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An Investigation of the Me_5Si_3-MeSi Region of the Mn-Fe-Si and some Related Systems

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From X-ray diffraction data it has been concluded that there is a Me_5Si_3-MeSi two phase region in the Mn—Fe—Si systems at 950°C. The lattice parameters of the MeSi and Me_5Si_3 phases as functions of composition have been determined as well as tie lines in the two phase region. Some observations on the corresponding part of the Cr—Mn—Si, Cr—Fe—Si and Cr—Co—Si systems have been made.

It has been found that the metal with the higher atomic number is enriched in the cubic MeSi phase which is the Si richest phase present in the investigated region of the systems mentioned. The relation of the lattice parameter variations of the Me_5Si_3 phases to the morphotropy of these phases is discussed.

The physical and chemical properties of the borides, carbides and nitrides of the first transition series metals show that the stability of these compounds decreases with increasing atomic number of the metal [1,2,21,22]. In accordance with this decrease in transition metal-non metal "affinity" it has been observed that in Me_1-Me_2-X systems (Me = transition metal from the first transition series, X = nonmetal) the metal with the lower atomic number is concentrated in the X richest phase present [3–6]. This was found to be so in the Me_2B-MeB two phase region of Me_1-Me_2-B systems, in which Hägg and Kiessling [6] determined the distribution of various metal pairs between the two phases mentioned. They found that the larger the difference in atomic number of the metals the more pronounced was the enrichment of the lower atomic number metal in the MeB phase.

In order to see if similar trends were displayed by Me_1-Me_2-Si systems, the Me_5Si_3-MeSi section of some ternary silicide systems has been studied. From older work it is known that Mn_5Si_3 [7] and Fe_5Si_3 [8] as well as MnSi [9] and FeSi [10] are isomorphous. Preliminary experiments indicated that there was a Me_5Si_3-MeSi two phase region in the Mn-Fe-Si systems. The main interest has been devoted to this system as the distribution of the Mn and Fe atoms could be determined in the same way as in the ternary boride systems [6].

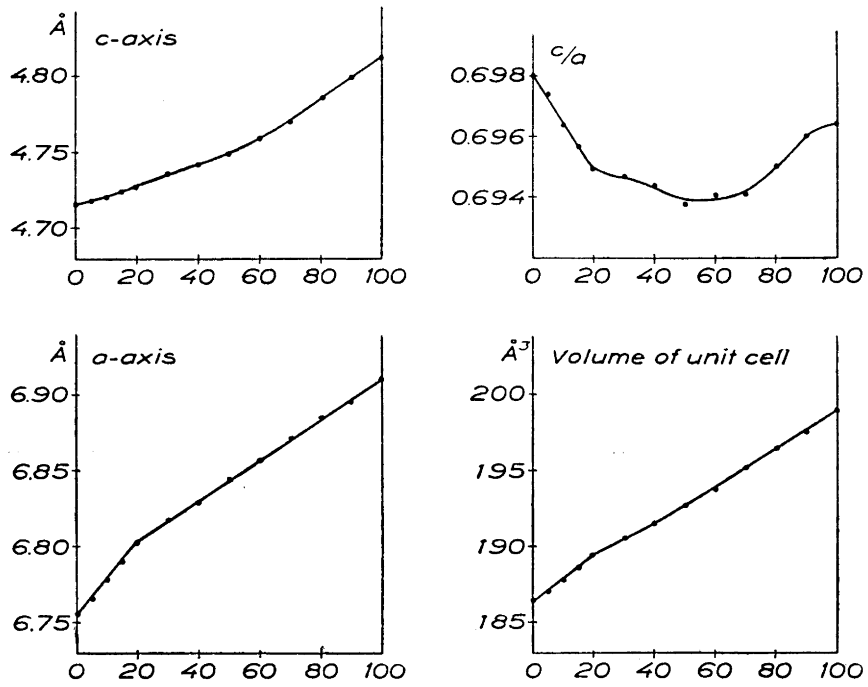

Fig. 1. Unit cell dimension of the Me_5Si_3 phase as function of the atomic ratio Mn/(Mn + Fe) × 100.

In connexion with these investigations information has been collected about the variation of the lattice parameters (l.p.) of the Me_5Si_3 phases with composition. Some relation between these l.p. variations and the morphotropy among the Me_5Si_3 phases has been found and is discussed in the last part of this paper.

EXPERIMENTAL

Weighed amounts of the elements in powder form (claimed purity $\geq$ 99.8 % except for Co which contained 0.45 % Ni) were melted twice in an arc furnace and subsequently annealed in evacuated silica tubes for 8 days at 950°C. As it was found that the compositions obtained from chemical analysis deviated very little from the nominal composition only six alloys were analysed. The analyses added up to 99.2 $\pm$ 0.5 %.

