Investigations on σ-FeCrSi

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The solubility of Si in σ-FeCr at 690° and the lattice dimensions of the sigma-phase as functions of the Si-content have been determined.

The distribution of the Si-atoms in σ-FeCrSi is discussed in comparison with some common transition metal silicide structures.

The brittle non-magnetic FeCr sigma phase was first reported by Bain and Griffiths [1] and Chevenard [2] in 1927. In the following years it was discussed whether this phase existed in the *pure* binary system or not. That the sigma phase did exist also when only very small amounts of impurities were present, was shown in 1936 by Jette and Foote [3], who pointed out the accelerating effect of Si and of cold work on sigma phase formation. In the same year, Andersen and Jette [4] investigated the Fe-Cr-Si system (mainly the Fe-rich corner). These authors found that considerable amounts of Si were dissolved in the sigma phase and they outlined the sigma phase region in the ternary system.

In connection with studies of transition metal silicides at this institute we decided to investigate more closely the solubility of Si in the sigma phase. The investigation was limited to the FeCr-Si section of the ternary system. Our results are presented in two parts — the first dealing with the lattice dimensions and the determination of the solubility limit, and the second dealing with our ideas of the distribution of Si-atoms in σ-FeCrSi. In the latter part, some aspects on the relation between the sigma phase structure and some common silicide structures are given.

I. THE SOLUBILITY OF Si IN σ-FeCr

(T. Lundström and B. Aronsson)

Experimental

Electrolytic Cr-powder and Baker's Fe (> 99.8 %) were used. The silicon was analysed and found to contain 98.92 % Si with iron as main impurity. The alloys were prepared by melting in an arc furnace. After annealing at the relevant temperature in evacuated silica tubes they were quenched in oil. The following annealing times were used: 690°,
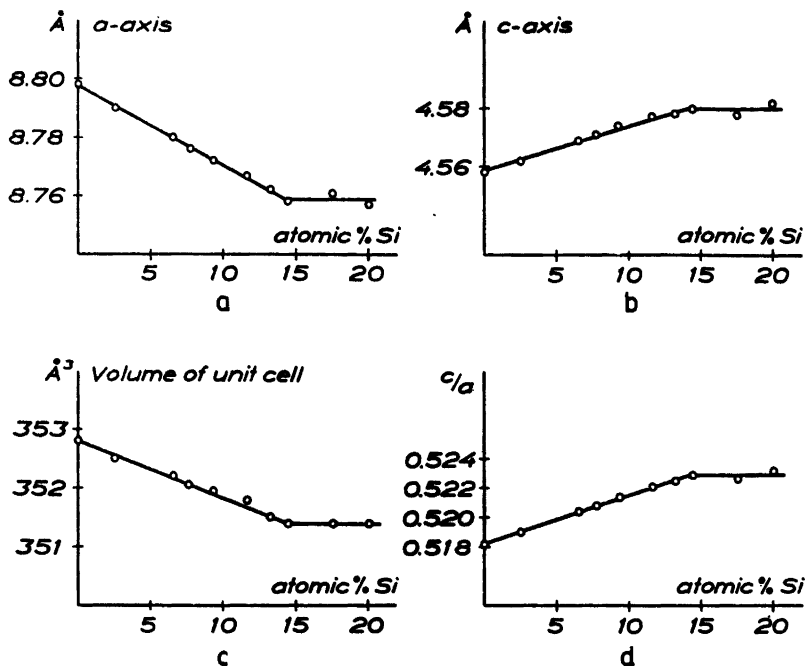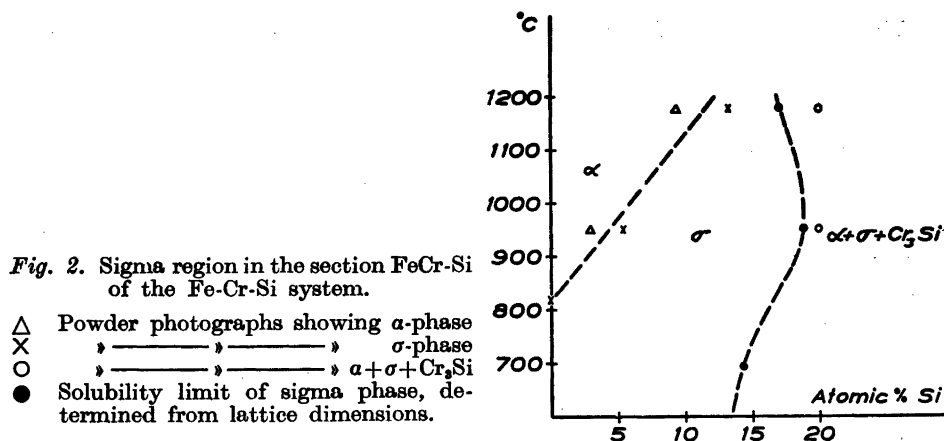
Fig. 1. Lattice parameters of σ-FeCrSi as functions of Si-content at 690°.

