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Abstract

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PHASE DIAGRAM OF IRON—HAFNIUM

Hafnium is a refractory, rare, dispersed metal. Its properties have as yet been studied insufficiently well, since until recently it could not be obtained without a significant amount of impurities (chiefly zirconium). The melting point of hafnium has not been identified; according to literature data it is: 2230° (1), 1975$±25°({2}), 2222±30({3}), 2130±15°({4}). Hafniumundergoesanallotropictransformation, thetemperatureofwhichhaslike
Like zirconium, the low-temperature modification of hafnium has a close-packed hexagonal lattice, while the high-temperature modification has a body-centered cubic lattice.

In the literature sources we found no information on the phase diagram of the iron—hafnium system. There are only contradictory data on the intermetallic compound Fe_2Hf. In paper (9) it is indicated that the intermetallic compound has two polymorphic modifications. The high-temperature modification has a hexagonal lattice ($a = 4.952$, $c = 8.087$ kX) and is observed in specimens quenched from 1600°. The low-temperature modification has a cubic lattice ($a = 7.011$ kX) and is observed in specimens quenched from temperatures of 600—1400°, together with a small amount of the high-temperature modification.

In paper (10) by the same author, the existence of a low-temperature modification in the intermetallic compound Fe_2Hf is not confirmed; it is stated only that the crystal lattice of the intermetallic compound is hexagonal, of the $MgZn_2$ type, and has the parameters: $a = 4.970$, $c = 8.109$ kX. The melting point of the intermetallic compound is 1650°.

In a recently published work (11) it is indicated that the solubility of hafnium in α-iron is approximately 0.2 wt.%.

Preparation of alloys and methods of investigation

Most of the alloys were prepared on the basis of electrolytic iron, purified by annealing in hydrogen and then in vacuum. The melting of this iron into compact specimens was carried out in an arc furnace. Some of the alloys were prepared on the basis of carbonyl iron. After the indicated purification of the iron, the content in it of carbon, silicon, manganese, sulfur, phosphorus, and nitrogen did not exceed 0.01% each.

As the second component of the alloys, metallic iodide hafnium was used, the

Fig. 1

Figure 1: Fig. 1

principal impurity of which was zirconium in an amount of 0.5% and molybdenum in an amount of 0.2%. The alloys were prepared in an arc furnace ([12]) in an atmosphere of pure argon. To achieve homogeneity of the ingot, 5-6 remeltings were used. In all, 25 alloys were prepared. The content of hafnium and carbon in the alloys was checked by chemical analysis, the results of which are given in Table 1.

Thermal analysis of the alloys was carried out on an apparatus described in work ([12]), using tungsten—iridium and BP 5/20 thermocouples (W + 5% Re—W + 20% Re). Dilatometric analysis was carried out

using the apparatus described in (12). For operation up to temperatures of 1000-1100°, a chromel-alumel thermocouple was used, and for 1100-1500°, a platinum-platinum-rhodium thermocouple. The transformation temperatures in the alloys obtained by the indicated methods may differ from equilibrium values, since

Table 1

No.	Hf, wt.%	C, wt.%	No.	Hf, wt.%	C, wt.%	No.	Hf, wt.%	C, wt.%
1	0.01		*9	1.08	0.010	17	28.70	0.010
2	0.02	0.008	10	1.85	0.007	18	45.27	
3	0.044	0.008	11	3.34	0.011	19	60.90	
4	0.048	0.008	12	5.67	0.007	20	70.40	
5	0.15	0.008	13	8.75	0.010	21	81.25	
6	0.16	0.007	14	14.99	0.008	22	90.85	
7	0.26	0.009	15	20.85	0.010	23	94.0	
8	0.53	0.007	16	25.15	0.007	24	97.0	

their determination was carried out under conditions of continuous heating at a rate of 20-30°/min in thermal analysis and 0.2-3°/min in dilatometric analysis. We considered sufficiently close to equilibrium those values of transformation temperatures that were obtained under conditions of the slowest heating.

Fig. 1

Deciphering the phase constituents of the alloys was carried out by X-ray structural analysis. X-ray patterns were taken in filtered cobalt $K\alpha$-radiation in a cylindrical camera 143.4 mm in diameter. Magnetic analysis (determination of the Curie point) of the alloys was carried out on an Akulov anisometer using the differential method described in (13).

