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Solid-Phase Wetting at Grain Boundaries in the Zr–Nb System

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Abstract—The microstructure of Zr–Nb polycrystalline alloys with niobium concentrations of 1, 2.5, 4, and 8 wt % is investigated in the temperature interval of 620–840°C. It is revealed that the second solid phase β-Nb forms either a chain of separate lens-like precipitates or continuous homogeneous layers at grain boundaries in zirconium, depending on the annealing temperature and the energy of the Zr/Zr grain boundary. It is shown that the greater the quantity of the second solid phase, the lower at which the temperature of the termination of grain-boundary wetting appears. A model is constructed that explains the dependence of the temperature of grain boundary wetting on the amount of wetting phase. It is found that the complete wetting of all grain boundaries in zirconium by the second solid phase does not occur in Zr–Nb alloys.

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INTRODUCTION

Zirconium–niobium alloys are widely used in building modern nuclear reactors. Their behavior upon thermomechanical treatment and the subsequent change in their properties during use (corrosion, hydride embrittlement) depend on the morphology of the α-Zr and β-Zr (β-Nb) phases. To achieve the optimum efficiency of reactor materials, we must therefore know the appropriate phase diagrams and feratures of phase transitions, both for bulk diagrams and transformations and for grain boundary transitions. It has recently been discovered that so-called grain boundary wetting phase transitions can occur in a wide variety of systems. When the temperature is higher than that of the grain boundary wetting phase transition, equilibrium layers of a second phase (a melt or a second solid phase) can form, separating the grains of the first phase from one another. Such grain boundary phase transitions strongly alter both the microstructure and the properties of two-phase materials. The creation of thermodynamically balanced layers of the second phase at a temperature above that of the grain boundary wetting phase transition changes the mechanical properties of the material (and can lead to both superplasticity and embrittlement of the material). It affects the corrosion stability, diffusion permeability; the recrystallization and growth of grains; the electric resistance of the material; and so on. The recently discovered grain boundary phase transitions of wetting by the second solid phase are especially important in this respect. In particular, they occur in such technologically important systems as iron–carbon, aluminum–zinc, aluminum–magnesium, etc.

Zirconium-based alloys are widely used in nuclear technology for the manufacturing of fuel claddings [1]. Zr–2.5 wt % Nb alloys are the ones used most widely for these purposes. These alloys are also used in combination with other alloying constituents, e.g., iron [2, 3], tin [4], chrome [5, 6], and copper [7]. These elements can be also used in different combinations with one another [8, 9]. Articles are manufactured from zirconium–niobium alloys mainly by means of mechanical extrusion in the two-phase region, where two solid phases of α-Zr and β-Zr (β-Nb) are at equilibrium [10]. The mechanical properties of the material upon deformation depend strongly on its structure and on the morphology of its constituent phases. The properties of zirconium–niobium alloys during their use are determined by degradation processes: (a) hydride creation in the material bulk [11] due to hydrogen diffusion through a protective layer of oxides [10]; (b) corrosion; and (c) creep [13]. All of these degradation processes are also determined by the morphology of the phases found in the material.

A fundamentally new phenomenon has recently been discovered: phase transitions of the wetting of grain boundaries by layers of the second solid phase [14, 15]. This implies that the second solid phase in the two-phase regions of phase diagrams can be located at grain boundaries of the initial phase, both in the form of equilibrium thin or thick layers and as separate lens-like particles. The second-phase morphology is determined by the ratio of the energies of the grain boundaries and the interphase borders, and can depend on both temperature and pressure, or on the concentration of alloying constituents.

Fundamental data on the arrangement of lines of such grain boundary transitions on traditional bulk phase diagrams can be used for application purposes in order to deliberately alter the properties of two-phase materials. For example, data on the grain boundary phase transitions of wetting by the second solid phase

are now being used to improve the technologies for producing mild ferrite-pearlitic steels for pipelines and hypereutectoid steels with high carbon content.