22—26 days; 950°, 7 days; 1 200°, 48 hours. All alloys containing less than 15 atomic % Si were analysed for Si and some alloys also for Fe and Cr. It was found that the atomic quotient Fe/Cr was constant = 1.01 with variations less than one per cent. This variation should not affect the lattice parameters more than within the experimental errors. Powder photographs were obtained in a Guinier type focusing camera, using CrKa-radiation. All specimens were mixed with some NaCl before the exposure and the camera constant was evaluated for each film, assuming the cube edge of NaCl to be 5.6394 Å (18° C) [5]. The agreement between observed and calculated $\sin^2\Theta$-values was ± 0.03 % and the lattice parameters were considered to be accurate to about 0.02 %. Because of the impurities present and a possible error in a_{NaCl}, all values may be subject to a small systematic error. These sources of error are, however, not likely to influence the changes of the lattice parameters.

Results

Alloys, annealed at 690°, showed only the sigma phase lines up to 14.4 atomic % Si. In the 17 % alloy the *110*-line of the α-phase could be observed. The changes of the lattice dimensions with Si-concentration are given in Fig. 1. The figure shows that σ-FeCr dissolves 14.2 % Si at 690° (estimated error about ± 0.5 %). Annealing of the 20 % alloy at 950° and 1 175° has shown that the upper solubility limit varies little with temperature (Fig. 2). At the lower solubility limit no two-phase range was observed between σ and α and for this reason the lower limit, outlined in Fig. 2, is only very approximate. In alloys, containing about 10 atomic % Si, the sigma phase is evidently

Fig. 2. Sigma region in the section FeCr-Si of the Fe-Cr-Si system.

△ Powder photographs showing α-phase
✕ 〃 ————— 〃 ————— 〃 σ-phase
○ 〃 ————— 〃 ————— 〃 $\alpha+\sigma+Cr_3Si$
● Solubility limit of sigma phase, determined from lattice dimensions.

stable up to near the melting point, since around this composition, this phase is the only one found even in the unannealed melts.

The changes of the lattice parameters with variation of the Si-concentration are small (Fig. 1 c). The unit cell volume decreases only 0.03 % per atomic % Si, which is about half the decrease when small amounts of Si ($<$ 10 atomic %) are dissolved in iron [6]. The axial ratio increases from 0.5181 to 0.5229 (Fig. 1 d) when the Si concentration is increased from 0 to 14 atomic % and the highest value of c/a which we have observed is 0.5246 (in an alloy annealed at 950°). The axial ratio is evidently very critical for the sigma structure. It is almost the same for all known sigma phases [7,7a] and the highest value hitherto reported is 0.5237 for σ-MoFe [8] which is only stable in a small temperature interval. It seems probable that when c/a exceeds 0.524 the sigma phase structure becomes energetically unfavourable and is not likely to be formed.

