Structural Investigations on the Monoclinic Sigma Phase in the Cr—Fe—Ni—Mo System

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The crystal structure of a σ-phase with the approximate composition $Cr_{11}Fe_{13}Ni_3Mo_3$ has been determined and refined from single-crystal data to an R-value of 0.073 in space group $P2$ (No. 3). A monoclinic deviation from the generally assumed tetragonal symmetry $P4/mnm$ for σ-phases was inferred from small splits in some of the powder diffraction lines. The monoclinic angle refined by least-squares profile analysis of Guinier-Hägg diffraction data is 90.15(1)°. The Mo atoms can be described as distributed within *one* of the two subsidiary layers situated between the pseudohexagonal main layers, causing a shift of the subsidiary layers of approximately 0.1 Å from a level halfway between the main layers.

The σ-phase with the approximate composition $Cr_{12}Fe_{13}Ni_3Mo_2$ has also been studied by single crystal diffraction. The result obtained confirms the general distribution scheme for the Mo atoms and the monoclinic space group as found for $Cr_{11}Fe_{13}$-Ni_3Mo_3. No significant deviation from 90° is found for the monoclinic angle, however.

The effect of Mo on the lattice parameters and on the chemical composition of σ-phase and $M_{23}C_6$ carbide in austenitic 25Cr-20Ni steel has been investigated by Andersson and Lundberg.[1] In

connection with these studies we decided to investigate the distribution of the Mo atoms in the σ-phases by X-ray diffraction techniques. We therefore made single crystal and powder diffraction studies on two samples with chemical compositions close to $Cr_{12}Fe_{13}Ni_3Mo_2$ and $Cr_{11}Fe_{13}Ni_3Mo_3$, named F and G by Andersson and Lundberg.[1]

EXPERIMENTAL

The concentrations of Cr, Fe, Ni and Mo in the F- and G-samples were determined on polished sections by electron-probe microanalysis using the procedure described by Andersson and Lundberg.[1] The analytical results, which should have relative errors less than 4 percent, are given in Table 1.

X-Ray powder diffraction patterns were obtained by a Guinier-Hägg focusing camera with $CrK\alpha_1$ radiation ($\lambda = 2.28970$ Å). Potassium chloride ($a = 6.2929$ Å)[2] was used as an internal theta-standard. The photographs were measured with a film scanner described by Johansson, Palm and Werner.[3] Small splits in some of the diffraction lines caused by a monoclinic deviation from tetragonal symmetry were observed for compound G (see Fig. 1).

Single crystals of the F- and G-samples were prepared by annealing in evacuated silica tubes for

Table 1. Chemical composition of σ-phase obtained by electron-probe microanalysis.

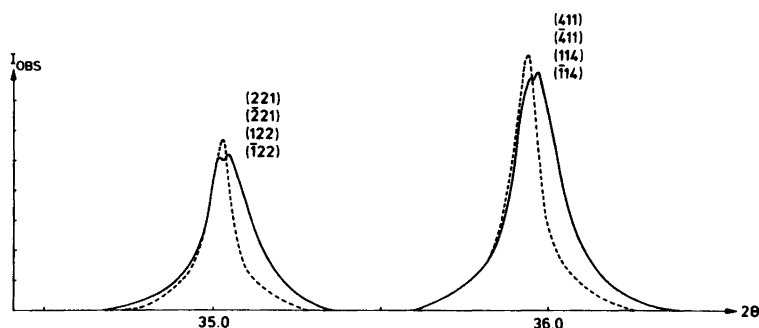| Sample	Cr	Fe	Ni	Mo	$Cr_xFe_yNi_zMo_t$
F Wt %	34.6	42.9	10.4	11.4	$Cr_{12}Fe_{13}Ni_3Mo_2$
At %	38.5	44.4	10.2	6.9	
G Wt %	32.7	41.3	10.9	15.5	$Cr_{11}Fe_{13}Ni_3Mo_3$
At %	36.7	43.1	10.8	9.4	

Fig. 1. Observed intensity curves, $34.5 - 36.5°$ in 2θ, for compound G (solid line) and compound F (dashed line). Small monoclinic splits are observed for G.

ten and six weeks, respectively, at 750 °C followed by quenching in water. X-Ray diffraction data were collected with a Philips diffractometer, PW 1100, using Mo$K\alpha$ radiation. Intensity data were recorded using the $\theta/2\theta$ scanning mode with a scan speed (2θ) of $0.9 - 1.8°$ min^{-1}. The upper limit of $(\sin \theta)/\lambda$ was 0.704 Å^{-1} for the F- and 1.078 Å^{-1} for the G-compound. Background counts were taken for 0.5 times the scan time at each end of the scan range, the latter being 1.8° and 1.4° for F and G, respectively. Reflexions with intensity greater than $2\sigma(I)$ were regarded as observed and used in the refinements. The number of observed independent reflexions was 846 for F and 1851 for G. The usual corrections were made for Lorentz and polarization effects as well as for absorption.

