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Grain Boundary Wetting by a Second Solid Phase in the Zr-Nb Alloys

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Zr-Nb alloys play the important role in the energy production being the main material for the cladding of nuclear fuel in the nuclear power plants. The thermo-mechanical treatment of these alloys proceeds in the (αZr) + (βZr, Nb) two-phase area of the Zr-Nb phase diagram. Therefore, the morphology and the mutual arrangement of the (Zr) and (Nb) phases play an extremely important role. The microstructure of binary Zr-Nb alloys with 2.5, 4, and 8 wt.% Nb after long anneals (720 h) was studied between 660 and 810 °C in the two-phase (αZr) + (βZr, Nb) area of the Zr-Nb phase diagram. (βZr, Nb)/(βZr, Nb) grain boundaries (GBs) completely or incompletely wetted by the αZr phase were observed. The portion of the completely wetted (βZr, Nb)/(βZr, Nb) GBs increases from 10% (at 660 °C) to 60% close to the upper border of the (αZr) + (βZr, Nb) two-phase area of the Zr-Nb phase diagram (850 °C). The temperature of the beginning of the GB wetting phase transition of (βZr, Nb)/(βZr, Nb) GBs by the αZr phase is $T_{ws} = 630 \pm 10$ °C. The αZr/αZr GBs completely wetted by a layer of (βZr, Nb) phase were not observed in the studied samples.

Keywords cladding of nuclear fuel, grain boundaries, wetting, Zr-Nb alloys

1. Introduction

Zr-Nb alloys play an important role in the energy production being the main material for the cladding of nuclear fuel in the nuclear power plants (Ref 1). Most common are the Zr-2.5wt.% Nb alloys. Frequently the Zr-2.5wt.% Nb alloy is additionally doped by Fe, Sn, Cr, Cu alone or in various combinations (Ref 2, 3). The parts of Zr-Nb alloys are usually produced by the mechanical extrusion in the in the (αZr) + (βZr, Nb) two-phase area of the Zr-Nb phase diagram (Ref 4). The mechanical properties of an alloy during the deformation are critically dependent on the morphology and mutual arrangement of the (Zr) and (Nb) phases, as well as the degradation processes of these materials during their life-time (like formation of hydrides due to the hydrogen diffusion, corrosion, and creep (Ref 4, 5)).

In turn, the morphology of the interpenetrating polycrystalline phases can be governed by the so-called grain boundary (GB) wetting phase transformations. For the liquid droplet on a solid substrate two situations are possible. If a liquid spreads on the surface, one can speak about full (or complete) wetting. The contact angle between liquid and solid in this case is zero. If a liquid droplet does not spread and forms a finite contact angle, it is a partial (or incomplete) wetting. Cahn (Ref 6) and Ebner and Saam (Ref 7) first assumed that the (reversible) transition from incomplete to complete wetting can proceed with increasing temperature, and it is a true surface phase transformation. The recent review of the works on the wetting phase transitions can be found in Ref 8.

The transition from incomplete to the complete wetting can also be observed within the GBs if the energy of two solid-liquid interfaces 2 σ_{SL} reduces to lower than the GB energy $\sigma_{GB} > 2\sigma_{SL}$. Cahn's idea (Ref 6) was the "driving force" for the experimental finding of GB wetting phase transformations, initially made in Zn-Sn, Zn-Sn-Pb, and Ag-Pb polycrystals (Ref 9, 10 and references therein). At a later state the original experimental data were reconsidered from this point-of-view, and numerous indications on the GB wetting phase transformations were found, particularly for Zn-Sn, Al-Cd, Al-In, Al-Pb (Ref 9 and references therein) and W-Ni, W-Cu, W-Fe, Mo-Ni, Mo-Cu, Mo-Fe (Ref 10, 11 and references therein) polycrystals. The exact measurements of the temperature dependence for the GB contact angle with the melt were made using the individual GBs in the specially grown bicrystals in the Cu-In, Cu-Bi, Al-Sn, Zn-Sn, Al-Zn, Sn-Bi, In-Sn, Zn-Sn, and Zn-In systems (Ref 12-16 and references therein). The GB

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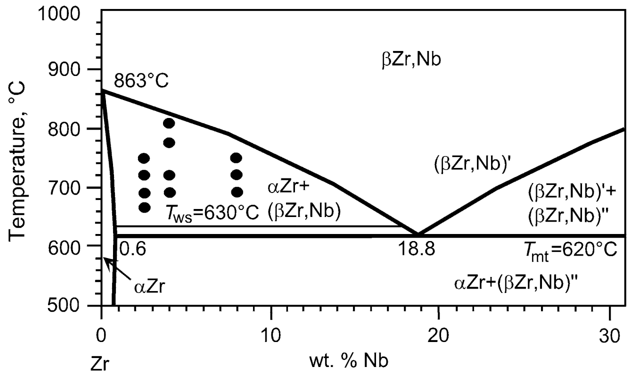

