Journal of Alloys and Compounds, 203 (1994) 259–265
JALCOM 877

Phases in rapidly cooled scandium–silicon samples

V. Kotroczo and I.J. McColm
Department of Industrial Technology, University of Bradford, Bradford BD7 1DP (UK)

(Received April 2, 1993; in final form July 8, 1993)

Abstract

Small, 0.5 g, samples of high purity Sc–Si compositions have been melted in an argon arc furnace and cooled at 150–200 °C s^{-1} while their surface temperatures have been monitored. From the cooling curves and microscopic, hardness, X-ray powder and differential thermal analyses, a phase diagram is suggested which has many similarities to the most recently proposed phase diagram, but does contain evidence for a peritectically formed Sc_5Si_4 phase. The highest silicide is non-stoichiometric within the range $ScSi_{1.22}$–$ScSi_{1.67}$.

1. Introduction

A recent review of the thermodynamic data for transition-metal silicides [1], emphasizes that uncertainty and controversy still exist over which phases occur in many lanthanide–silicon systems, while the melting points for several compounds are as yet undetermined. Where more detailed studies have been reported [2–4] lanthanide silicides are usually characterized by high melting points and very small ranges of non-stoichiometry. The normally congruent melting Ln_5Si_3 phase in some cases has a potentially useful reaction with hydrogen [4–6]. Although Sc_5Si_3 does not easily absorb hydrogen [7], it has been shown to have a beneficial effect on the hydrogen reactivity of other Ln_5Si_3 phases [6].

In the course of making Sc_5Si_3 for hydride studies it was possible to make a more extensive thermal analysis, as well as X-ray, metallographic and hardness investigation of the Sc–Si system. Some of this data is reported here because, in part, it supports the most recent investigation given in ref. 2, adds to it, and helps to clarify the "$ScSi_2$" controversy. The investigation by Eremenko *et al.* of the Sc–Si system [2] reports three stable compounds: a congruently melting Sc_5Si_3 phase, melting point 2060 °C; a peritectic phase ScSi with a peritectic temperature of 1785 °C; and a peritectic phase Sc_2Si_3, that is formed by the reaction: liquid + ScSi $\rightarrow$ β-Sc_2Si_3 at 1260 °C, but is peritectoidally decomposed at 925 °C to ScSi plus Si after first undergoing a solid-state transformation at 1070 °C. All the experimental work reported in ref. 2 was undertaken with scandium of relatively low purity, and when some samples were re-made with high purity sublimed scandium decreases of some 75 °C in the cooling arrest temperatures were noted. Furthermore it was mentioned that several unaccounted for lines occurred in X-ray patterns obtained for samples in the composition range Sc_5Si_3 to ScSi. In an examination of the Y–Si system [3] a Y_5Si_4, peritectically formed, phase was noted, and, since scandium and yttrium have many similarities the absence of such a phase in the Sc–Si system might be unexpected.

Earlier reports describe a stable Sc_3Si_5 phase [7, 8], rather than the Sc_2Si_3 reported in ref. 2. Earlier Schob and Parthe [9] suggested that the highest silicide had the composition $ScSi_{1.50}$. After long annealing, 350–750 h at 800 °C, the highest silicon content silicide is reported as decomposing into ScSi plus silicon when studies were made in ternary systems such as Sc–Cr–Si [10] and Sc–Fe–Si [11]. Eremenko *et al.* [2] confirmed this behaviour in the phase diagram resulting from their work. Furthermore, when investigating the thermodynamics of alloys in the Sc–Si system containing more than 50 at.% Si, Lukashenko *et al.* [12] found the e.m.f. to be independent of composition in the temperature range 840–980 K; from which they concluded that $ScSi_{1.5}$ was unstable. Moreover, Lukashenko noted that two stable phases Sc_5Si_3 and ScSi were formed from the elements accompanied by significant heat effects and a considerable decrease in entropy to give thermodynamically, very stable compounds; Sc_5Si_3 had $\Delta H_f = -102.8$ kJ mol^{-1} and ScSi had ΔH_f -87.1 kJ mol^{-1}; because of the perceived instability of the $ScSi_{1.67}$ phase no enthalpy of formation value was quoted. Here we report new results from higher purity elements, which although obtained from the molten state with relatively rapid cooling rates, 150–200 °C s^{-1}, contribute

SSDI 0925-8388(93)00877-2

to the knowledge of the phase relationships in the scandium–silicon system.

