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Abstract

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A NEW COMPOUND IN THE RHENIUM–IRON SYSTEM

The study of rhenium alloys with iron is of great importance for establishing the features of the interaction of rhenium with transition metals. The binary rhenium–iron system was first studied by Eggers ([1]), who constructed the phase diagram up to 70 wt.% rhenium by means of thermal, metallographic, and X-ray analyses. In that work it was shown that two compounds are formed in the system: an η-phase (20-60 wt.% rhenium), stable at high temperatures up to 1200°, and an ε-phase (70 wt.% rhenium), stable in the temperature interval investigated. J. Nemec and V. Tschebjatowski ([2]) established that the crystal structure of the ε-phase is analogous to the known σ-phases. Work carried out at the A. A. Baikov Institute of Metallurgy confirmed the data concerning the structure of the ε-phase ([3]). Further investigations showed that the available information concerning the rhenium–iron diagram is inaccurate.

X-ray diffraction and metallographic investigations were carried out on alloys containing 40, 50, and 60 wt.% rhenium, which according to the phase diagram belong at temperatures below 900° to the two-phase region $\alpha + \varepsilon(\sigma)$. The specimens were prepared by melting in a high-frequency furnace charges pressed from powders of carbonyl iron and rhenium of 99.9% purity. The melts were made in a helium atmosphere in corundum crucibles. The specimens obtained were annealed in evacuated quartz ampoules at temperatures of 750, 800, 950, and 1050°, with cooling in air or with the furnace. Quenching from 1200 and 1300° was also carried out. X-ray patterns were taken in an RKD camera using CoK radiation without a filter from powder specimens rolled, in the form of a column, onto a thin glass fiber. The powders were obtained with the aid of a fine grinding wheel, followed by removal of magnetic material from the specimen.

On the X-ray patterns of specimens quenched from 1200 and 1300° or annealed at 1050°, two systems of lines were observed, corresponding to a solid solution based on γ-Fe and to the σ-phase. After annealing of cast specimens at 750, 800, and 950°, the X-ray patterns do not reveal lines of the σ-phase. In these photographs, along with the lines of the α- (750 and 800°) and γ- (950°) solid solutions, reflections appear that correspond to a new phase. Comparison of the line intensities shows an increase in the amount of this phase with increasing rhenium content. The alloy with 60 wt.% rhenium, judging from the X-ray pattern, contains an insignificant amount of solid solution and is located close to the single-phase region of the new compound. Figure 1 shows X-ray patterns of this alloy in the cast state and after annealing at 1050 and 750°. The duration of each anneal was 1 hour. The positions of the lines on the X-ray pattern show that the compound (hereinafter designated as the χ'-phase) apparently has a cubic structure with large unit-cell dimensions. A calculation was carried out which showed that all lines are well indexed on the basis of a body-centered cubic (bcc) lattice (see Table 1). By back-reflection photography in a KROS camera with a platinum standard, the unit-cell parameter of the χ'-phase was determined. For the measurements the doublet of the lines (941, 853, 770) was used at angles $\theta_{\alpha_1} = 80°36'$ and $\theta_{\alpha_2} = 81°30'$. The value obtained was $a = 8.960$ kX.

On the basis of data on the unit-cell dimensions and the chemical composition of the alloy, as well as the results of pycnometric measurements,

Table 1

hkl	$h^2+k^2+l^2$	d, kX	$\sin^2\theta_{\text{exp}}$	$\sin^2\theta_{\text{calc}}$	I_{exp}	I_{calc}	hkl	$h^2+k^2+l^2$	d, kX	$\sin^2\theta_{\text{exp}}$	$\sin^2\theta_{\text{calc}}$	I_{exp}	I_{calc}
110	2	6,645	0,018	0,020	very weak		721, 633, 552	54	1,219	0,536	0,537	46	27
200	4	4,670	0,036	0,040	very weak		642	56	1,194	0,559	0,557	weak	
211	6	3,632	0,060	0,060	medium	12	730	58	1,174	0,578	0,577	medium	
220	8	3,101	0,082	0,080	weak	2	732, 651	62	1,138	0,616	0,616	medium	
310	10	2,807	0,101	0,099	very weak		811, 741, 554	66	1,102	0,656	0,656	strong	
321	14	2,379	0,141	0,139	3	3	820, 644	68	1,084	0,682	0,676	strong	
400	16	2,216	0,162	0,159	2,5	2	653	70	1,071	0,696	0,696	weak	
411, 330	18	2,092	0,182	0,179	100	100	822, 660	72	1,055	0,716	0,716	strong	
332	22	1,898	0,221	0,219	11	10	831, 750, 743	74	1,040	0,736	0,736	strong	
422	24	1,815	0,242	0,239	13	12	662	76	1,027	0,757	0,755	weak	
510, 431	26	1,751	0,260	0,258	4	2	752	78	1,015	0,775	0,775	strong	
521	30	1,645	0,294	0,298	very weak		840	80	1,000	0,797	0,795	weak	
530, 431	34	1,531	0,340	0,338	weak	0,3	910, 833	82	0,989	0,815	0,815	weak	

