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Corresponding Member of the Academy of Sciences of the USSR N. V. AGEEV and V. Sh. SHEKHTMAN

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Abstract

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ON THE QUESTION OF THE NATURE OF SIGMA PHASES

In a number of works devoted to compounds between transition metals ($^{1-5}$), it is noted that the existence of σ-phases is to a considerable degree connected with the electronic structure of the components. Certain conclusions concerning the nature of these compounds can be obtained on the basis of a study of ordering. The study of the atomic distribution in the cells of σ-phases formed by elements of the first long period, by the methods of X-ray and neutronographic analysis, has shown the presence of an ordered arrangement of atoms ($^{6-8}$). According to the data obtained, atoms occupy crystallographically different positions in the cells depending on the position of the given element in D. I. Mendeleev's periodic system relative to subgroup VIIA (^{8}). Rhenium is an element highly inclined to form σ-phases in binary systems (^{9}); however, in these phases ordering has not so far been detected, with the exception of the Re–Mo alloy ($^{10-12}$).

We carried out an X-ray study of ordering of σ-phases in the chromium–rhenium, manganese–rhenium, and iron–rhenium systems. Binary alloys were studied containing 37 at.% Cr* (annealing for 500 hours at 1000°), 47.7 at.% Mn (annealing for 360 hours at 1000°), and 55 at.% Fe (annealing for 6 hours at 1500°), which, according to microstructural and X-ray analysis, belong to single-phase regions of σ-phases on the phase diagrams. In accordance with these compositions, for calculation of the structural amplitudes formulas were chosen which were conventionally assigned to these compounds on the basis of crystallochemical data on the number of atoms per cell and the number of correct systems of points in the structure: $Re_{18}Cr_{12}$, $Re_{16}Mn_{14}$, $Re_{12}Fe_{18}$. In Table 1

Table 1

Ordering variants of σ-phases

Position	Coord. number	$Re_{18}Cr_{12}$ 1*	$Re_{18}Cr_{12}$ 2	$Re_{18}Cr_{12}$ 3	$Re_{18}Cr_{12}$ 4	$Re_{16}Mn_{14}$ 1	$Re_{16}Mn_{14}$ 2	$Re_{16}Mn_{14}$ 3	$Re_{16}Mn_{14}$ 4	$Re_{16}Mn_{14}$ 5	$Re_{16}Mn_{14}$ 6*	$Re_{12}Fe_{18}$ 1	$Re_{12}Fe_{18}$ 2	$Re_{12}Fe_{18}$ 3*	$Re_{12}Fe_{18}$ 4
2(a)	12	2 Re	2 Re	2 Re	2 Cr	2 Mn	2 Mn	2 Mn	2 Re	2 Mn	2 Mn	2 Fe	2 Fe	2 Fe	2 Re

Position	Coord. number	$Re_{18}Cr_{12}$ 1*	$Re_{18}Cr_{12}$ 2	$Re_{18}Cr_{12}$ 3	$Re_{18}Cr_{12}$ 4	$Re_{16}Mn_{14}$ 1	$Re_{16}Mn_{14}$ 2	$Re_{16}Mn_{14}$ 3	$Re_{16}Mn_{14}$ 4	$Re_{16}Mn_{14}$ 5	$Re_{16}Mn_{14}$ 6*	$Re_{12}Fe_{18}$ 1	$Re_{12}Fe_{18}$ 2	$Re_{12}Fe_{18}$ 3*	$Re_{12}Fe_{18}$ 4
$4(f)$	15	4 Cr	4 Re	4 Cr	4 Re	4 Mn	4 Re	4 Mn	4 Mn	4 Re	4 Re	4 Fe	4 Fe	4 Re	4 Fe
$8(i_C)$	14	8 Re	8 Re	4 Re4 Cr	6 Re2 Cr	8 Re	8 Re	4 Re4 Mn	6 Re2 Mn	4 Re4 Mn	6 Re2 Mn	8 Fe	8 Fe	4 Re4 Fe	6 Re2 Fe
$8(i_D)$	12	8 Re	8 Cr	8 Re	8 Cr	8 Mn	8 Mn	8 Re	8 Re	4 Re4 Mn	8 Mn	8 Fe	8 Re	8 Fe	8 Re
$8(j)$	14	8 Cr	4 Re4 Cr	4 Re4 Cr	8 Re	8 Re	4 Re4 Mn	4 Re4 Mn	8 Mn	4 Mn4 Re4 Mn	6 Re2 Mn	8 Re	4 Re4 Fe	4 Re4 Fe	8 Fe

Note. The asterisk * denotes ordering schemes chosen for the corresponding phases on the basis of experimental data.

are presented the considered variants of ordered arrangement of atoms in these compounds, satisfying the symmetry of the space group $P4_2/mnm$, to which the structure of the σ-phase belongs. Calculation of the inten-

of intensities was carried out for reflections corresponding to a group of 6 strong lines lying in a narrow interval of angles θ. The calculations showed that in most cases it is possible, from the intensity ratios of the selected lines, to distinguish a statistical distribution of atoms from an ordered one and to identify a definite ordering scheme. However, in the case of the rhenium–iron alloy it proved necessary also to include the (311) and (002) lines in the consideration. The line intensities were determined on a URS-50I diffractometer with an MSTR-4 counter and recording of the curves on an EPP-09 potentiometer. The areas bounded by the peaks on the diffractometric curve were measured with a planimeter. Comparison of the experimental and calculated line-intensity values showed the presence of ordering in the alloys studied (Table 2).

Table 2

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* The Re–Cr specimen was obtained from the laboratory of Prof. E. M. Savitskii.