2. Experimental details

Small samples in the weight range 0.2–0.5 g were prepared from silicon lump of purity 99.999% and sublimed scandium pieces of purity 99.99%, both supplied by Johnson Matthey Ltd. Compositions were prepared without filing, mainly by shearing in an argon-filled glovebox to reduce contamination. Melting was achieved in a very small argon arc furnace of unique design [4], utilizing an argon atmosphere in excess of 1 atm pressure flowing over the melt. To ensure homogeneity, each sample was melted three times, turning over between melts without opening the furnace and so limiting possible contamination. Only samples where the decrease in final weight after the three melts was less than 0.3% were taken for further investigation. By monitoring the surface of the small beads after the arc was switched off, using an IRCON pyrometer, cooling curves for each composition were established. In order to compensate for the emission effect some samples were calibrated on the differential thermal analysis (DTA) apparatus.

A very limited number of compositions were examined on the Linzeiss high temperature DTA apparatus capable of operating up to 2200 °C in an argon atmosphere. The heating and cooling rates used were 10 °C min^{-1}. Surface-oxidized tantalum crucibles were used with a tungsten powder standard and samples approximately 0.2 g. Samples were prepared for optical and microhardness measurements by polishing with diamond paste down to 1/2 μm grit size. A Leitz miniload hardness tester was used with a Vickers diamond and a 1.96 N load applied for 15 s. This load produced well-defined, crack-free indents for scandium-rich alloys but had to be reduced to 0.98 N to obtain clear indents on silicon-rich samples. No etching was necessary when plane polarized light was used to view the surface. The values for hardness used to construct Fig. 5 were the mean of 16 indents made at random positions on the surface.

All the samples were subjected to X-ray powder analysis using Cu Kα_1 radiation in an XDG-700 Guinier–Hägg focusing camera.

3. Results

Figure 1 is a collection of all the observed arrest temperatures on the cooling curves and Fig. 2 shows two typical cooling curves indicating liquidus and solidus points for samples containing 10 and 14 at.% Si; it was from these and other curves of samples between

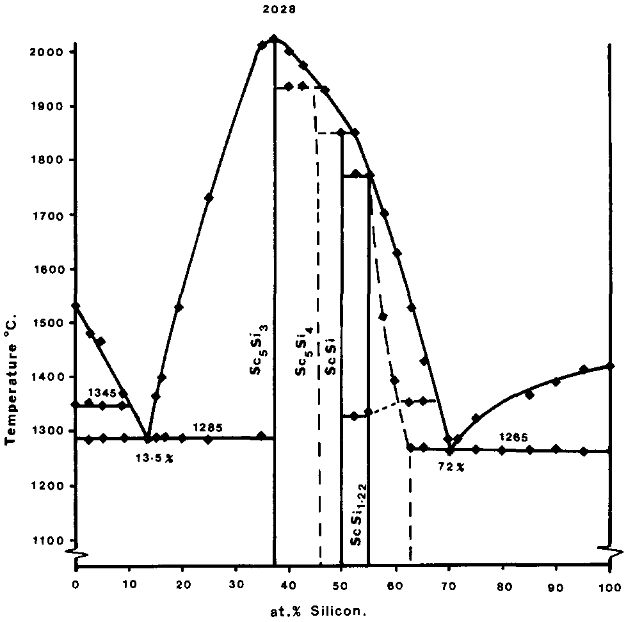

Fig. 1. A diagram showing phase relationships for rapidly cooled samples in the Sc–Si system compiled from cooling curve data.

