidly solidified alloy consists of very fine mixed phases. Furthermore, the electron diffractions reveal that the fine grains of the fcc-type phase are oriented randomly. The fine phase is an fcc-type one in the rapid solidified alloy, as similarly observed in the as-cast alloy. The fcc-type phase has granular morphology and its grain size is estimated as about 100 nm.

A number of fine precipitates are observed in the fcc-type grains, as can be clearly seen in an enlarged bright-field image of Fig. 7. The precipitates indicated by arrowheads

Fig. 5 A lattice image of the LaNi₃-type phase in the as-cast alloy, and enlarged one in inset. Arrowheads indicate twin boundaries.

Fig. 6 A bright-field TEM image the rapidly solidified alloy and the corresponding electron diffraction pattern in inset. The electron diffraction pattern was taken from the area of about 1 μm in the diameter.

Fig. 8 A bright-field TEM image of the cold-rolled ribbon alloy and a corresponding electron diffraction pattern. The electron diffraction pattern was taken from the area of about 1 μm in the diameter.

Fig. 7 An enlarged bright-field image of Fig. 6. Arrowheads indicate La precipitates.

are composed of La phase with an approximate size of 5 nm. The La precipitates do not exist in the region close to phase boundaries and lie in inner region of the fcc-type grains. This microstructure suggests that during solidification, La atoms close to the grain boundaries have diffused to the outside of the fcc-type phase so as to form the LPS phase, while La atoms left in the inner region of the fcc-type grains have cohered as La precipitates.

Figure 8 shows a BF image of the cold-rolled ribbon sample. Although the grain size of the fcc-type phase remains almost unchanged even after the cold rolling treatment, the fcc-type phase is significantly deformed, compared to the rapidly solidified alloy.

To summarize the features of their microstructures, Fig. 9 shows schematic illustrations of microstructural features for the $\text{Pd}_{47.5}\text{Ag}_{47.5}\text{La}_5$ alloy; (a) the as-cast, (b) the rapidly solidified and (c) the cold-rolled states. One can recognize that the size and outer shape of the fcc phase are significantly dependent on the procedure methods, though the fcc phase has the similar curved interface without distinct difference in all the three states.

Fig. 9 Schematic illustrations of microstructures for $\text{Pd}_{47.5}\text{Ag}_{47.5}\text{La}_5$ alloys; (a) the as-cast, (b) the rapidly solidified and (c) the cold-rolled ribbon alloys. Black small ovals indicate La precipitates.

4. Conclusion

We prepared the rapidly solidified ribbon alloy of Pd_{47.5}Ag_{47.5}La₅ with a thickness of 30 μm. From TEM observations, the rapidly solidified alloy consisted of a non-equilibrium mixture of fcc- and long periodic stacked LaNi₃-type phases. The fcc phase has a small grain size of about 100 nm and includes very fine precipitates of La phase. Because of the finely mixed microstructure of the thin ribbon alloy, the rapidly solidified Pd-Ag-La alloy ribbon is expected to be a candidate for good hydrogen permeator.

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