24 alloys were made in the Mn—Fe—Si system, 13 on the Me_5Si_3 line (4 analysed), 4 on the MeSi line (2 analysed) and 7 with compositions $MeSi_{0.75}$ or $MeSi_{0.80}$. Four of the Me_5Si_3 alloys contained traces of a (FeMnSi) and one of (Mn, Fe)Si. For these alloys the Mn/Fe ratio in the Me_5Si_3 phase may be slightly different from that in the alloy. However, this difference was estimated to be too small to affect the l.p. of Me_5Si_3 significantly. In each of the Cr—Me′—Si systems (Me′ = Mn, Fe, Co) four alloys were made with compositions $Cr_{0.2}$ $Me'_{0.8}$ $Si_{0.63}$, $Cr_{0.4}$ $Me'_{0.6}$ $Si_{0.63}$, $Cr_{0.6}$ $Me'_{0.4}$ $Si_{0.63}$ and $Cr_{0.8}$ $Me'_{0.2}$ $Si_{0.63}$.

Powder photographs were taken in a Guinier type focussing camera, using Cr$K\alpha$-radiation. All powder samples were mixed with some CaF_2 before the exposure and the l.p. which are thought to be reliable to about $\pm$ 0.03 % are given assuming the cube edge of CaF_2 to be 5.4630 Å [11] at 21°C.

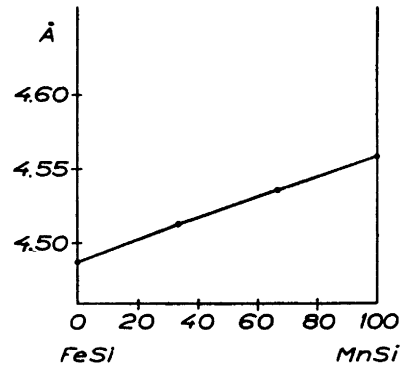

Fig. 2. Cube-edge of the MeSi phase as function of the atomic ratio Mn/(Mn + + Fe) × 100.

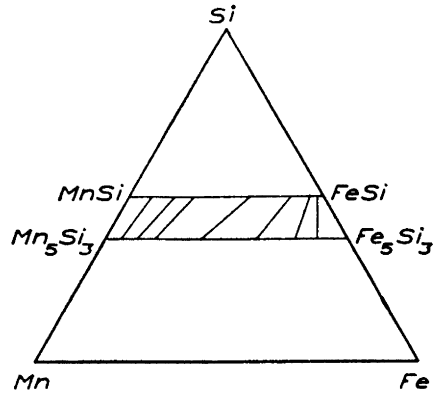

Fig. 3. Some tie lines in the Me_5Si_3-MeSi region of the Mn—Fe—Si system at 950°C.

RESULTS

The Mn-Fe-Si system. All the Me_5Si_3 alloys showed sharp and unsplit powder lines corresponding to the $D8_8$-structure [8]. The variations of the unit cell constants with composition are given in Fig. 1. It was concluded that, at 950°C, the Me_5Si_3 line in the Mn-Fe-Si system is a single phase line (or very nearly so). Similarly it was found that the MeSi line is a single phase line (Fig. 2). For the alloys in the two phase region the l.p. (lattice parameters) of the two phases were determined. From the curves in Fig. 1 and 2 the composition of the two phases in equilibrium with each other was obtained and tie-lines in the Me_5Si_3-MeSi two phase region could be drawn (Fig. 3).

The distribution ratios have been defined and determined as in the paper by Hägg and Kiessling [6]. Let x'_{Mn} be the atomic fraction Mn/(Mn + Fe) and x'_{Fe} the atomic fraction Fe/(Mn + Fe) in the Me_5Si_3-phase. x''_{Mn} and x''_{Fe} are the corresponding fractions in the MeSi phase. In order to be ≤ 1 the distribution ratios are defined as $\alpha_{Mn} = x''_{Mn}/x'_{Mn}$ and $\alpha_{Fe} = x'_{Fe}/x''_{Fe}$. The variations of the distribution ratios as function of $(x'_{Mn} + x''_{Mn})/2$ are given in Fig. 4.

As seen from Fig. 3 and 4, iron is enriched in the MeSi phase. At small Fe concentrations about twice as much iron will be found in this phase as in the Me_5Si_3 phase.

The Cr-Me'-Si systems (Me' = Mn, Fe, Co). Besides the cubic MeSi phase the (Cr, Mn)$Si_{0.63}$ and (Cr, Fe) $Si_{0.63}$ alloys were found to contain Cr_5Si_3 with dissolved Mn or Fe (T 1 (W_5Si_3)-type structure) [12–14] and (or) Mn_5Si_3 (Fe_5Si_3) with dissolved Cr ($D8_8$-type structure [7]). In these systems there are probably a T 1-MeSi two phase region, a T 1-$D8_8$-MeSi three phase region and a $D8_8$-MeSi two phase region. The composition of the MeSi phase could be estimated from its l.p. which was assumed to vary according to Vegard's law from

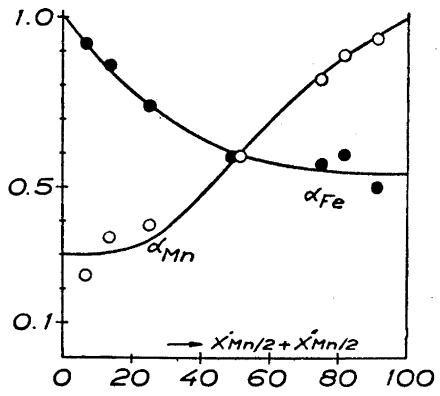

Fig. 4. The distribution ratios α_{Fe} and α_{Mn} as function of $(x'_{Mn} + x''_{Mn})/2$ (See text).