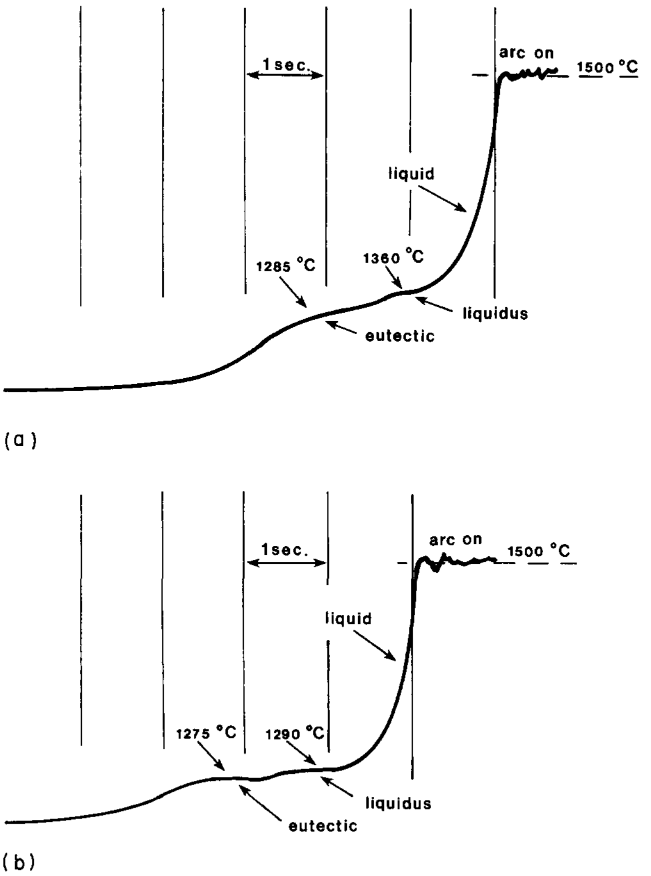

Fig. 2. Two typical cooling curve traces for samples cooled at rates in the range 150–200 °C s^{-1}; (a) for 10 at.% Si; (b) for 14 at.% Si.

10 and 14 at.% Si that the eutectic was established at 13.5 at.% Si and 1285 °C. The DTA traces for compositions between Sc and Sc_5Si_3 confirm that the region of the diagram drawn as Fig. 1 is in agreement with ref. 2, even though slow cooling and heating rates 10 °C min^{-1} were used compared to the 150–200 °C s^{-1} cooling rates apparent from Fig. 2. The congruent melting of the Sc_5Si_3 at 2028 °C was confirmed by the DTA method. Two peaks for 11.5 at.% Si and the sharp melting point at 2025 °C for Sc_5Si_3 are shown in Fig. 3.

Metallographic examination and the X-ray powder results all confirmed a simple eutectic behaviour for the composition range Sc to Sc_5Si_3. In the composition range between Sc_5Si_3 and ScSi the cooling curves reveal two regions of quite complex behaviour on either side of the sample containing 45 at.% Si.

Between the composition corresponding to Sc_5Si_3 and that of Sc_5Si_4 the cooling curves are characteristic of a peritectic process and the microstructures of such samples do not disagree with such an interpretation as Fig. 4 indicates. Figure 4 is a micrograph of the preparation containing 45 at.% Si; a light-grey phase forms in the core leading to a darker-grey material and is probably the phase with the highest melting point, Sc_5Si_3. Reaction of this solid with liquid of composition of about ScSi probably results in the dark-grey phase which, by analogy with the Y–Si system [3], is Sc_5Si_4. The darkest areas on Fig. 4 are believed to account for ScSi which was identified in the X-ray films arising from samples in this composition range.