The first clear evidence that wetting-by-solid-phase grain boundary phase transitions or envelopment actually exists was obtained quite recently [14, 16]. It was shown in direct experiments on Zn–5 wt % Al polycrystals that below a certain temperature T_{WS}, the solid phase (Al) at the zinc grain boundaries takes the form of individual isolated particles [14, 16]. At temperatures above T_{WS}, Zn/Zn grain boundaries appear in the polycrystal, on which the phase (Al) takes the form of a continuous layer. The fraction of such boundaries in the Zn/Zn polycrystal increases continuously as the temperature grows. The wetting-by-solid-phase grain boundary phase transition is reversible. If samples that have already been annealed at a temperature below T_{WS} are annealed once more at a temperature above T_{WS}, the individual particles (Al) at the grain boundaries merge rapidly with each other, creating a continuous layer. In contrast, if samples that have already been annealed at a temperature above T_{ws} are annealed once more at a temperature below T_{WS}, the continuous layer (Al) at the boundaries disperses into individual particles. A similar grain boundary phase transition from incomplete wetting by a solid phase to complete wetting has been also observed in systems of aluminum–magnesium [17, 18] and cobalt–copper [19].

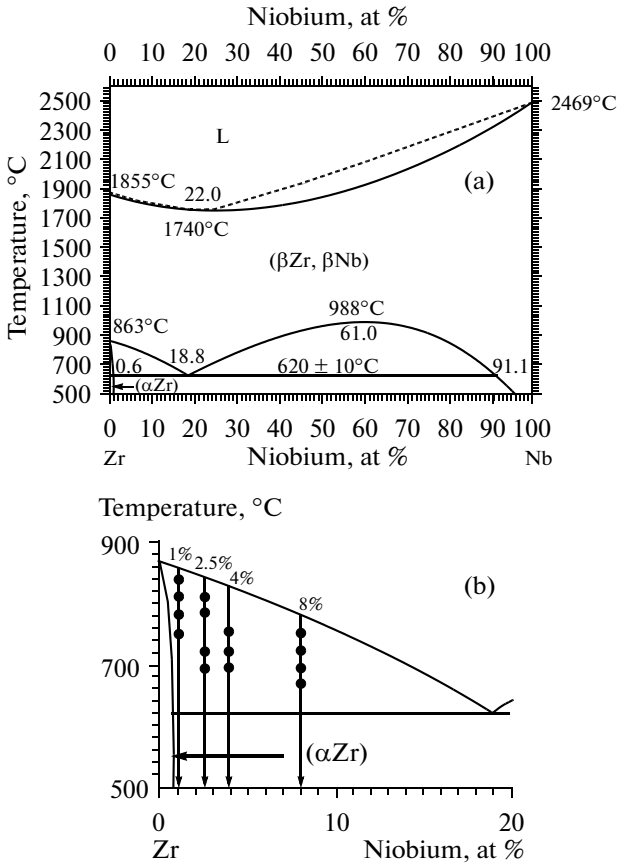

Fig. 1. (a) Zr–Nb bulk phase diagram and (b) portion of the Zr–Nb phase diagram with dark circles corresponding to the annealing temperatures.

EXPERIMENTAL

For our microstructure investigations, Zr–1 wt % Nb, Zr–2.5 wt % Nb, Zr–4 wt % Nb, and Zr–8 wt % Nb alloys were prepared by means of induction melting. Flat rings 5 mm thick were cut from the manufactured rods. The polycrystalline samples were then sealed in quartz ampoules (residual pressure $P = 4 \times 10^{-4}$ Pa) and annealed in the two-phase region of the Zr–Nb bulk phase diagram, (annealing time, 720 h). Figure 1a shows the Zr–Nb bulk phase diagram, while Fig. 1b shows part of the Zr–Nb phase diagram in which the annealing temperatures of the investigated samples are marked with dark circles. After hardening in water, the microstructure of the polycrystalline samples was examined using optical and scanning electron microscopes (the Oxford Instruments Tescan Vega TS5130 MM scanning microscope, which enabled us to perform a phase analysis, and the Neophot-32 optical microscope equipped with a Canon 10 Mpix Digital Rebel XT camera).

RESULTS AND DISCUSSION

Figure 2 presents optical microphotographs of Zr–1 wt % Nb alloy for four annealing temperatures: 750, 780, 810, and 840°C. It can be seen that the fraction of wetted grain boundaries increases as the annealing temperature grows. The fractions of the fully wetted grain boundaries were calculated using the series of microphotographs taken for each annealing temperature. The grain boundaries were assumed to be fully wetted if the second-phase layer ran along them continuously from one triple boundary joint to another.