The influence of Si on FeCr-sigma phase formation is quite different from that of carbon [9] and nitrogen [10]. (Recent investigations at this institute indicate that boron behaves similarly to these elements.) When these small non-metals are present, Cr-rich carbides and nitrides are formed, thereby lowering the amount of Cr, available for sigma formation. Silicon, on the other hand, is dissolved in the sigma phase and expands its region of existence appreciably. When the solubility limit is exceeded we have found — confirming the results of Andersen and Jette [4] — that Cr-rich Cr_3Si and Fe-rich α-phase with about the same Si-content are formed. Thus, the equilibria in this part of the Fe-Cr-Si system indicate that Fe and Cr have about the same "affinity" towards Si.

The stabilizing effect of Si on the sigma phase is also revealed in the Cr-Ni-Si system, where this phase is easily formed when small amounts of Si are present but has not been found in the binary Cr-Ni system.

II. THE STRUCTURE OF σ-FeCrSi AND ITS RELATION TO SOME SILICIDE STRUCTURES

(B. Aronsson)

The crystal structure of the sigma phase has been determined by Bergman and Shoemaker [8] and by Dickins, Douglas and Taylor [11]. The unit cell is tetragonal and the space group is D_{4h}^{14}—$P4/m$ n m. The atomic parameters of FeCr, according to B. and S., are given in Table 1 together with the coordination numbers (C.N.) and the number of electrons which these authors have found in the different maxima of the electron density function. As pointed out in Refs.[8,11] the structure resembles that of β—U [12]. (The details of this structure are still under discussion [13].)

Following the nomenclature of Tucker [12], the structure can be described as built up of *main layers*, pseudohexagonal layers from which some atoms have dropped out. Between these are the *subsidiary layers*, the atoms of which are placed above and beneath the holes of the main layers. Atoms of successive subsidiary layers have close contact with each other and form straight rows, perpendicular to the layers.

The ordering in the sigma phase has been discussed in Refs.[8,11]. More definite results on this point have been obtained by Kasper and Waterstrat [14], who investigated the sigma phases, appearing in the Ni-V, Fe-V and Cr-Mn systems, using neutron diffraction. The conclusions of the latter authors are, that V, Cr and Mo (A metals) prefer the positions with the highest C. N. (II, III and V), while Fe, Co and Ni (B metals) prefer the positions with the lowest C. N. (I and IV). Mn can behave both as an A- and a B-metal. The sigma phase appears at different compositions in different systems. Of course, this affects the distribution of the atoms so that III and V may be more or less mixed positions. We have tried to determine if Si behaves as an A-metal, as a B-metal or as Mn.

Experimental

Powder photographs of alloys containing 0, 9.3 and 14.4 atomic % Si were microphotometered and the intensities determined. It was found that the intensity of the *002* powder line of the sigma phase decreased 33 ($\sim \pm 10$) % when its Si concentration increased from 0 to 14.4 %. This shows that the Si-atoms chiefly substitute atoms in the main layers. This is also to be expected from the lattice spacing relations. In order to get some information of the substitution within the main layers a single crystal investigation was undertaken.

A small crystal fragment was picked out of the 11.6 % alloy. When a narrow collimator was used the spots were split into triplets at high glancing angles. This did not affect the intensity measurements appreciably but made an accurate determination of the composition from its lattice parameters difficult. With a method described by Weisz, Cochran and Cole [15] (Θ-method) the a-axis of the crystal was found to be 8.758 Å ($\sim \pm 0.010$ Å), corresponding to a composition of 12—14 atomic % Si or 3.5—4 Si-atoms per unit cell. In this determination Cu$K\alpha$-radiation and the reflexion *11, 1, 0* were used. Efforts to get a better crystal were unsuccessful.