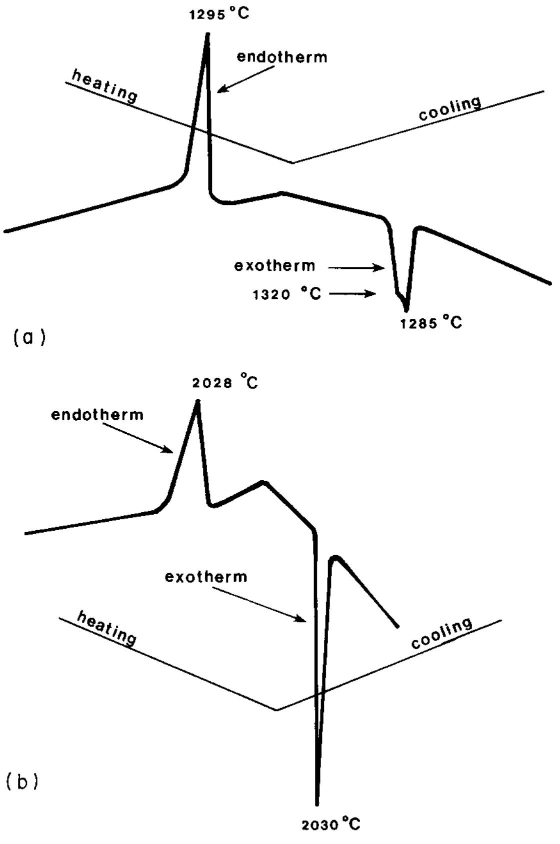

Fig. 3. Two high temperature DTA traces for (a) 11.5 at.% Si; (b) congruently melting Sc_5Si_3.

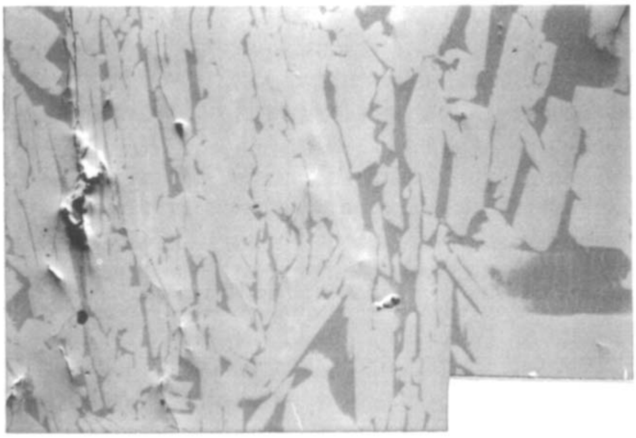

Fig. 4. Micrograph of an arc cast sample containing 45 at.% Si.

TABLE 1. Observed and calculated $Sin^2\theta$ values for lines from an orthorhombic Sc_5Si_4 phase

hkl	Relative intensity	$Sin^2\theta$ (obs)	$Sin^2\theta$ (calc)[a]
102	vf	0.0611	0.0609
201	vf	0.0642	0.0638
032	vf	0.0785	0.0790
050	m	0.0865	0.0863
132	s	0.0921	0.0920
150	f	0.0990	0.0991
042	f	0.1038	0.1032
310	m	0.1092	0.1095
212	vf	0.1128	0.1130
241	f	0.1187	0.1188
060	n	0.1240	0.1240
320	vf	0.1300	0.1298
014	vf	0.1950	0.1954
303	vf	0.2239	0.2241
360	vf	0.2400	0.2401
063	vf	0.3278	0.3280
225	vf	0.3649	0.3653
512	vf	0.3741	0.3739

[a] The calculated values are for an orthorhombic unit cell; $a = 0.678(2)$ nm, $b = 1.311(4)$ nm, $c = 0.703(1)$ nm; vf = very faint; f = faint; m = medium; s = strong.

All X-ray powder analyses made on samples in the range of 37.5 to 50 at.% Si were quite complex but were indexed satisfactorily if Sc_5Si_3 and ScSi were assumed to be present with a hitherto unencountered orthorhombic phase. Table 1 shows the lines which were left when all reflections from Sc_5Si_3 were removed from the pattern and had good agreement with a calculated pattern for an orthorhombic unit cell with the parameters given in Table 1. The quality and intensity of the lines on the films from this phase improved when the composition was closest to Sc_5Si_4. Despite this observation, the several annealing procedures to which these samples were subjected produced almost no change in the phase distribution. Annealing in vacuum at 1600 °C for 24 h, or for 48 h at 1500 °C, with slow cooling at 1 °C min^{-1}, was tried to little effect. At 50 at.% Si even the fast-cooled samples were almost single-phase ScSi with an orthorhombic X-ray unit cell, and to obtain effectively phase-pure material at 50 at.% Si composition, only a very short anneal in vacuum at 1500 °C was required.