hkl	$h^2+k^2+l^2$	d, kX	$\sin^2\theta_{exp}$	$\sin^2\theta_{calc}$	I_{exp}	I_{calc}	hkl	$h^2+k^2+l^2$	d, kX	$\sin^2\theta_{exp}$	$\sin^2\theta_{calc}$	I_{exp}	I_{calc}
600, 442	36	1,492	0,358	0,358	11	6	842	84	0,978	0,834	0,835	weak	
611, 532	38	1,451	0,380	0,378	8	6	921, 761, 655	86	0,966	0,854	0,855	weak	
541	42	1,378	0,420	0,417	5	2	664	88	0,955	0,874	0,875	medium	
622	44	1,348	0,439	0,437	8	3	930, 851, 754	90	0,943	0,895 (α_1)	0,895 (α_1)	strong	
631	46	1,319	0,458	0,457	3	1,5	932, 763	94	0,924	0,935	0,934	medium	
444	48	1,292	0,477	0,477	8	5	844	96	0,914	0,954	0,954	weak	
750, 550, 543	50	1,265	0,498	0,497	9	2,5	941, 853, 770	98	0,905	0,972 (α_1)		very strong	

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a

b

c

d

Fig. 1. X-ray diffraction patterns taken in an RKD camera: a —Re—Fe alloy (60 wt.% Re) in the cast state; b —the same alloy after annealing at 1050° for 1 h (σ-phase + austenite); c —the same alloy after annealing at 750° for 1 h (γ'-phase + ferrite); d —electrolytic manganese

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Fig. 1. Electron diffraction patterns of polyvinyl chloride films: a —at a monomer : aldehyde ratio of 1 : 1 and with excess aldehyde; b —with some excess of monomer; c —at a monomer : aldehyde ratio of 1 : 0.7 and with a further increase in monomer content

Fig. 2. Electron diffraction pattern of a polyvinyl chloride film. (The polymer was obtained at a monomer : chloral ratio of 1 : 1.)

(d = 12.92 g/cm^3) the number of atoms in the cell was calculated. The value obtained, z = 58.1, gives grounds to assume that the compound belongs to the structural type α-Mn, which is characterized by 58 atoms per unit cell of a body-centered cubic lattice. Indeed, comparison of the X-ray diffraction patterns of the γ'-phase and α-Mn (see Fig. 1) shows a definite similarity of the diffraction patterns. At the same time, a number of differences are observed in the intensity ratios of certain lines. Since the intensity distribution in the X-ray pattern of α-Mn corresponds to a statistical arrangement of atoms, it may be supposed that the observed differences in intensities are connected with the ordering of rhenium and iron atoms in the structure of the γ'-phase. To verify this assumption it is necessary to compare the calculated and measured line intensities in the X-ray pattern.

Table 2

Position	Coord. number	Distribution of atoms
$2(a)$	16	2 Re
$8(c)$	16	8 Re
$24(g)$	13	8 Re, 16 Fe
$24(g')$	12	24 Fe

The corresponding calculation was carried out for a group of lines located in the angular interval $\theta = 14 \div 47^\circ$, on the basis of the scheme of atomic distribution presented in Table 2. According to this scheme, rhenium, which has the larger atomic radius, is located in the unit cell in positions corresponding to large values of the coordination number and of the mean interatomic distance. This type of distribution, associated with the size ratios of the components, is well known for phases with the α-Mn type structure ([3]).

In calculating the structural amplitudes, the coordinates of the atoms in the cell were taken to be the same as in the α-Mn structure. The measure of the calculated intensity was the quantity $I \sim Lp|F|^2$, where

$$L = \frac{1 + \cos^2 2\theta}{\sin 2\theta \cdot \cos\theta},$$

p is the multiplicity factor, and $|F|$ is the modulus of the structural amplitude. The intensities were measured with an MF-4 recording microphotometer. Both in the calculation and in the measurement, the intensity of the $(411, 330)$ line was taken as 100.

Table 1 presents data showing generally satisfactory agreement between the calculated and experimental intensity values. The best agreement is observed for lines with $h^2 + k^2 + l^2 = 14, 16, 22, 24, 26$, located in a small angular interval that includes the standard line. The results obtained make it possible to conclude that the new compound found in the rhenium—iron system has a structure close to the α-Mn type, with an ordered distribution of atoms in the unit cell.

The formation of such a rhenium compound with iron should be compared with the available data on phases in binary systems based on rhenium ([3]). In particular, it is necessary to take into account that compounds belonging to the same structural type have been found in all systems with metals of subgroups IVA, VA, and VIA, with the exception of vanadium and chromium. This indicates a special tendency of rhenium to form the structure characteristic of its analogue in the periodic system—manganese.

It may also be noted that, as in some other systems, in the rhenium—iron system a structure of the α-Mn type is observed alongside the σ-phase, which confirms the closeness in the nature of these compounds.

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