REFINEMENTS

The unit cell dimensions (*cf.* Table 2) used in the least-squares refinements of the single-crystal data

were obtained from profile refinements of the powder diffraction data using the program described by Werner *et al.*[4] No significant deviations in cell parameters were found from profile refinements using preliminary or final positional coordinates obtained from single-crystal data. A monoclinic angle of 90.15(1)° was found for compound G.

The preliminary assumption was that the atoms Cr, Fe, Ni and Mo are distributed at random over the atomic sites of the structure. The scattering factor curve for Mn[5,6] was used for all metal atoms, and the distribution of the Mo atoms was determined from refinements of the formal occupancy factors. The Mn scattering factor was chosen as a weighted average of Cr, Fe and Ni, whose scattering powers are quite similar. Preliminary refinements showed that the occupancy factors for the four twofold positions derived from position III (*cf.* Table 3) were almost equal. In order to facilitate a comparison between the F- and G-compounds

Table 2. Crystal data.

Compound	F	G
Approximate composition	$Cr_{12}Fe_{13}Ni_3Mo_2$	$Cr_{11}Fe_{13}Ni_3Mo_3$
F.W.	1722.4^a	1755.6^a
a(Å)	8.8544(20)	8.8915(8)
b(Å)	4.5920(2)	4.6088(2)
c(Å)	8.8447(19)	8.8618(8)
β(°)	90.03(8)	90.15(1)
V(Å^3)	359.62(5)	363.15(5)
μ(Mo$K\alpha$)(cm^{-1})	272	273
D_x(g cm^{-3})	7.952	8.027
Space group	$P2$ (No. 3)	$P2$ (No. 3)

^{a} Calculated from the compositions given in Table 1.

these "occupancy factors" were normalized to 1.0 in both refinements. The start parameters for the single crystal refinements were derived from the data published by Bergman and Shoemaker[7] for tetragonal σ-FeCr. The splitting of point positions from $P4/mnm$ to $P2$ is illustrated in Table 3, where the refined parameters for compound G are also listed. For compound F, only the refined occupation factors are reported in the table. The conventional R-values obtained for isotropic refinements were 0.120 and 0.073 for F and G, respectively.

DISCUSSION

As stated above, a monoclinic deviation from the generally assumed tetragonal symmetry for σ-phase is obviously present in G (cf. Fig. 1). This fact, however, could hardly have been detected from single crystal data alone as the small deviation of 0.15° from 90° in the β angle made it impossible to refine the unit cell parameters from single crystal data. Refinement of unit cell parameters by profile analysis of powder diffraction data was also facilitated by the longer wavelength used in the powder data collection.

The σ-phase structure can be described as built up of pseudo-hexagonal main layers perpendicular to the monoclinic b axis. Between them are subsidiary layers, whose atoms are located above and beneath holes in the main layers (Fig. 2). The atoms in the subsidiary layers have close interlayer contact with each other, leading to improved overall packing and to rather short distances along vertical rows in the structure.[7,8] This feature is also observed in the present study. Thus, in compound G, the shortest Me−Me distances 2.277(11), 2.297(11), 2.315(11) and 2.333(11) Å are the four vertical distances between the subsidiary layers. The corresponding atomic parameters are those originating from point position 8(j) in $P4/mnm$ (cf. Table 3). As a comparison, the shortest distance between two atoms within a main layer, (1/2, 1/2, 1/2) to (0.5659, 0.5179, 0.7609) (see Table 3), is found to be 2.385(2) Å. The average Me−Me contact distance in G is 2.637 Å.

The most pronounced effect of the monoclinic deviation from tetragonal symmetry is that the two subsidiary layers are displaced about 0.1 Å along [010] in the same direction, thus keeping the interlayer distance constant.