Fig. 1. Rhenium content in the σ-phase as a function of the group number of the second component

Figure 1: Fig. 1. Rhenium content in the σ-phase as a function of the group number of the second component

Line indices	I_{calc} for a statistical distribution	Cr—Re I_{calc} 1	Cr—Re I_{calc} 2	Cr—Re I_{calc} 3	Cr—Re I_{calc} 4	Cr—Re I_{exp}	Mn—Re I_{calc} 1	Mn—Re I_{calc} 2	Mn—Re I_{calc} 3	Mn—Re I_{calc} 4	Mn—Re I_{calc} 5	Mn—Re I_{calc} 6	Mn—Re I_{exp}	Re—Fe I_{calc} 1	Re—Fe I_{calc} 2	Re—Fe I_{calc} 3	Re—Fe I_{calc} 4	Re—Fe I_{exp}
311	4													19	<1	19	<1	13
002	15													<1	17	11	29	17
112	84	51	57	85	129	56	172	76	122	51	87	112	70	189	154	86	52	68
410	34	19	33	32	56	26	78	33	34	18	29	46	30	74	35	34	17	34
330	31	14	40	24	63	23	74	37	21	13	27	51	53	88	20	42	12	41
202	65	22	43	59	113	36	93	57	76	26	78	89	89	223	126	80	39	68
212	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
420	50	46	31	54	44	49	30	39	74	49	62	42	50	60	101	46	60	50

Analysis of the ordering schemes selected on the basis of experimental data (see Table 1) shows that the distribution of atoms in the cells of the σ-phase exhibits a correlation with the coordination number. In particular, positions $2(a)$ and $8(i_D)$, corresponding to the smallest coordination number, and positions $4(f)$, corresponding to the largest coordination number, are always occupied by atoms of different kinds. In this case chromium atoms occupy positions with coordination number 15, while manganese and iron atoms occupy positions with coordination number 12. Thus, similarly to the data of (^{8}), the ordering scheme of the σ-phase proves to be connected with the positions of the components in the periodic system. The results obtained, as well as data on the compositions of compounds in binary alloys of rhenium with vanadium, chromium, manganese, and iron, may be considered on the basis of concepts developed as applied to σ-phases in alloys of transition metals of the first long period (^{1}, ^{3}, ^{4}).

Fig. 1. Rhenium content in the σ-phase as a function of the group number of the second component

If the average concentration of rhenium in the σ-phases V—Re, Cr—Re, Mn—Re, Fe—Re ($^{13-15}$) is plotted as a function of the group number of the second component (Fig. 1), it may be noted that the rhenium content decreases as the group number increases. In explaining this fact, apparently, one should adhere to the point of view of those investigators who regard σ-phases as a certain modification of electron compounds (Hume-Rothery phases) for transition-group metals. In this case it may be assumed that σ-phases are characterized by a definite level of the number of outer-

electrons per atom in them, and their stability depends on the volume of the Brillouin zone. Thus rhenium in systems with vanadium, chromium, manganese, and iron appears as an element possessing an excess of electrons in comparison with the assumed (hypothetical) level.

The higher the group number (valence) of the second component, the smaller the amount of rhenium required to attain the electron concentration characteristic of σ-phases. The idea that rhenium in the systems under consideration has a higher valence than its partners finds some confirmation in the results of an analysis of interatomic distances in the crystal cells of the σ-phases rhenium—chromium and rhenium—iron by means of Pauling' s equation. The number of valence bonds was calculated on the basis of the ordering data presented above. It is possible that it is precisely the increased metallic valence of rhenium, in comparison with the elements of the first transition series, that can explain the formation of σ-phases in the systems rhenium—manganese and rhenium—iron, which do not satisfy the known rule that the elements entering into σ-phases are located in the periodic system on opposite sides of the line separating subgroups VIA and VIIA.

Institute of Metallurgy named after A. A. Baikov
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CITED LITERATURE

1. A. H. Sully, *J. Inst. Metals*, **80**, 173 (1951—1952).
2. V. Yu. M-Rozen, G. Reinor, *Struktura metallov i splavov*, Moscow, 1959.
3. P. Greenfield, P. Beck, *J. Metalls*, **6**, 2 (1954).
4. D. Bloom, N. Grant, *Trans. Am. Inst. of mining and metall. Engineers*, **197**, 88 (1953).
5. C. Haworth, W. Hume-Rothery, *Philos. Mag.*, **3**, 33, 1013 (1958).
6. G. Bergman, D. Shoemaker, *Acta Crystallogr.*, **7**, 12 (1954).

7. B. Decker, R. Waterstrat, J. Kasper, *J. Metalls*, **6**, 12 (1954).
8. J. Kasper, R. Waterstrat, *Acta Crystallogr.*, **9**, 3, 297 (1956).
9. N. V. Ageev, Ch. V. Kopetskii, E. M. Savitskii, V. Sh. Shekhtman, *DAN*, **129**, No. 3 (1959).
10. R. Waterstrat, J. Kasper, *Trans. Am. Inst. of mining and metall. Engineers*, **209**, 872 (1957).
11. Ya. Nemets, V. T. Shebyatovskii, *Byull. Pol' sk. Akad. nauk*, **6**, 4 (1958).
12. N. V. Ageev, V. Sh. Shekhtman, *Izv. AN SSSR, ser. fiz.*, **23**, No. 5 (1959).
13. M. A. Tylkina, K. B. Povarova, E. M. Savitskii, *DAN*, **131**, No. 2 (1960).
14. E. M. Savitskii, M. A. Tylkina, K. B. Povarova, *ZhNKh*, **4**, issue 8 (1959).
15. N. V. Ageev, Ch. V. Kopetskii, E. M. Savitskii, V. Sh. Shekhtman, *DAN*, **125**, No. 1 (1959).

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