Fig. 2

Figure 2: Fig. 2

Results obtained and discussion

By the methods of differential thermal and dilatometric analysis it was established that in alloys containing up to 45% hafnium there are four transformations in the solid state. Of these, two are magnetic—in α-iron and in the intermetallic compound, the third is associated with the transformation of α-iron into γ-iron, and the fourth with the transformation of γ-iron into δ-iron. The temperature of the $\alpha \rightarrow \gamma$ transformation was determined by the dilatometric method on heating at a rate up to 0.5°/min. In Fig. 1a the experimental data are presented. Solid dots denote the temperatures of the beginning of the transformation, and circles the temperatures of the end of the transformation. On the basis of these data, a portion of the iron–hafnium diagram, presented in Fig. 1b, was developed.

The $\alpha \rightarrow \gamma$ transformation in the starting iron, containing up to 0.01% carbon, when heated at a rate of 0.2–0.3°/min was observed in the temperature interval 894–905°. From the thermograms and dilatograms of heating and cooling of the alloys it was not possible to distinguish the transformations $\alpha + \varepsilon \rightarrow \gamma + \varepsilon$ from $\alpha \rightarrow \gamma$. The maximum solubility of hafnium in α-iron (the peritectoid point), equal to 0.2%, was determined from the intersection of the peritectoid horizontal with the extrapolated curve of the $\alpha \rightarrow \gamma$ transformation. Characteristic

A special feature was the increase in the temperature of the transformation $\alpha + \varepsilon \rightarrow \gamma + \varepsilon$ with increasing hafnium content in the alloys, and the extension of the transformation over a noticeable temperature interval.

Therefore, the temperature of the transformation $\alpha + \varepsilon \rightarrow \gamma + \varepsilon$, equal to $935 \pm 5°$, was determined from the dilatogram of a two-phase $(\alpha + \varepsilon)$ alloy closest in composition to the peritectoid point.

The transformation $\gamma + \varepsilon \rightarrow \delta$ proceeds by a eutectoid reaction at a temperature of $1330 \pm 5°$. The composition of the eutectoid alloy is 2.8% hafnium. The maximum solubility of hafnium in γ-iron is 1.6% at 1330°. In alloys containing from 70 to 99% hafnium, two transformations in the solid state were found. The first is associated with the magnetic transformation of the intermetallic compound and is accompanied by a substantial change in the coefficient of thermal expansion. The second transformation in the above-mentioned alloys is eutectoid and occurs at a temperature of $1235 \pm 10°$ according to the reaction: $\varepsilon + \alpha_{\mathrm{Hf}} \rightleftarrows \beta_{\mathrm{Hf}} + \varepsilon$. It is accompanied by a noticeable thermal effect and a considerable increase in volume (on heating). This eutectoid transformation is observed even in an alloy containing 99% hafnium. Consequently, the solubility of iron in hafnium is small and is certainly less than 1%.

Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 3

The melting diagram was constructed exclusively by the method of differential thermal analysis. It was thereby established that in the iron—hafnium system there exist two eutectic transformations: $L \rightleftarrows \delta+\varepsilon$ at $1350 \pm 10^\circ$ and $L \rightleftarrows \beta_{\mathrm{Hf}}+\varepsilon$ at $1300 \pm 10^\circ$. The hafnium contents in the eutectic alloys are 21.5 and 85%, respectively.

X-ray structural analysis of alloys Nos. 17-22, whose phase composition includes the intermetallic compound Fe_2Hf (ε-phase), showed that the crystal lattice of the ε-phase is hexagonal, of the $MgZn_2$ type. The parameters of the crystal lattice of the ε-phase were determined from the lines (226), (233), (118), and (232). These parameters proved to be different in alloys of different composition, namely:

Parameters	a	c	c/a
Alloy No. 18	4.9116	8.0013	1.629
Alloy No. 19	4.9565	8.0964	1.6335
Alloy No. 21	4.9756	8.1288	1.6338

The parameters of the crystal lattice of the ε-phase of alloy No. 17 practically coincide with the parameters of the ε-phase of alloy No. 18. Coincidence of the parameters of the ε-phase was also established in alloys Nos. 20–22. Preliminary treatment

The treatment of these alloys consisted of annealing at 1200° followed by quenching. Since alloys Nos. 17 and 18 are two-phase ($\alpha + \varepsilon$), during annealing the maximum possible iron concentration at this temperature was established in the ε-phase. In alloys Nos. 20–22, in addition to the ε-phase, the α_{Hf} phase is present; therefore, during annealing of these alloys the maximum possible solubility of hafnium at this temperature was established in the ε-phase.