Weissenberg photographs were taken around the c-axis, using Mo$K\alpha$-radiation. The layer lines 0—4 were recorded. The multiple film method was used and the intensities of 110 nonequivalent reflexions were visually estimated. No deviation in the linear dependence of $\log \frac{I_{obs}}{I_{calc}}$ on $\left(\frac{\sin \Theta}{\lambda}\right)^2$ was observed. The temperature constant B was found to be

0.77 Å^3. Using the structure of Bergman and Shoemaker [9], the observed F-values were put on an absolute scale. The temperature factors were divided out and a threedimensional Fourier-synthesis $\left(\dfrac{x}{60}\ \dfrac{y}{60}\ \dfrac{z}{24}\right)$ was made with the aid of the Hägg-Laurent [16] machine. The number of electrons in the different maxima of the electron density function were summed. With these atomic numbers and the parameters of Bergman and Shoemaker a three-dimensional $F_0 - F_c$ synthesis was worked out in the section $xy0$. Small maxima of nearly the same height were found at the assumed atomic positions — confirming that the result of the electron counts fitted well to the intensity data. The atomic coordinates, determined from the difference synthesis, were not significantly different from those of Bergman and Shoemaker. The background indicated that a standard deviation in number of electrons of 0.5 e for the atoms II, III and IV and of 1.0 e for the atom I was reasonable. The same value was obtained with a formula given by Cruickshank [17].

The distribution of Si-atoms may, of course, vary with annealing temperature and Si-content. It should be emphasized that the results of this investigation have been obtained from a 12 % alloy, annealed 22 days at 690°.

Results and discussion

The result of the electron counts is given in Table 1, column 5. The number of electrons found in position IV is about 10 % lower than the numbers found in the other positions. The considerations of the preceding paragraph indicate that this difference is significant. Certainly there are many factors which may influence the result of electron counts, but the most reasonable interpretation

Table 1.

	Position [8]	Parameters [8]		C.N. [8]	Atomic number in σ-FeCr [8]	in σ-FeCrSi $_{0.25}$
I	2(a)			12	28.1	26.0
II	4(f)	$x = 0.3981$		15	23.8	23.8
III	8(i)	$x = 0.4632,$	$y = 0.1316$	14	25.8	24.2
IV	8(i)	$x = 0.7376,$	$y = 0.0653$	12	25.8	21.6
V	8(j)	$x = 0.1823,$	$z = 0.2524$	14	23.3	24.1

of the above mentioned result is that the Si-atoms mainly occupy IV-positions. That is, Si behaves as a B metal. If the metal atoms are ordered as Kasper and Waterstrat [14] suggest, the approximate distribution of atoms in σ-FeCrSi— should be: mainly Fe in I, mainly Cr in II, about 3 Si- and 5 Fe-atoms in IV and a mixture of Fe and Cr (and perhaps a little Si) in the III- and V-positions.

That silicon behaves as a B-metal in σ-FeCr is in accordance with the facts that the solubility of Si is greater in Fe (26 atomic %)[6] than in Cr (< 14 %)[18] and that the highest coordination number of Si in any known silicide structure is 12. At first glance, it seems curious that no Si-atoms are found in I-positions. Inspecting Fig. 3 a more closely we see, however, that if more than two Si atoms shall be placed in the unit cell the IV-positions alone permit a more even distribution of the Si-atoms in the structure, than does a combination of I- and IV-positions. If Si-Si contacts are to be avoided, a maximum of four Si-atoms per unit cell can occupy the positions, having 12 coordination, and this can only be achieved if IV-positions alone are occupied. It must be mentioned that the solubility limit corresponds to about four Si-atoms per unit cell.

