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Short Communication

Microstructure dependent hydrogen permeability in eutectic $Nb_{30}Ti_{35}Co_{35}$

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ABSTRACT

$Nb_{30}Ti_{35}Co_{35}$ eutectic composites with various structure patterns were produced by directional solidification (DS), rolling and annealing. The relationship between structure and hydrogen permeability is investigated and discussed on the basis of the mixing rule. The measured hydrogen permeability of the parallel-type structure with the two eutectic phases aligned in parallel to the hydrogen permeation direction (generated by DS) is significantly higher than those measured for the other structure types. In contrast, a series-type structure with the two phases aligned perpendicular to the hydrogen permeation direction (generated by rolling) induces the lowest permeability. The variation of hydrogen permeability with different structure patterns is quantitatively explained by the mixing rule.

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Introduction

Pd-based alloys, in particular Pd–Ag alloys, are commercially used as hydrogen permeation membranes for separation and purification of hydrogen gas produced by steam reforming of natural gas [1–3]. However, due to the scarcity and high cost of Pd it is desirable to develop low cost membrane materials with comparable hydrogen permeation properties, but containing either less Pd or preferably no Pd at all. Group V metals, such as V, Nb and Ta, are promising substitutions for Pd-based membranes considering their high hydrogen permeability and relatively lower cost. In their pure form, these metals are prone to hydrogen embrittlement, which is connected with their excessive hydrogen absorption. Hence, various V- [4–6], Nb- [7,8] and Ta-based [9] solid solution alloys have been designed, based on the concept that additional elements improve the resistance to hydrogen embrittlement by the reduction of

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hydrogen solubility. Meanwhile, multiphase membrane materials, such as Nb–Ti–Ni [10,11], Nb–Ti–Co [12], V–Ti–Ni [13,14], Ta–Ti–Ni [15], among others, are also drawing wide attention. These alloys are generally characterized either by the coexistence of a primary bcc-Nb/V/Ta phase and a surrounding binary eutectic structure (bcc-Nb/V/Ta + B2–TiNi/TiCo), or by a fully eutectic structure. The bcc-Nb/V/Ta phase is mainly responsible for the hydrogen permeability, and the B2 phase in the eutectic and the eutectic structure itself impart resistance against hydrogen embrittlement [16–18]. Consequently, such alloys are promising to achieve a sound combination of high hydrogen permeability and excellent embrittlement resistance via a pertinent microstructure.

It is evident that the microstructure strongly affects the hydrogen permeation performance. Correspondingly, the microstructural parameters should be controlled, such as the distribution, volume fraction, chemical composition, etc. of the constituting phases. These parameters can change drastically upon variation of the initial alloy composition and the alloy processing conditions. Thus, a quantitative description correlating microstructure and hydrogen permeability is expected to guide the development of high performance hydrogen permeable alloys. Ishikawa and co-authors [19] first built a relationship between two-phase composite structures and hydrogen permeability on the basis of the mixing rule using effective medium theory [20]. Five types of representative structures and the hydrogen permeability equations are tabulated in Table 1. It has been found that the mixing rule is effective to predict the hydrogen permeability of as-cast Nb–TiNi alloys [19] which are considered as a composite of primary phase bcc-(Nb,Ti) and eutectic {bcc-(Nb, Ti) + B2–TiNi}. Although two phases are involved in the eutectic part, the eutectic structure was assumed as a single "phase" and its hydrogen permeability is approximated as a constant in the mixing rule. This is only appropriate for the eutectic when it exhibits a rather low permeability compared with primary bcc phase, as that in Nb–Ti–Ni alloys [10]. However, when it comes to Nb–Ti–Co alloys, the constant approximation for the permeability of the eutectic in the mixing rule induced large deviations between prediction and experimental results [21]. Further refinement is thus necessary to enhance the effectiveness of the mixing rule for various multiphase alloy systems. This in turn requires to elucidate the relationship between different types of fully eutectic structures and the resulting hydrogen permeability.

