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Abstract

Full Text

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THE IRON-ZIRCONIUM PHASE DIAGRAM

We have already been engaged in developing a partial phase diagram of Fe-Zr alloys rich in iron, in the region of 0.16% Zr ([1]), as a particular problem in the systematic study of the influence of alloying elements on the polymorphism of iron. In connection with the problem of constructing the Fe-Cr-Zr phase diagram, we subsequently encountered the need to develop the remaining regions of the complete diagram, in greater detail in the 16-52% Zr region and approximately in the 52-100% Zr region. In the concentration interval 16-52% Zr, the primary interest was the presence here of intermediate phases, concerning whose number and composition there were contradictions in the literature. In formulating the problem and choosing the research method we took into account the work of our predecessors ([2-4]).

The alloys were prepared from electrolytic iron refined in hydrogen and iodide zirconium by cruciibleless melting in an arc furnace with a nonconsumable tungsten electrode and a water-cooled copper hearth in an atmosphere of purified argon. In all, 22 alloys were prepared, of which 13 were subjected to a control chemical analysis for zirconium content.

The melting diagram was constructed from data of differential thermal analysis on heating (at a rate of 40-50°/min) using original apparatus ([5]), without contamination of the product of cruciibleless melting.

After preliminary experiments in thermal analysis on alloys in the initial cast state* in the decisive experiments we performed thermal analysis on alloys subjected to preliminary annealing (1250°, 18 h), carried out in a modernized TVV-2M furnace in an argon atmosphere at a constant temperature monitored by a thermocouple. On the differential heating curves of alloys annealed under the indicated regime, peaks were detected that signaled the occurrence in alloys with 20-40% Zr of a transformation at a practically constant temperature of 1470-1485°, independent of alloy composition. These peaks were not present on the heating thermograms of the same alloys in the initial cast state; they were also absent on the thermograms of cooling subsequent to melting. At the same time, on the differential heating curves of alloys containing 30% zirconium and more, a decrease was observed in the peak corresponding to the temperature 1325°, at which the eutectic transformation occurs. Investigation of the microstructure in the initial annealed state of these alloys showed a decrease in the content of the eutectic constituent in it. Such a result of thermal analysis and of analysis

Fig. 1. Phase diagram of the Fe–Zr system

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Fig. 2. Microstructure of cast (a) and annealed (b) alloy containing 34% Zr. 400×

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of the microstructure of the alloys could be explained by assuming the formation in the alloys, in the concentration interval under study, of an intermediate chemical compound melting with decomposition at a temperature of 1480° by a peritectic reaction. Bearing this in mind and taking into account that the transformation effect at 1480° and the simultaneous

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* In the structure of which, at Zr content > 30%, grains of a third phase were observed in small quantity.

a decrease in the effect of the eutectic transformation in alloys with a Zr content > 30% was not observed in alloys in the initial cast state, whereas in alloys preliminarily annealed according to the indicated regime it was observed in an incomplete form; the conclusion was drawn that the annealing was insufficient. Alloys with a zirconium content > 29% were, in an exploratory procedure, subjected to an additional prolonged anneal (1250°, 56 h), and then to a further high-temperature anneal (1450°, 8 h), the temperature of which was 125° above the eutectic temperature. This anneal achieved the intended purpose and brought the alloys to a state sufficiently close to equilibrium. In this state the alloys were subjected to microstructural, X-ray structural, dilatometric, and repeated differential thermal analysis on heating.

Fig. 1. Phase diagram of the Fe–Zr system

On the basis of the data of this analysis and with the use of data from our preceding work[(1)], a complete phase diagram of Fe–Zr alloys was constructed, shown in Fig. 1. The existence of two intermediate phases has been established. One of them, based on the chemical compound $ZrFe_2$, melting congruently at a temperature of 1675°, has a homogeneity range within ∼ 40–48% Zr (ε-phase). In determining the formula of this intermetallic compound we disagreed with the conclusions of works[(2)] and [(3)] and confirmed the conclusion of work[(4)]. The boundaries of the phase homogeneity were determined on the basis of microstructural and X-ray structural analysis. The second intermediate phase, according to our microstructural-analysis data, has a homogeneity range within 30–34% Zr (η-phase). It melts with decomposition at a temperature of 1480° by the peritectic reaction $\eta \rightarrow Zh_{20} + \varepsilon$. Thus the existence of a second intermetallic compound, first predicted in

Fig. 3. Change in the hardness of alloys and in the parameter of the crystal lattice of the ε-phase as a function of alloy composition

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Fig. 2. Microstructure of a cast (a) and annealed (b) alloy containing 34% Zr. 400×

in work (4), by X-ray structural analysis data, and by direct experiment the temperature of incongruent melting of the η-phase, which is based on this intermetallic compound, was determined. At the same time, the scheme of transformations of this phase proposed in work (4) was confirmed. The region of homogeneity of the η-phase found by us apparently does not include a composition expressed by a simple stoichiometric formula. It should be noted that determination of the boundaries of its homogeneity from microstructural and X-ray structural analysis data encounters certain contradictions that have not yet been eliminated. Alloys with 30 and 34% Zr, according to microstructural analysis data, were single-phase, while at the same time X-ray structural analysis of alloys within this concentration interval did not reveal any noticeable change in the magnitude of the lattice parameters. The microstructure of a cast and annealed alloy containing 34% Zr is shown by the micrographs in Fig. 2. The change in hardness of the alloys and in the parameter of the crystal lattice of the ε-phase as a function of alloy concentration is presented in Fig. 3.

Fig. 3. Change in the hardness of alloys and in the parameter of the crystal lattice of the ε-phase as a function of alloy composition

The ε-phase has a cubic lattice of the $MgCu_2$ type. The complex (noncubic) lattice of the η-phase has not been deciphered by us at this stage of the investigation. In microhardness the ε- and η-phases practically did not differ.

In conclusion it should be noted that, as was already indicated above, the part of the diagram pertaining to alloys lying on the diagram to the right of the intermetallic compound $ZrFe_2$ has been sketched only approximately, from thermal-analysis data for just five alloys, which moreover were not subjected to preliminary annealing. It is not excluded that here as well, on further more detailed investigation, the existence of a chemical compound will be revealed.

In the light of the investigation carried out by us, the discrepancies between us and the authors of work (2) in the construction of the diagram in the region of alloys with concentrations in the range 16–50% Zr are explained by the fact that the diagram constructed by them from thermal-analysis data under rapid cooling of the alloys is a diagram of metastable states.

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CITED LITERATURE

1. V. N. Svechnikov, A. Ts. Spektor, *Problems of the Physics of Metals and Metallurgy*, Collection of Scientific Works of the Institute of Metallophysics, Academy of Sciences of the Ukrainian SSR, No. 11, 1960, p. 30.

2. R. Vogel, W. Tonn, *Arch. Eisenhüttenw.*, **3**, 87 (1932).

3. E. T. Hayes, A. H. Roberson, W. L. O'Brien, *Trans. ASM*, **43**, 888 (1951).

4. H. J. Wallbaum, *Arch. Eisenhüttenw.*, **14**, 521 (1941); H. J. Wallbaum, *Zs. Kristallogr.*, **103**, 391 (1941).

5. V. N. Svechnikov, Yu. A. Kocherezhinskiy et al., *Mechanical Engineering*, Scientific-Technical Collection No. 5. Institute of Technical Information, Kiev, 1960, p. 76.

Note: Figure translations are in progress. See original paper for figures.