There are some interesting common features in the sigma- and the cubic A 15-(or W_3O-[19]) structures in both of which straight rows of metal atoms with close contact are found. Inspecting Figs. 3 a and 3 d and Table 2, we see that the III-atoms of the sigma phase have two close and eight remote A-metal neighbours as well as four B-metal neighbours at "normal" distances, while the Cr-atoms of Cr_3Si [18] (W_3O-type) are surrounded by $2 + 8$ Cr-atoms and 4 Si-atoms at similar distances. The figures further show that the spatial arrangements of atoms around the III- and V-atoms are roughly the same as around the Cr-atoms of Cr_3Si. On the other hand, the I- and IV-atoms have environments, similar to that of the Si-atom of Cr_3Si. These similarities are only qualitative, but it is interesting to note that — following the nomenclature of Kasper and Waterstrat [14] — all the hitherto reported phase of W_3O-type [20,20a,20b,31] can be written A_3B, where we have to add Ti, Zr, Nb, Ta and W to the A-metals and Ru, Rh, Os, Ir, Pt, Au, Hg, Ga, Sn, Si, As and

Table 2. Interatomic distances (in Å units).

	Sigma-structure [6]								Cr_3Si [18]		
I—IV	2.380	(4)		IV—I	2.380	(1)			Si—Cr 2.55	(12)	
—V	2.542	(4)	} 2.51	—IV	2.453	(1)					
—II	2.603	(4)		—III	2.470	(2)					
				—III	2.476	(1)					
				—III	2.483	(1)	} 2.53				
				—V	2.538	(2)					
				—V	2.562	(2)					
				—II	2.695	(2)					
III—III	2.404	(1)	} 2.41	V—V	2.253	(1)	} 2.27				
—II	2.414	(1)		—V	2.294	(1)			Cr—Cr 2.28	(2)	
—IV	2.470	(2)		—IV	2.538	(2)					
—IV	2.476	(1)	} 2.48	—I	2.542	(1)	} 2.55	Cr—Si 2.55	(4)		
—IV	2.483	(1)		—IV	2.562	(2)					
—V	2.763	(2)		—III	2.763	(2)					
—V	2.768	(2)	} 2.80	—III	2.768	(2)					
—III	2.838	(4)		—II	2.833	(2)	} 2.81	Cr—Cr 2.79	(8)		
				—II	2.920	(1)					

Sb to the B-metals given by these authors. Perhaps, some general principle accounts for the structural similarities between V_3Ni [21] (W_3O-type) and σ-NiV [14] as well as between Cr_3Si and σ-FeCrSi.