The difference in the crystal-lattice parameters of the ε-phase in several alloys indicates the existence of a appreciable homogeneity range of the ε-phase. Determination of the boundaries of the single-phase region of the intermetallic compound at 1200° was carried out by directly determining the hafnium content in the ε-phase in alloys Nos. 17, 18, and 21 annealed at 1200°. The chemical composition of the ε-phase was determined by I. D. Marchukova by the method of local x-ray spectral analysis on an RSASH-2 apparatus at the Institute of Metallurgy of the Academy of Sciences of the USSR.

The hafnium content in the ε-phase of alloy No. 18 was determined to be 50%, and in the ε-phase of alloy No. 21, 64%. Figure 2 shows the dependence of the lattice parameters of the ε-phase a, c, and c/a on the composition of the intermetallic compound. As already indicated above, it was established that the intermetallic compound Fe_2Hf is ferromagnetic. By magnetic analysis the Curie point of the ε-phase was determined in different alloys, i.e., for different compositions of the ε-phase. Thus it was established that, as the hafnium content in the intermetallic compound changes from 50 to 64%, the Curie point decreases from 405 to 145° (Fig. 2). As a result of prolonged (more than 100 h) annealing of the alloys at 850°, the composition of the ε-phase in them changed, and at the same time the Curie point also changed. In alloy No. 18 the Curie point decreased (compared with the state after annealing at 1200°) from 405 to 377°, while in alloy No. 21 it increased from 145 to 170°. This change in the Curie point occurred as a result of an increase in the hafnium content in the ε-phase of alloy No. 18 from 50 to 55% and a decrease in the hafnium content in the ε-phase of alloy No. 21 from 64 to 63.5% (see Fig. 2). In this way the boundaries of the single-phase region of the intermetallic compound were outlined.

The hardness of the intermetallic compound, determined on a Vickers instrument, is 650 kg/mm^2, and its melting temperature is $1810\pm20°$ (for the composition corresponding to the stoichiometric composition Fe_2Hf). This temperature is considerably higher than the value 1650° obtained in Ref. 10).

The phase diagram of the iron–hafnium system, constructed from the results of the present work, is presented in Fig. 3.

In conclusion, we consider it a pleasant duty to express our gratitude to I. B. Borovskii for carrying out the local x-ray spectral analysis in his laboratory and for the guidance provided in this work.

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CITED LITERATURE

1. I. H. De Boer, J. D. Fast, *Zs. anorg. u. allgem. Chem.*, **187**, 193 (1930).
2. H. K. Adenstedt, *Trans. Am. Soc. Metals*, **44**, 949 (1952).
3. D. K. Deardorf, E. T. Hayes, *J. Metals*, **8**, No. 5, Sec. 2, 509 (1956).
4. F. B. Liton, *J. Electrochem. Soc.*, **98**, 488 (1951).
5. P. Duwes, *J. Appl. Phys.*, **22**, No. 9, 1174 (1951).

6. A. E. Van Arkel, *Reine Metalle*, Berlin, 1939.
7. D. K. Deardorf, H. Katto, *Trans. Am. Inst. of Mining and Metall. Engineers*, **215**, 876 (1959).
8. J. D. Fast, *J. Appl. Phys.*, **23**, No. 3, 350 (1952).
9. R. P. Elliott, *Techn. Report*, No. 1, Contract No. AF18(600) 642, Project No. BO53 (1954); cited in: W. B. Pearson, *Handb. of Lattice Spacings and Structures of Metals and Alloys*, London—N. Y.—Paris—Los Angeles, 1958.
10. R. P. Elliott, W. Rostocker, *Trans. Am. Soc. Metals*, **50**, 617 (1958).
11. R. Reinbach, *Zs. Metallkunde*, **51**, No. 5, 292 (1960).
12. V. N. Svechnikov, Yu. A. Kocherzhinskii, A. K. Shurin, et al., *Mashinostroenie*, No. 5, 76 (1960).
13. V. G. Permyakov, Yu. V. Naidich, S. A. Rybak, *Zav. lab.*, **21**, No. 6, 695 (1955).

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