The results from our calculations are displayed in Fig. 3, where T_{ES} is the temperature of eutectoid transition. For all of the investigated alloys (Zr–1 wt % Nb, Zr–2.5 wt % Nb, Zr–4 wt % Nb, and Zr–8 wt % Nb), the temperatures T_{WS0} = 770, 660, 655, and 635°C, respectively, (where T_{WS0} is the temperature at which the fraction of fully wetted grain boundaries in the alloy is zero) were found by extrapolation. It was thus shown that the grain boundary phase transition of Zr/Zr boundary wetting by the second solid phase (Nb) occurs in this system.

We also observed that the dependences for Zr–1 wt % Nb, Zr–2.5 wt % Nb, Zr–4 wt % Nb, and Zr–8 wt % Nb are displaced to the region of lower temperatures as the fraction of the second component

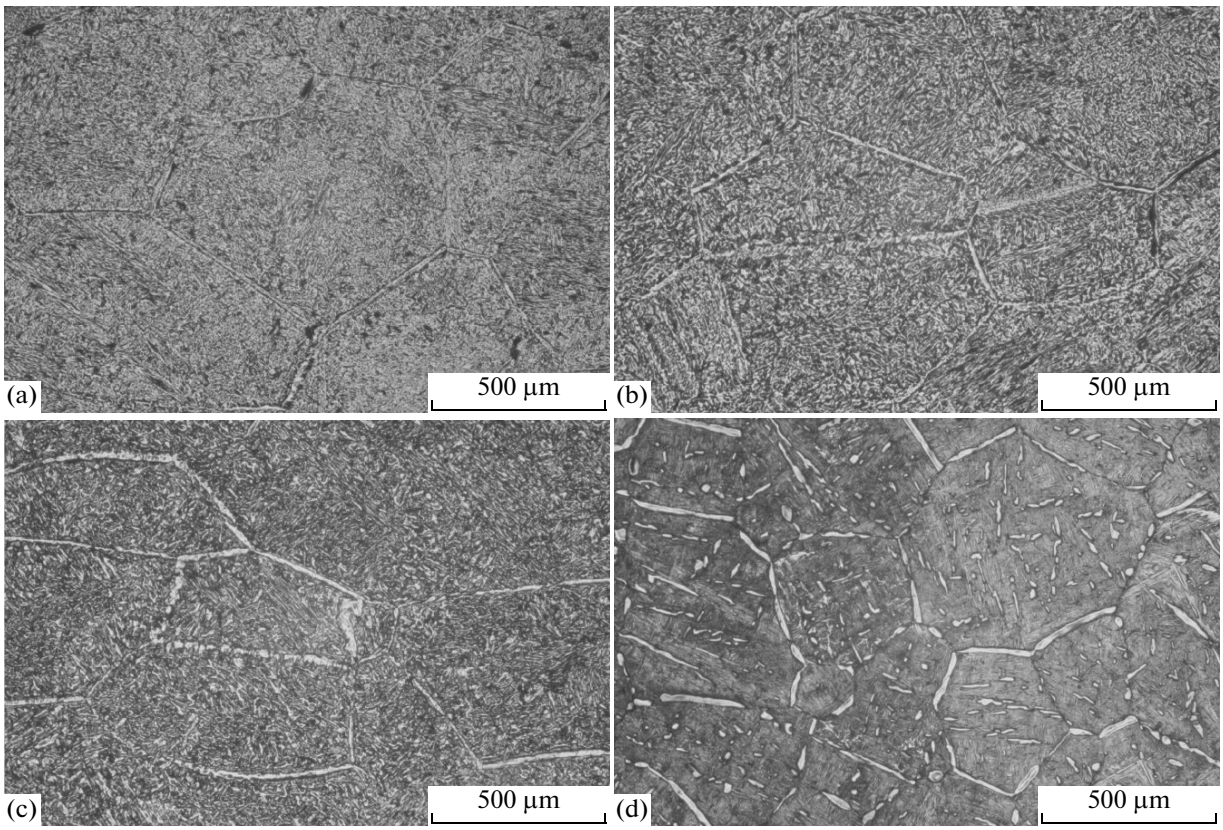

Fig. 2. Optical microphotographs of Zr 1 wt % Nb polycrystalline samples annealed at temperatures of (a) 750°C, (b) 780°C, (c) 810°C, and (d) 840°C, with annealing times of 624, 573, 271, and 668 h, respectively.