The region between ScSi and $ScSi_2$ was characterized by cooling curves that were more difficult to interpret and provided observations most in conflict with the data in ref. 2. The cluster of variable thermal effects between 1325 and 1350 °C in samples within the composition range $ScSi_{1.1}$–$ScSi_{1.86}$ is most perplexing and is perhaps best interpreted in terms of a $\beta \rightarrow \alpha$ phase transition of the highest silicon content silicide phase. Some tentative possibilities are suggested by the dotted lines in Fig. 1. X-ray powder analyses of these samples could be interpreted as mixtures of ScSi, silicon and an 'AlB_2'-type structure material which was the highest silicon content silicide.

The data was more carefully examined for samples in the composition range $ScSi_{1.11}$ to $ScSi_{1.66}$ and the following features emerge. First an AlB_2-type hexagonal phase can be identified in all samples, with the lattice parameters increasing as the silicon content increases. This supports the view that the highest silicon content phase is non-stoichiometric. The $ScSi_{1.11}$ composition has a very strong pattern of lines for ScSi plus a weak AlB_2-type phase with $a = 0.3656$ nm and $c = 0.3872$ nm, whereas at $ScSi_{1.66}$ the AlB_2-type phase is very strongly present, $a = 0.3662(9)$ nm and $c = 0.3879(5)$ nm, plus lines from free silicon and one or two very faint extra lines. Between these compositions the parameters change for the AlB_2-type phase as indicated in Table 2, but for all three compositions between $ScSi_{1.11}$ and $ScSi_{1.16}$ a varying number of unindexed lines occur, none of which correspond to ScSi or silicon. The calculated lattice parameter for $ScSi_{1.22}$, assuming an AlB_2-type phase, is out of line and on re-examination indexing of almost all lines in the pattern can be achieved for an orthorhombic cell with $a = 0.827(9)$ nm, $b = 0.869(7)$ nm, $c = 0.998(9)$ nm. This could be the result of $ScSi_{1.22}$ being the quenched high temperature form of "$ScSi_{1.66}$". All materials with greater silicon contents than 62.5 at.% Si contained free silicon.

From the complete range of arc-melted samples made here it was possible to establish the composition–hardness plot which is shown as Fig. 5. Phases shown to exist in this work have the hardness values listed in Table 3, from which it can be seen that free Sc metal, free silicon and the peritectically formed ScSi are relatively easy to identify when present in mixtures. The hardness technique was useful in helping to confirm the X-ray phase analysis for some compositions exhibiting complex freezing processes; Fig. 6 shows indents made in the ScSi phase surrounded by areas of the $ScSi_{1.22-1.67}$ phase.

TABLE 2. X-ray phases and lattice parameters for the AlB_2-type phase in samples containing 52–63 at.% silicon

Composition	AlB_2-type phase			Other phases
	Intensity	Lattice parameters (nm)		
		a	c	
$ScSi_{1.11}$	VVW	0.3656	0.3872	very strong ScSi
$ScSi_{1.22}$	VS	0.3842(9)	0.4145(7)	many unidentified lines[a]
$ScSi_{1.35}$	M	0.3660(8)	0.3876	few weak orthorhombic lines
$ScSi_{1.50}$	M	0.3665(9)	0.3880	one or two weak lines
$ScSi_{1.66}$	S	0.3662(9)	0.3879(5)	silicon plus two very weak lines

[a] When re-indexed as orthorhombic ($a = 0.827(9)$ nm, $b = 0.869(7)$ nm, f.c.c. $= 0.998(9)$ nm) almost all the lines are accounted for and no AlB_2-type phase remains.

