Investigation of the System Zr-Fe-Si*

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The isothermal section of the system Zr-Fe-Si has been in-
vestigated using X-ray diffractometry and film technique. The
results were complemented with micrographic data. The existence
of the compounds found previously: $Zr_4Fe_4Si_7$ (V), $ZrFe_2Si_2$ (D),
ZrFeSi (E), Zr_2Fe_3Si (λ_1) was definitely confirmed. A new ternary
phase of the composition $Zr_6Fe_{16}Si_7$ belonging to the $Mg_6Cu_{16}Si_7$-
type was found ($a = 11.53 \pm 0.01$ Å). Zirconium stabilizes the
crystal structure of Fe_5Si_3 which as a pure phase exists only in
the interval from 1090 to 825° C. The isoconcentration tie-line at
66.7 a/o Zr indicates the existence of an unbroken series of solid
solutions between Zr_2Fe and Zr_2Si. $ZrFe_2$ dissolves approx. 5 p.c.
of silicon. The solubility of the third component in all other
binary phases was found to be very small.

INTRODUCTION

Partial investigations in the system Zr-Fe-Si revealed the existence of
the following five phases: $Zr_4Fe_4Si_7$[1], $Zr_2Fe_3Si_2$[2], ZrFeSi[3-5], $ZrFe_2Si_2$[6] and
$ZrFeSi_2$.[5]

About the existence of the last phase there are some contradictory data
in the literature. According to some authors[7] this phase does not exist at all,
but others[1] have found that in the silicon-rich region there is a compound
possesing a tetragonal structure ($a = 13.056 \pm 2$, $c = 5.090 \pm 1$) which very
probably corresponds to the structure of the $Zr_4Co_4Ge_7$-type. In another paper[5]
it is mentioned that this phase has a certain range of homogeneity due to the
variation of the content of silicon and iron.

This study was undertaken in order to clarify the phase relationships
within the whole ternary isothermal section at 800° C. Table I is presented to
illustrate the extreme complexity of both metal-silicon and metal-metal
systems.

MATERIALS AND METHODS

The alloys in the whole system (110 samples) were prepared by arc-melting in
an argon atmosphere (1 at). Iodide zirconium (99.98%, USSR, carbonyl iron (99.98%,
USSR) and extrapure silicon (99.99%, USSR) were used for all preparation. The
weight loss (mostly due to evaporation of silicon) was compensated for by the ad-
dition of an extra quantity as determined by weighing some representative samples
before and after alloying. Therefore the composition is accurate within 1 p.c.

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* The results of this investigation were presented at the Vth Conference of the
Yugoslav Center for Crystallography, Bled, October 1970.

TABLE I

The Characteristic Data for the Bynary Phases Found in the Systems Zr-Fe, Zr-Si and Fe-Si

Compo- sition	Conditions and temp. of for- mation	Structure type	Lattice parameters (Å)			References
			a	b	c	
Zr_6Fe_{23}	1480, P	Th_6Mn_{23}	11,69	—	—	8
$ZrFe_2$	1645, L	$MgCu_2$	7,010	—	—	9
Zr_2Fe	~ 1100, P	$CuAl_2$	6.457	—	5.542	10
$ZrSi_2$	1520, P	$ZrSi_2$	3,72	14.76	3.67	11, 12
$ZrSi$	2095, P	FeB	6.982	3.789	5.302	11, 13
$ZrSi$	— , P	CrB	3.754	9.892	3.746	12, 13
Zr_5Si_4	2250, P	Zr_5Si_4	7.123	—	13.002	11, 14, 15
Zr_3Si_2	— , P	U_3Si_2	7.082	—	3.714	11, 14, 15
Zr_5Si_3	2210, L	Mn_5Si_3	7.886	—	5.558	11, 13—15
Zr_2Si	2110, P	$CuAl_2$	6.612	—	5.294	13—15
Zr_3Si	1630, P	Ti_3P	11.01	—	5.45	13—15
Fe_3Si	1275, P	CsCl	—	—	—	16, 17
Fe_3Si	1150, P	BiF_3	5.644	—	—	16
Fe_2Si	1215, L	Fe_2Si	5.619	—	—	9, 11, 16
Fe_5Si_3	1040, E 1090, Pd 825, E	Mn_5Si_3	6.755	—	4.717	9, 11, 16
$FeSi$	1410, L	Fesi	4.489	—	—	11, 16
$FeSi_2$ (ξ_α)	1220, L 960, E	$FeSi_2$	2.698	—	5.147	9, 16
$FeSi_2$ (ξ_β)	995, Pd	$FeSi_2$	9.8792	7.7991	7.8388	16, 18, 19

P-peritectic, Pd-peritectoidal, E-eutectoidal decomp., L-from melt, S-solid state transformation.

All samples, subjected to annealing treatment at 800° C during 500 hours, were subsequently quenched in cold water.

X-ray phase analysis was done using film (CrKα) and a diffractometer technique (General Electric XRD-6 with nickel filtered CuKα radiation).