In the present work, a eutectic $Nb_{30}Ti_{35}Co_{35}$ (all compositions in atomic percent) alloy is chosen as a prototype to investigate the microstructure dependent hydrogen permeability. Various types of two-phase structures are produced by directional solidification (DS), rolling and annealing. These structures are introduced and treated with the aid of the mixing rule. Thus, the structure/hydrogen permeability relationship is discussed on the basis of the mixing rule. Different hydrogen permeability values are theoretically predicted and experimentally confirmed for different types of two-phase structures.

Experimental

Ingots of about 40 g of $Nb_{30}Ti_{35}Co_{35}$ were prepared by arc melting in a purified Ar atmosphere using Nb, Ti and Co (99.99 mass% purity for all) which is termed as "as-cast" in the present work. The as-cast $Nb_{40}Ti_{30}Co_{30}$ ingots were then hot-rolled to about 1 mm thickness at 1073 K. The hot-rolled samples are termed as "as-rolled". Parts of the rolled sheet were then annealed at 1273 K for one week under Ar atmosphere, which is termed as "rolled-annealed" in the following.

Directionally solidified (DS) $Nb_{30}Ti_{35}Co_{35}$ ingots, 15 mm in diameter and 120 mm in length, were prepared in a Bridgman-type furnace at a growth rate of 0.5 μm/s. More details of the DS experimental procedure can be found in Refs. [22,23]. Disks, 12 mm in diameter and 0.6 mm in thickness, were cut from the as-cast, as-rolled, rolled-annealed and DS ingots by a spark erosion wire-cutting machine. The disks from the DS ingots were sliced both perpendicular to and parallel to the growth direction, which generates parallel- and series-type structures (see Table 1), respectively. Table 2 shows the information of all the samples in the present work. Additionally, as-cast $Nb_4Ti_{47}Co_{49}$ and $Nb_{90}Ti_8Co_2$ ingots were also prepared by arc melting, which represents B2–TiCo and bcc-(Nb, Ti) respectively.

Microstructural and crystallographic analyses were carried out in a scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (EDX) and X-ray diffractometry (XRD), respectively. The volume fraction of the constituent phases was analyzed using image J from SEM data. Both sides of the disks were ground, polished and then coated with 190 nm of Pd by a radio frequency (RF) sputtering device to prevent oxidation during the hydrogen permeation/absorption tests and to act as catalyzer for hydrogen uptake into the material. The disks were sealed with copper gaskets and set into a hydrogen permeation measurement apparatus (cf. Ref. [10,11]). The hydrogen flux, J, passing through the disks was measured by a hydrogen flow meter at 673 K, 623 K, 573 K and 523 K, respectively. The pressure-composition-temperature (PCT) curves were measured using a Sieverts-type apparatus at 673 K in a pressure range from 0.01 to 0.9 MPa (cf. Ref. [17,18,23]). The amount of absorbed hydrogen was calculated from the pressure drop in a constant inner volume chamber.

Results and discussion

Microstructures

In Fig. 1, the microstructures of the as-cast, as-rolled and rolled-annealed $Nb_{30}Ti_{35}Co_{35}$ samples are shown. A fully lamellar cellular eutectic structure with varying orientation of the lamellae is observed in as-cast $Nb_{30}Ti_{35}Co_{35}$, Fig. 1(a). XRD patterns in combination with EDX identify the dark phase as B2–TiCo and the white phase as bcc-(Nb, Ti). The equilibrium chemical compositions of the TiCo and (Nb, Ti) phases are $Nb_4Ti_{47}Co_{49}$ and $Nb_{90}Ti_8Co_2$, respectively. The fully lamellar structure is still maintained in the as-rolled $Nb_{30}Ti_{35}Co_{35}$, but the lamellar boundaries are drastically extended in the rolling direction, Fig. 1(b). After a subsequent annealing of the rolled $Nb_{30}Ti_{35}Co_{35}$ at 1273 K for one week, the lamellar structure is replaced by a duplex structure consisting of white granular bcc-(Nb, Ti) in a contiguous black B2–TiCo matrix, Fig. 1(c). Such a change in eutectic structure during annealing is

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