Fig. 1 Part of the Zr-Nb phase diagram. Thick lines denote the bulk phase transitions and are taken from Ref 22. Circles denote the points where the Zr-Nb alloys were annealed. Thin line at T_{ws} = 630 °C denote the tie-line of the start of the GB wetting phase transition of (βZr, Nb)/(βZr, Nb) GBs by the second solid phase (αZr)

can also be wetted not by liquid, but by a solid phase like in the Zn-Al (Ref 17), Al-Zn (Ref 11), Al-Mg (Ref 18), and Co-Cu (Ref 19) alloys or even by an amorphous phase (Ref 20, 21). From the point of view of Cahn's generic phase diagram (Ref 6), the Zr-Nb is quite "suspicious." In other words, it can be expected that the GB wetting by a second solid phase can proceed in the (αZr) + (βZr, Nb) two-phase area of the Zr-Nb phase diagram. To check this possibility is the goal of our work.

2. Experimental

The Zr-Nb alloys with 2.5, 4, and 8 wt.% Nb were investigated. The alloys were prepared of high-purity components (4N Zr and 4N Nb) by the vacuum induction melting. The 2 mm thick slices were also cut from the ∅ 15 mm cylindrical ingots, then divided into four parts and sealed into evacuated silica ampoules with a residual pressure of approximately 4×10^{-4} Pa at room temperature. Samples were annealed at temperatures 660, 690, 720, 750, 780, and 810 °C for 720 h, and then quenched in water. The accuracy of the annealing temperature was ±2 °C. The annealing points were in the two-phase (αZr) + (βZr, Nb) area of the Zr-Nb phase diagram (Fig. 1) (Ref 22). After quenching, samples were embedded in resin and then mechanically ground and polished, using 1 μm diamond paste in the last polishing step, for the metallographic study. After etching, samples were investigated by means of the optical microscopy and by scanning electron microscopy (SEM). SEM investigations have been carried out in a Tescan Vega TS5130 MM microscope equipped with the LINK energy-dispersive spectrometer produced by Oxford Instruments. Light microscopy has been performed using a Neophot-32 light microscope equipped with a 10 Mpix Canon Digital Rebel XT camera. A quantitative analysis of the wetting transition was performed adopting the following criterion: every (βZr, Nb)/(βZr, Nb) GB was considered to be completely wetted only when a layer of αZr-rich film had covered the whole GB (Fig. 2c); if such a layer appeared to be interrupted, then the GB was regarded as incompletely (Fig. 2a, b) wetted. At least 100 GBs were analyzed at each temperature. Typical micrographs obtained by SEM are shown in Fig. 2. In the as-cast alloys, the (βZr, Nb)/(βZr, Nb) GB did not contain neither chains of the αZr particles nor the continuous αZr layers. They formed during the annealing by the bulk and GB diffusion. The Zr-depleted zone along the (βZr, Nb)/(βZr, Nb) GB is clearly visible, for example, in Fig. 2(b). The formation of GB chains or continuous αZr layers proceeds mainly in the first 200-300 h. Afterwards the amount of completely and incompletely wetted GBs did not change much. Therefore, we chosen the annealing duration of 720 h to measure the equilibrium portion of completely and incompletely wetted (βZr, Nb)/(βZr, Nb) GBs.

3. Results and Discussion

SEM micrographs of the Zr-4wt.% Nb and Zr-8wt.% Nb alloys annealed at 660, 690, and 720 °C are shown in Fig. 2. The (βZr, Nb) grains (matrix) appear light gray. The αZr phase between (βZr, Nb) grains appear dark gray. In Fig. 2(a) and (b) both completely and incompletely wetted (βZr, Nb)/(βZr, Nb) GBs are visible. The elongated areas of the αZr phase form chains along the incompletely wetted (βZr, Nb)/(βZr, Nb) GBs (Fig. 2a, b). The majority of (βZr, Nb)/(βZr, Nb) GBs are completely wetted by the αZr phase. In this case, the αZr phase forms the continuous layer separating the (βZr, Nb) grains. A triple joint of the (βZr, Nb)/(βZr, Nb) GBs completely wetted by the αZr phase is shown in Fig. 2(c). Therefore, the complete wetting of (βZr, Nb)/(βZr, Nb) GBs by the αZr phase exists in the αZr + (βZr, Nb) two-phase region of the Zr-Nb bulk phase diagram. This phenomenon can be observed even on the "microscopic" scale, like in Zn-Al (Ref 17), Al-Zn (Ref 11), Al-Mg (Ref 18), and Co-Cu (Ref 19) systems where we observed the GB wetting by a second solid phase earlier. However, like in the case of the GB wetting by a liquid phase (melt) (Ref 11, 15, 16 and references therein), one can expect also the existence of the nanometric thin GB films of a second wetting phase. The complete GB wetting on the "microscopic" scale is the necessary condition for the existence of nanometric thin GB films. Such GB nanolayers appear in two cases: (1) if the grain size is small and the amount of second wetting phase is low and not sufficient to form the "thick" GB layers (like it has been observed in Cu-Bi or ZnO-Mn_3O_4 systems (Ref 16, 20)); (2) in the one-phase solid solution area of a phase diagram between bulk solidus and GB solidus lines (like it has been observed in Cu-Bi or Al-Zn systems, Ref 11, 15, 16 and references therein). Possible presence of such nanometric thin GB films in the Zr-Nb system will be studied in the future.