As seen from Figs. 3 b and 3 e, the concepts of main and subsidiary layers are also very suitable for the description of two other silicide structures, namely the W_5Si_3—[22,23] (T1-) [24] and $D8_8$[25]-structures. The main layers are more irregular than in the sigma phase, but the short distances between atoms of successive subsidiary layers and the characteristic 14-coordination around these atoms are also found here. In W_5Si_3, the structure of which can be described as a combination of the sigma- and the $CuAl_2$-structures, both Me- and Si-rows are found. In order to be stable such a structure probably demands shorter distances in the rows than do structures which contain only Me-rows (*e. g.*, $D8_8$). The discussion of the sigma- and W_3O-structures has shown that rows with the closest interatomic contact are most easily formed by the metals
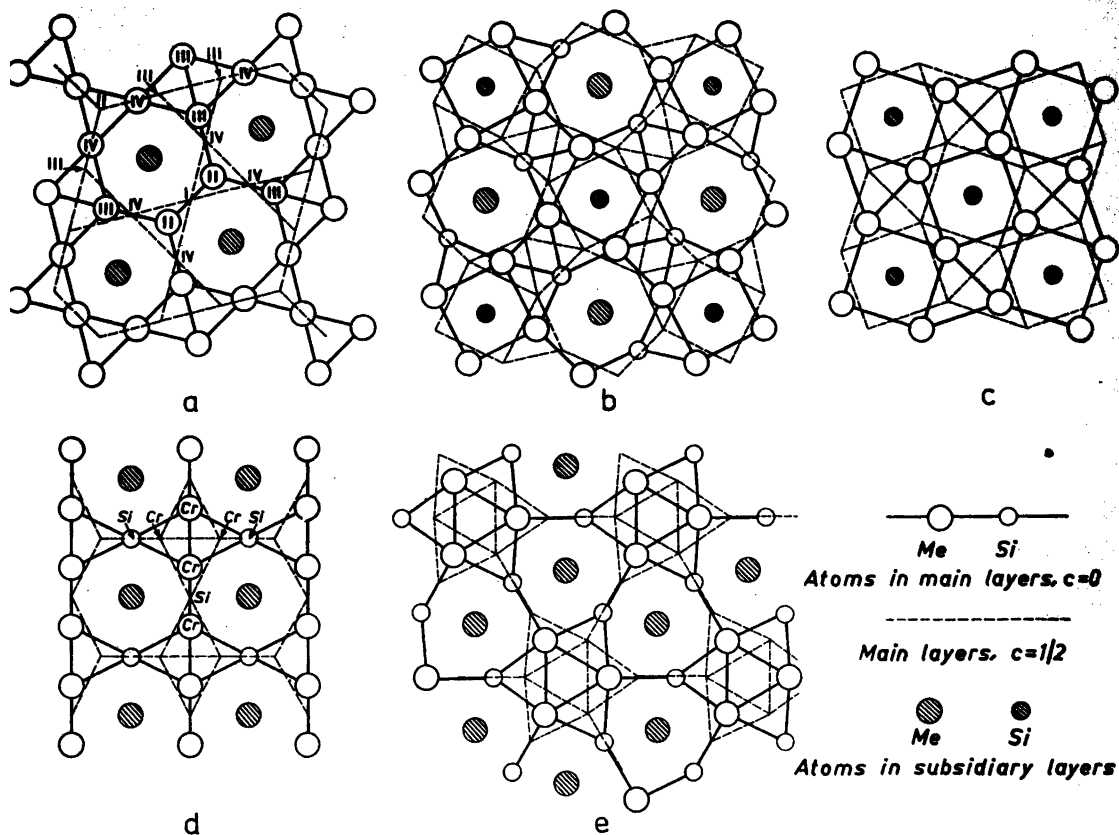
Fig. 3. The sigma structure and some silicide structures. a. σ -FeCr [8]. b. W_5Si_3 [22,23]. c. Ta_2Si [30] (CuAl$_2$-type). d. Cr_3Si [18]. e. Mn_5Si_3 [25]. The layers are parallel to the plane of the paper. (In $D8_8$ the main layers are found in the planes $c = 1/4$ and $c = 3/4$.)

of the Va and VIa groups. This may be part of the explanation of the curious morphotropy among the Me_5Si_3-phases: Ti_5Si_3 [26] $(D8_8)$, V_5Si_3 [27] $(T1)$, Cr_5Si_3 [22] $(T1)$, Mn_5Si_3 [25] $(D8_8)$ and Fe_5Si_3 [6] $(D8_8)$ with the following interatomic distances in the metal rows: 2.58 Å, 2.37 Å, 2.30 Å, 2.40 Å and 2.36 Å. Recently these phases have been comprehensively discussed by Nowotny and his school [24,28].

As pointed out by Bergman and Shoemaker [8], Fe_7W_6 is structurally related to the sigma phases. In the rhombohedral Fe_7W_6 [25]-structure, groups of four W-atoms are found on the trigonal axis. The distances between adjacent atoms of such a group are less than in elementary W.

The most conspicuous structural feature of all these metallic phases are the straight rows of atoms with close contact. These rows are most easily formed by the transition metals of the Va- and VIa-groups. They are found in a number of common silicide structures, which indicates that silicon has

some beneficial effect on the stability of these rows. As long as so little is known about the electronic structures of the transition elements, it is probably meaningless to try to give a more fundamental explanation of the mentioned facts.

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