increases. Consequently, the greater the amount of the second component, the lower the temperature of the transition from the incomplete wetting of Zr/Zr boundaries by the second solid phase (Nb) to their full wetting. It thus turns out that a change in Nb concentration at the same annealing temperature affects the energy of Zr/Zr grain boundaries, which is impossible.

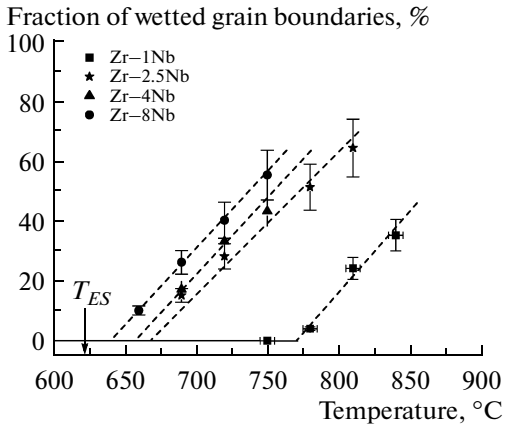

Fig. 3. Temperature dependence of the fraction of wetted grain boundaries for Zr 1 wt % Nb; Zr 2.5 wt % Nb; Zr 4 wt % Nb; and Zr 8 wt % Nb alloys.

At the same time, it is known that if the component concentrations in the two-phase region change, the quantitative ratio of phases is affected. The number of phases in the two-phase region is calculated according to the rule of segments. It may seem from the above that the amount of the second solid phase (Nb) affects the structural formation during the wetting phase transition. In reality, it is more advantageous energetically for the lens-like precipitates and layers of this phase to spread over the grain boundary during an increase in the amount of the second phase, instead of expanding it. The joining of layers with nonzero contact angles occurs at a certain critical increase in the amount of the second solid phase (Nb). As a consequence, we observe the grain boundary wetting phase transition at a substantially lower temperature than the actual temperature of termination of the wetting phase transition.

Figure 4 shows a model of the merging of the second solid phase layers at nonzero contact angles when the amount of a given phase increases. We can be sure of the wetting phase transition occuring in the Zr–Nb

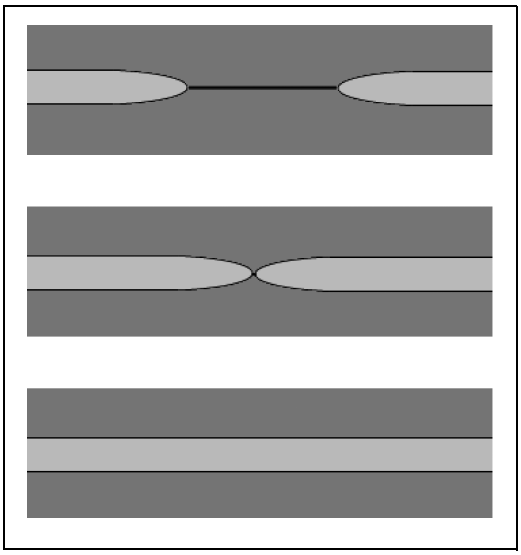

Fig. 4. Model showing the merging of layers of the second solid phase with nonzero contact angles as the amount of the wetting phase increases.

system only from the dots for Zr–1 wt % Nb alloy, since it contains a fraction of the Zr/Zr boundaries wetted with the second solid phase (Nb).

CONCLUSIONS

The grain boundary wetting solid-phase transition in the Zr–Nb system was observed. Complete wetting of grain boundaries was not achieved in the investigated alloys. Temperature T_{WS0} was displaced to the region of lower temperatures as the fraction of the second solid phase increased.

ACKNOWLEDGMENTS

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