It has been stated by Kasper and Waterstrat[9]

Table 3. Final atomic parameters (e.s.d.'s in parentheses).

| Splitting of point positions			Compound G					Compound F
Position	$P4/mnm$	$P2$	x	y	z	$B/\text{Å}^2$	"Occup. factors"	"Occup. factors"
I	2(a)	1(a)	0	0	0	0.29(3)	1.05(2)	1.07(2)
		1(d)	0.5	0.5	0.5	0.29(3)	1.05(2)	1.07(2)
II	4(f)	2(e)	0.3987(2)	0.0052(19)	0.3985(2)	0.37(3)	0.97(1)	0.96(2)
		2(e)	0.8987(2)	0.5059(19)	0.1015(2)	0.37(3)	0.97(1)	0.98(2)
III	8(i)	2(e)	0.4638(2)	0.0093(21)	0.1314(2)	0.38(2)	1.0[a]	1.0[a]
		2(e)	0.9636(2)	0.5039(18)	0.3684(2)	0.38(2)	1.0[a]	1.0[a]
		2(e)	0.1312(2)	0.0192(16)	0.4630(2)	0.38(2)	1.0[a]	1.0[a]
		2(e)	0.6314(2)	0.5132(21)	0.0366(2)	0.38(2)	1.0[a]	1.0[a]
IV	8(i)	2(e)	0.7390(2)	0.0053(19)	0.0664(2)	0.38(2)	1.06(1)	1.06(2)
		2(e)	0.2392(2)	0.5168(17)	0.4340(2)	0.38(2)	1.06(1)	1.07(2)
		2(e)	0.0656(2)	0.0158(19)	0.7389(2)	0.38(2)	1.06(1)	1.07(2)
		2(e)	0.5659(2)	0.5179(17)	0.7609(2)	0.38(2)	1.05(1)	1.08(2)
V	8(j)	2(e)	0.1833(5)	0.2709(18)	0.1797(6)	0.32(2)	0.86(3)	0.96(3)
		2(e)[b]	0.6789(4)	0.7665(16)	0.3166(4)	0.32(2)	1.15(3)	1.13(3)
		2(e)[b]	0.1821(4)	0.7648(15)	0.1853(5)	0.32(2)	1.09(3)	1.09(3)
		2(e)	0.6880(5)	0.2646(19)	0.3182(6)	0.32(2)	0.82(3)	0.90(3)

[a] Fixed parameter. [b] Preferably occupied by Mo atoms.
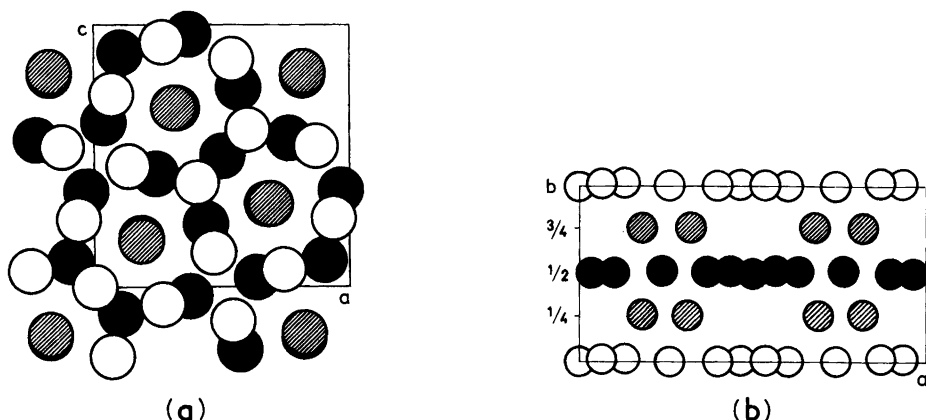
Fig. 2. The structure of the monoclinic σ-phase. (a) Projection along [010]. (b) Projection along [001]. Unfilled circles represent atoms in the main layers at $y=0$; filled circles, atoms in the main layers at $y=1/2$; and shaded circles, atoms in the subsidiary layers at $y\approx 1/4$ and $y\approx 3/4$ [almost coincident in (a)].

that the metals to the left of manganese in the periodic table (Cr, Mo) occupy the position of type II (see Table 3) and those to the right (Fe, Ni) occupy positions of type I and IV. The remaining positions, III and V, are termed mixed positions and they contain varying proportions of the component atoms. These statements were made for binary, tetragonal, σ-phases and may not be strictly valid for the present type of quaternary phases. No definite conclusions about the distribution of Cr, Fe and Ni can be drawn from the present study because of the small differences in scattering power these atoms exhibit. From the occupancy parameters reported in Table 3, however, it can be inferred that the Mo atoms are situated in the subsidiary layer at $y=0.76$. As can be seen from the table, the same type of Mo concentration is found from the occupancy parameters of the less molybdenum-rich F-compound. Thus, the Mo atoms are located in a "mixed" position of type V. The distribution of the relatively large Mo atoms in one of the subsidiary layers excludes short Mo−Mo contact in the [010] direction.

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