4. Discussion

Considering all the cooling curves that were obtained in conjunction with the annealing experiments and the limited number of DTA scans, Fig. 1 is an attempt to rationalize the data. It produces a diagram for the system which has several features in reasonably close agreement with that produced by Eremenko *et al.* [2] and can be discussed in terms of their interpretation. In such a comparison the following points emerge:

(1) At the scandium-rich end of the diagram there is surprisingly good agreement considering the great differences in technique and material purity used in the two studies. Here the eutectic is placed at 13.5 at.% Si and 1285 °C, whereas in ref. 2 it was 12 at.% Si and 1275 °C. However, the metal $\beta \rightarrow \alpha$ transformation, detected in both investigations only for samples up to the eutectic composition, shows a marked difference; in this work a mean transition temperature of 1345 °C was found from four samples, compared with 1430 °C found from two samples in ref. 2. Sig-

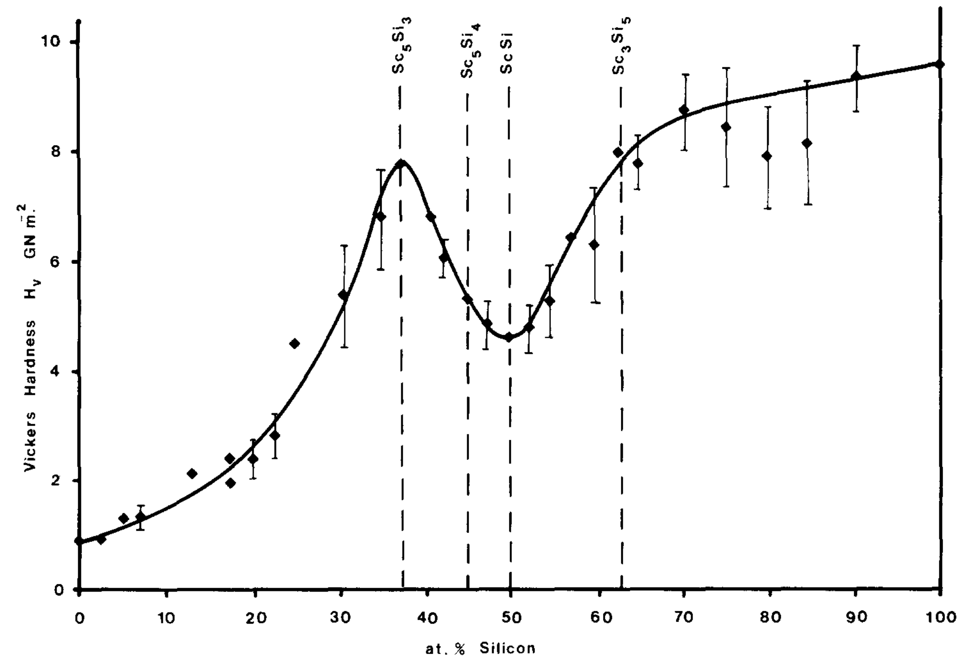

Fig. 5. The Vickers microhardness as a function of composition for arc cast Sc–Si samples.

TABLE 3. Vickers hardness of phases found in the Sc–Si system

Composition	Hardness GN m^{-2}
Sc	0.785 ± 0.09
Sc_5Si_3	7.61 ± 0.5
ScSi	4.22 ± 0.59
$ScSi_{1.67}$	8.24 ± 0.29
Si	9.13 ± 0.29

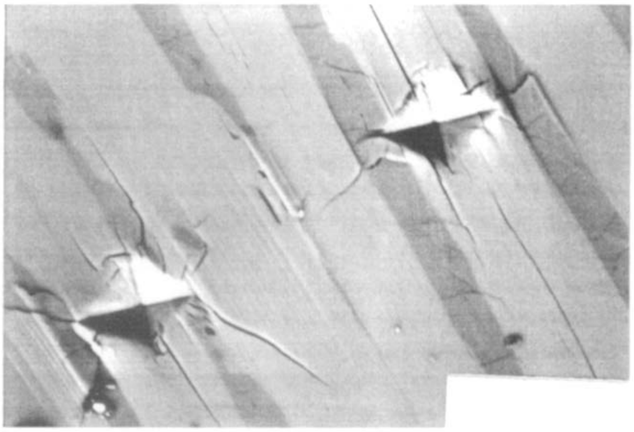

Fig. 6. Indent made in the ScSi phase surrounded by the non-stoichiometric phase $ScSi_{1.22-1.67}$.