CrSi to MnSi and from CrSi to FeSi. It was found that Mn and Fe, respectively, were enriched in this phase and this enrichment was more marked for Fe.

In all the (Cr, Co)$Si_{0.63}$ alloys the MeSi phase had a cube edge of 4.449 ± 0.004 Å which corresponds closely to that of pure CoSi (4.447 Å) [9]. Therefore, in the Cr-Co-Si system practically pure CoSi is in equilibrium with some Si poorer phase (or phases).

Thus, it has been found that in the investigated part of the Cr-Me'-Si systems the metal with the higher atomic number is concentrated in the MeSi phase.

The l.p. vs composition curves. The unit cell constants of the $D8_8$ phase vary quite irregularly from Mn_5Si_3 to Fe_5Si_3. Especially remarkable is the variation of c/a which goes through a minimum at about $(Fe_{0.5}Mn_{0.5})_5Si_3$. No careful determinations of l.p. variations of the Me_5Si_3 phases in the other systems were made but it was observed that when Cr was dissolved in Mn_5Si_3 or Fe_5Si_3 there was a decrease in c/a for the $D8_8$ phase while the solution of Mn or Fe in Cr_5Si_3, on the contrary, increased the c/a ratio for the latter phase.

DISCUSSION

This study of the Me_5Si_3-MeSi region of some Me_1-Me_2-Si systems (Me = Cr, Mn, Fe, Co) has revealed regular trends in the distribution of the metals: The larger the difference in their atomic number the more pronounced is the enrichment of the *higher* atomic number metal in the MeSi phase. This behaviour is opposite to that found in ternary boride and carbide systems of the same metals: In these systems the *lower* atomic number metal is always concentrated in the nonmetal richest phase. Results of investigations of this type certainly depend on the parts of the ternary systems which are actually studied and no farreaching conclusions can be drawn from the above observations. It seems, however, as if the silicides of Cr, Mn, Fe, Co do not show the same decrease in stability with increasing atomic number of the metal as do the borides, carbides and nitrides.

The l.p. variations of the T 1 and $D8_8$ phases may be worth a few comments. Of the Me_5Si_3 silicides of the first series transition elements Ti_5Si_3 [15], Mn_5Si_3 [7] and Fe_5Si_3 [8] have the $D8_8$ structure while V_5Si_3 [16] and Cr_5Si_3 [13] have the T 1 (W_5Si_3) structure. In the presence of small amounts of carbon, V_5Si_3 (C) [17] and Cr_5Si_3(C) [18] also crystallize in the $D8_8$ structure. The Me_5Si_3 phases belong to a group of phases the structures of which are characterized by straight rows of atoms. In the T 1 and $D8_8$ phases these rows run parallel to the c-axis and the smaller c/a-value these phases have, the shorter are the interatomic distances in the rows ($= c/2$) compared with the average interatomic distances in the structure. Looking at the c/a values of the $D8_8$ phases (V_5Si_3 and Cr_5Si_3 contain some C) we see that the smallest values are found for V and Cr

		Ti	V	Cr	Mn	Fe
$D8_8$	c/a	0.691	0.679	0.676	0.696	0.698
	$c/2$	2.59 Å	2.42 Å	2.36 Å	2.41 Å	2.36 Å
T 1	$c/2$		2.38 Å	2.30 Å		

This gives sense to the fact that c/a for Mn_5Si_3 and Fe_5Si_3 decreases (to about 0.684 and 0.693, respectively) when Cr is dissolved in these phases. It is also compatible with the general observation that rows with the closest contacts between the row atoms are formed by the Va and VIa groups metals (*e.g.* in phases of the β-W and σ-type).

As seen from the table the distances between row atoms ($= c/2$) in the V_5Si_3 and Cr_5Si_3 T 1 phases are still shorter than in the $D8_8$ phases of these metals, which indicates that the atomic arrangement in the T 1 structure is such that the row atoms are closer to each other than they would be in a $D8_8$ structure of the same elements. The Va and VIa group metals being those which form rows with the shortest contact, it is not surprising that the T 1 structure is chosen by V_5Si_3 and Cr_5Si_3 while Ti_5Si_3, Mn_5Si_3 and Fe_5Si_3 crystallize in the $D8_8$ structure.

In a number of investigations it has been shown that several $D8_8$ phases only exist as ternary phases [*e.g.* V_5Si_3 (C) [17] and Cr_5Si_3 (C) [18]] containing small amounts of a third component (B, C, N or O) [19,20]. It is possible that Ti_5Si_3, Mn_5Si_3 and Fe_5Si_3 are in reality ternary phases, too, owing their existence to the presence of small non metals such as C, N or O, but this has not yet been proved.

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