In Fig. 3, the temperature dependence for the fraction of (βZr, Nb)/(βZr, Nb) GBs completely wetted by the αZr phase is shown. The amount of completely wetted GBs increases form 10% (660 °C, Zr-8wt.% Nb) to about 60% (810 °C, Zr-2.5wt.% Nb). The extrapolation of the solid line towards 0% at lower temperature shows that slightly above the monotectoid temperature $T_{mt} = 620 \pm 10$ °C (Ref 22) the portion of completely wetted (βZr, Nb)/(βZr, Nb) GBs reaches zero. It means that the starting temperature of the GB wetting phase transition of (βZr, Nb)/(βZr, Nb) GBs by αZr can be estimated as $T_{ws} = 630 \pm 10$ °C. Therefore, the finishing temperature of this GB wetting phase transition cannot be estimated, since only about a half of (βZr, Nb)/(βZr, Nb) GBs are completely wetted by αZr at the upper border of the (αZr + βZr, Nb) two-phase area of the Zr-Nb phase diagram. The αZr/αZr GBs completely wetted by a layer of (βZr, Nb) phase were not observed in the studied samples.

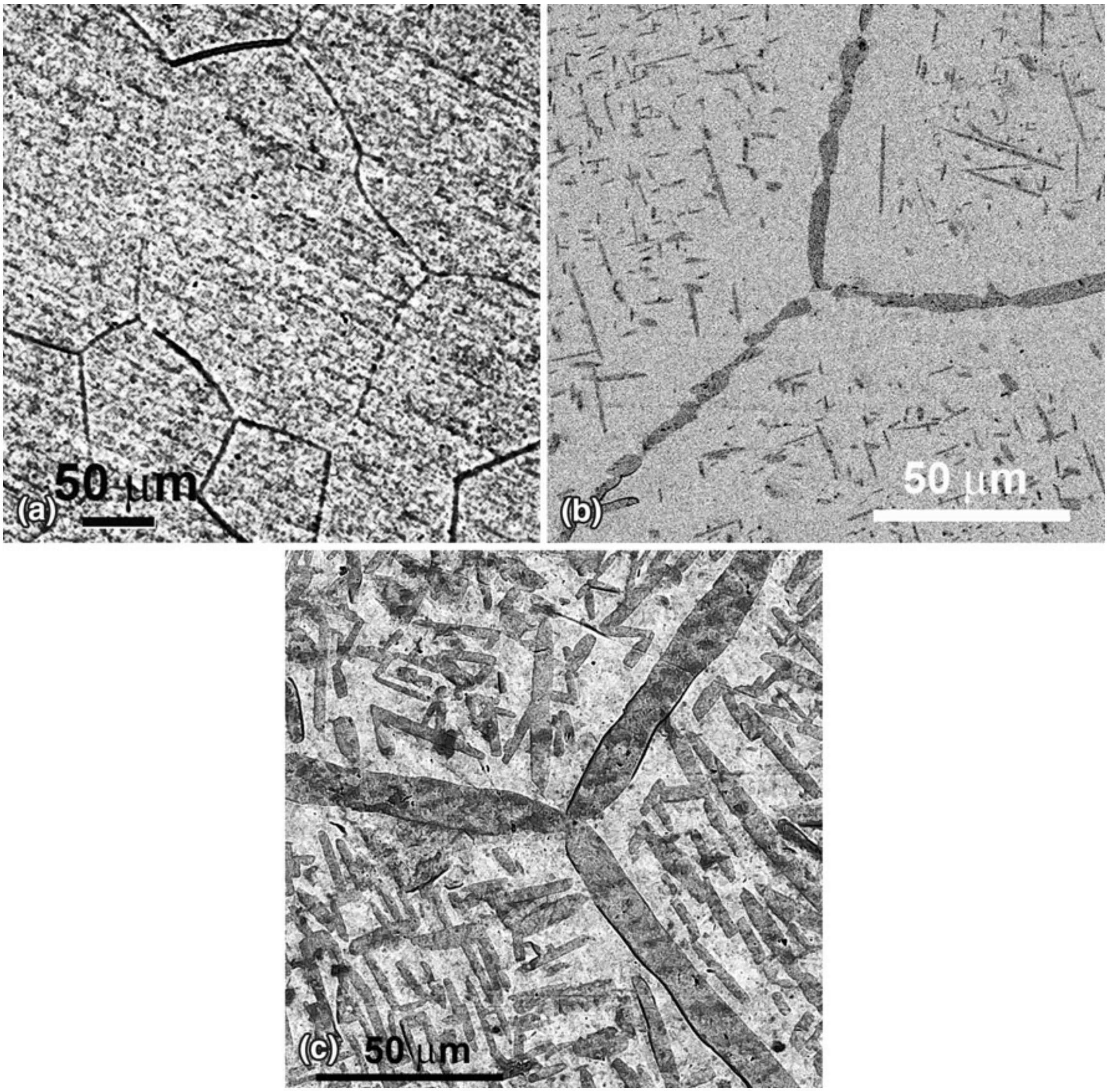

Fig. 2 SEM micrographs of the Zr-Nb alloys. (a) Zr-8wt.% Nb annealed at 660 °C, (b) Zr-8wt.% Nb annealed at 690 °C, (c) Zr-4wt.% Nb annealed at 720 °C. The (βZr, Nb) grains (matrix) appear light gray. The αZr phase between (βZr, Nb) grains appear dark gray

At each temperature above T_{ws} both completely and incompletely wetted GBs exist. Most probably this difference is due to the scatter of specific enthalpy (excess energy for the unit area) of different (βZr, Nb)/(βZr, Nb) GBs. For example, we observed earlier that the GBs with low energy (like twin GBs) cannot be completely wetted by a second solid phase and contain only the chains of the solid particles instead of continuous layers of a second solid phase (Ref 17). The increase of the amount of completely wetted GBs with increasing