nificantly, when Eremenko *et al.* used a purer, sublimed formed of scandium, they reported a melting point of 1540 °C and a $\beta \rightarrow \alpha$ transformation at 1338 °C, whereas for the scandium used in the main investigation these temperatures were reported at 1615 °C and 1442 °C respectively. Hence when using sublimed, purer scandium, both investigations report close results and are in agreement with earlier reports of these properties [13]. Two considerations emerge from this. First, there seems to be a significant impurity in the scandium used by Eremenko *et al.* [2] which raises the temperatures observed for cooling effects, and this may be the cause of more significant divergence in the observations made in the two investigations of higher silicon content samples. Second, from the constant value of the transformation which at 1345 °C is only slightly above the 1338 °C found elsewhere, there is little evidence for silicon solution in the metal.

(2) The only congruent melting phase in the system is Sc_5Si_3 with a melting point of 2028 ± 5 °C from the cooling curve analysis and from the DTA method. This value is some 30 °C lower than that reported in ref. 2 and probably reflects again the impurities present in the scandium used by Eremenko *et al.*

(3) The liquidus curve in Fig. 1 strongly suggests a peritectic around 1935 °C which was not reported in ref. 2. A suggested composition for the peritectic is close to Sc_5Si_4 which is a metal:silicon ratio known to occur as an orthorhombic phase in the Y–Si system [3]. Although large amounts of this phase could be seen in the quenched sample, none of the annealing methods tried was able to produce a phase-pure sample. Elimination of lines in the X-ray powder diffraction films arising from Sc_5Si_3 and ScSi from samples containing this phase, left a pattern that could be indexed on an orthorhombic unit cell with parameters similar

to those of other Ln_5Si_4 phases. Thus it is suggested from this data that a reaction

Sc_5Si_3 + liq.

leads to Sc_5Si_4 and this is removed by a reaction

$Sc_5Si_4 + \text{liq.} \longrightarrow ScSi$

at 1850 °C. The obvious shoulder on the liquidus of Fig. 1 at 1850 °C supports this suggestion.

(4) The peritectic observed by Eremenko *et al.* [2] at 1785 °C and believed to represent

$\text{liq.} + Sc_5Si_3 \longrightarrow ScSi$

was never observed in the rapidly cooled samples of composition between Sc_5Sc_3–ScSi prepared in this work. For samples at the composition ScSi, or very close to it, almost phase-pure ScSi was prepared even at rapid cooling rates and only short, relatively low temperature, annealing was needed to produce ScSi as a single-phase product.

(5) For compositions containing more silicon than ScSi the variety and inconsistency of thermal effects observed on cooling make it difficult to do other than suggest a series of events; these are indicated by dotted lines in Fig. 1. The complicated appearance of the phase diagram, suggested by Eremenko *et al.* to contain a series of solid-state phase changes and peritectoid reactions beyond ScSi was not mirrored in this research. Furthermore, the eutectic temperature in this work of 1255 °C, while being 100 °C above the eutectic reported in ref. 2 is close to the peritectic,

$\text{liq.} + ScSi \longrightarrow ScSi_{1.5}$

at 1260 °C reported by ref. 2.

The confused picture for compositions above ScSi, as far as the cooling curve analyses are concerned, became clearer only when X-ray, microscopy and microhardness data were combined. Particular attention was paid to X-ray data obtained from samples in the three distinct composition ranges Sc_5Si_3–Sc_5Si_4, Sc_5Si_4–ScSi and ScSi–$ScSi_2$. All samples within any one of these ranges gave rise to powder X-ray films where the relative intensities varied as might be expected when a mixture is variously sampled. In the first two composition ranges, when the lines arising from Sc_5Si_3 and ScSi were identified, there still remained many lines unaccounted for, which were well-defined and of good intensity, especially in samples close to Sc_5Si_4 in composition. The fact that all the remaining lines could be accounted for on a pattern given by an orthorhombic unit cell only slightly smaller in volume than that for Y_5Si_4, is taken as strong evidence for the existence of this phase in these samples despite there being no mention of its existence in ref. 2. The rapid cooling of the samples prepared in this work is most likely the cause of this discrepancy.

In the light of the X-ray evidence, the microstructures seen, and the cooling curve features, a dotted line is included in Fig. 1 to indicate an Sc_5Si_4 phase formed from Sc_5Si_3 + liquid at approximately 1920 °C and the conversion of this phase at 1850 °C by reaction with a liquid containing approximately 55 at.% silicon to form ScSi. In the diagram by Eremenko *et al.* ScSi is formed from liquid of 55 at.% Si reacting with Sc_5Si_3 at 1785 °C. In either case, for compositions close in stoichiometry to ScSi the orthorhombic monosilicide phase is relatively easily produced. Mild annealing produces a twinned form of ScSi as Fig. 6 shows. This is the softest phase in the system which, when indented, clearly shows slip bands around the indent.

The X-ray data was unambiguous in always showing the free silicon in samples of composition richer in silicon than $ScSi_{1.67}$. Considering the cooling curve data and X-ray patterns together, the most consistent interpretation is that the highest silicon content phase has the disilicide structure and is widely non-stoichiometric within the limits $ScSi_{1.22}$–$ScSi_{1.67}$. This phase forms a eutectic with silicon at 77 at.% Si, a point of agreement in both this and the investigation by Eremenko *et al.* [2]. However, there is disagreement over the eutectic temperature which was found to be 1265 °C here and only 1155 °C in ref. 2. Thermal effects at 1260 °C were interpreted by ref. 2 as a peritectic reaction between ScSi and liquid to produce $ScSi_{1.67}$. Here the erratic cooling effects between 1325 and 1350 °C are taken as a reaction between ScSi and a silicon-rich liquid leading to the highest silicon-content silicide. None of the low temperature changes, from 1150 to 925 °C, reported in ref. 2 were ever observed in the samples prepared for this work and cooled at the fast rates used here. This is perhaps not surprising in view of the exceedingly long annealing times that appear to be needed in order to reveal the metastability of $ScSi_{2-x}$ with respect to ScSi and silicon.

References

1 M.E. Schlesinger, *Chem. Rev., 90* (1990) 607.

2 V.N. Eremenko, K.A. Meleshevich, Yu.I. Buyanov and P.S. Martsenyuk, *Porosh. Metall., 12* (1988) 52.

3 T.W. Button, I.J. McColm and J.M. Ward, *J. Less-Common Met., 159* (1990) 205.

4 V. Kotroczo, I.J. McColm, M. Rebbeck and J.M. Ward, *J. Alloys Comp., 189* (1992) 87.

5 I.J. McColm and J.M. Ward, *J. Alloys Comp., 178* (1992) 91.

6 I.J. McColm and V. Kotroczo, *J. Less-Common Met., 131* (1987) 191.

7 V. Kotroczo, I.J. McColm and N.J. Clark, *J. Less-Common Met., 132* (1987) 1.

8 L. Topor and O.J. Kleppa, *J. Chem. Thermo., 19* (1987) 69.

9 O. Schob and E. Parthe, *Monatsh. Chem., 95* (1964) 1466.

10 O.I. Bodak and B.Yu. Kutor, *Kokl. An. Ukr. SSR Ser. A, 7* (1976) 656.

11 E.I. Gladyshevskii, *Dokl. An. Ukr. SSR Ser. A, 8* (1978) 751.

12 G.M. Lukashenko, R.I. Polotskaya and V.R. Sidorko, *J. Alloys Comp., 179* (1992) 299.

13 G.V. Samsonov, Yu.B. Panderao and T.S. Verkhoglyadova, *Dop. Akad. Nauk. Ukr. RSR, 2* (1963) 224.