temperature can be explained by the fact that GBs with different energies have also different temperatures of wetting transition T_w. For example, GBs with higher energy possess the lower T_w (Ref 12, 13). The relative quantity of a second phase can in principle influence the amount of completely wetted GBs. However, the experimental points in Fig. 3 for three different alloys do not scatter much around the obtained straight line. It means that in the studied concentration and temperature interval the influence of the relative quantity of a second phase is low. At least it does not change much the estimated value of T_{ws}.

4. Conclusions

1. In the (αZr + βZr, Nb) two-phase field of the Zr-Nb phase diagram the αZr phase can either completely or incompletely wet the (βZr, Nb)/(βZr, Nb) GBs.
2. The portion of the completely wetted (βZr, Nb)/(βZr, Nb) GBs increases from 10% (at 660 °C) to 60% close to the upper border of the (αZr + βZr, Nb) two-phase area of the Zr-Nb phase diagram (850 °C). The temperature of the beginning of the GB wetting phase transition of (βZr, Nb)/(βZr, Nb) GBs by the αZr phase can be estimated as $T_{ws} = 630 \pm 10$ °C.
3. The αZr/αZr GBs completely wetted by a layer of (βZr, Nb) phase were not observed in the studied samples.

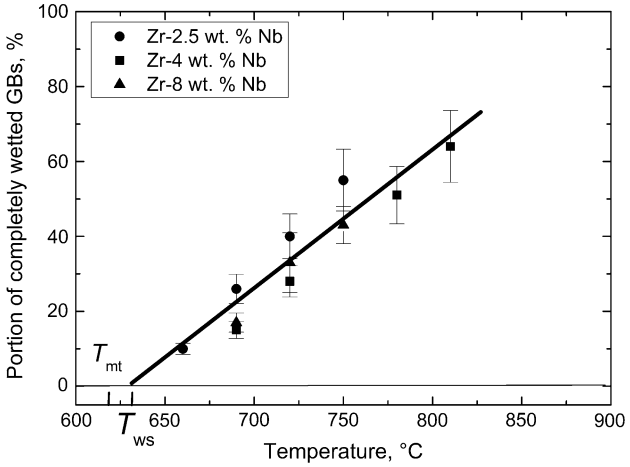

Fig. 3 Temperature dependence for the fraction of (βZr, Nb)/(βZr, Nb) GBs completely wetted by the αZr phase. Circles denote the Zr-2.5wt.% Nb alloy, squares denote the Zr-4wt.% Nb alloy, triangles denote the Zr-8wt.% Nb alloy. T_{ws} = 630 °C is the temperature of the start of the GB wetting phase transition of (βZr, Nb)/(βZr, Nb) GBs by the second solid phase (αZr). The temperature $T_{mt} = 620 \pm 10$ °C (Ref 22) of monotectoid transformation is also shown

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