For the micrographic examinations samples were etched in a mixture of HF, HNO_3, glycerol, ethanol and water. When necessary, photographs were taken with MIM-7 (USSR) or Officine Galileo (Italy) reflecting microscopes.

RESULTS AND DISCUSSION

In order to confirm the literature data for the binaries, 25 alloys were prepared, corresponding to the composition of the phases found previously.

The X-ray phase analysis showed that all compounds, except Zr_6Fe_{23} and Zr_3Si, are easy to prepare. The latter two compounds were not detected.

The only possible explanation is that these two peritectoidal phases form only if the temperature is very high (cca 1400—1500° C) or if they are stabilized by the presence of some impurities.

Fig. 1 shows the isothermal section of the ternary system Zr-Fe-Si at 800° C. As seen, there are five intermetallic compounds in this system *i. e.* $Zr_4Fe_4Si_7$ (V), $ZrFe_2Si_2$ (D), $ZrFeSi$ (E), Zr_2Fe_3Si (λ_1) and $Zr_6Fe_{16}Si_7$ (T). Only Zr_2Fe_3Si (λ_1) is characterised by some extended region of homogeneity.

The phase T fits the cubic indexing ($a = 11.53 \pm 0.01$ Å) for which the X-ray data are presented in Table II. A simple analysis of the extinct reflections suggests that one is dealing with a face-centered Bravais-lattice. The
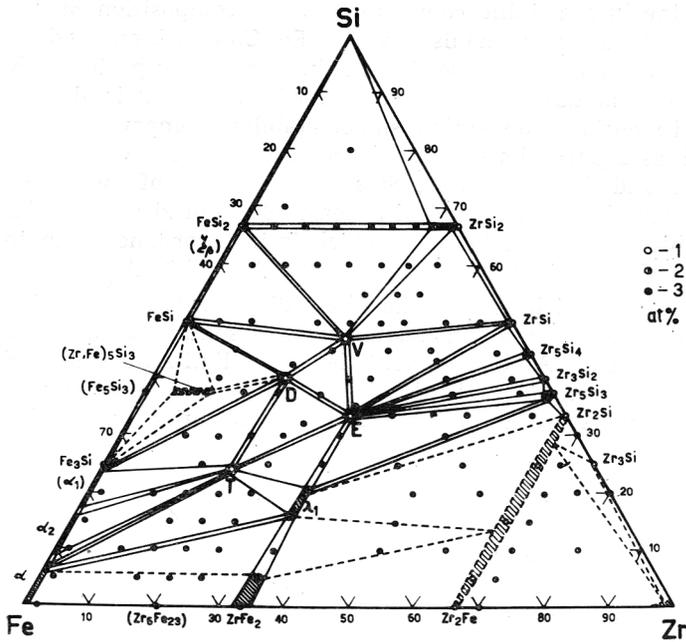
Fig. 1. Isothermal section at 800° C of the system Zr—Fe—Si.

TABLE II

X-Ray Data for $Zr_6Fe_{16}Si_7$ (CrKα)

HKL	$\sin^2 \Theta_{obs.}$	$\sin^2 \Theta_{calc.}$	$I_{obs.}$
133	0.1881	0.1865	1
204	0.1950	0.1964	1
224	0.2381	0.2356	3
333	0.2668	0.2651	10
440	0.3143	0.3142	10
531	0.3405	0.3436	2
600, 442	0.3521	0.3534	2
620	0.3927	0.3927	1
533	0.4235	0.4222	1
622	—	0.4320	—
444	—	0.4713	—
551, 711	0.5017	0.5007	2
640	—	0.5105	—
642	—	0.5498	—
731, 553	0.5817	0.5793	3
800	—	0.6284	—
733	0.6579	0.6578	3
820, 644	—	0.6676	—
822, 660	0.7066	0.7069	7
751	0.7379	0.7364	6
662	—	0.7456	—
840	0.7826	0.7854	3
+ 6 more lines			

formation of the intermetallic compounds of the composition $M_6X_{16}Si_7$, where M can be any of transition metals and X is Fe, Co or Ni, ensured us to ascribe the crystal structure of the phase T to the known binary prototype $Mg_6Cu_{16}Si_7$. This compound is actually a superstructure of Th_6Mn_{23}. It is also possible that the compound mentioned above is a silicon stabilized binary of the composition Zr_6Fe_{23} which as a pure phase could not have been prepared.

We also found that at 37.5 a/o Si a ternary phase of the Fe_5Si_3 structure is being stabilized by the addition of at least 10 a/o of zirconium. The relevant crystallographic parameters increase which is in accordance with the relative sizes of iron and zirconium atoms ($R_{Fe} = 1.26$, $R_{Zr} = 1.60$ Å).

In the zirconium-rich part of the phase diagram two isostructural phases, i. e. Zr_2Fe and Zr_2Si, form a continuous series of solid solutions with a certain range of homogeneity. At the moment the exact limits of this solid solutions field can not be given precisely due to the fact that the number of samples was not sufficient. As seen from Fig. 2, the substitution of iron by silicon in
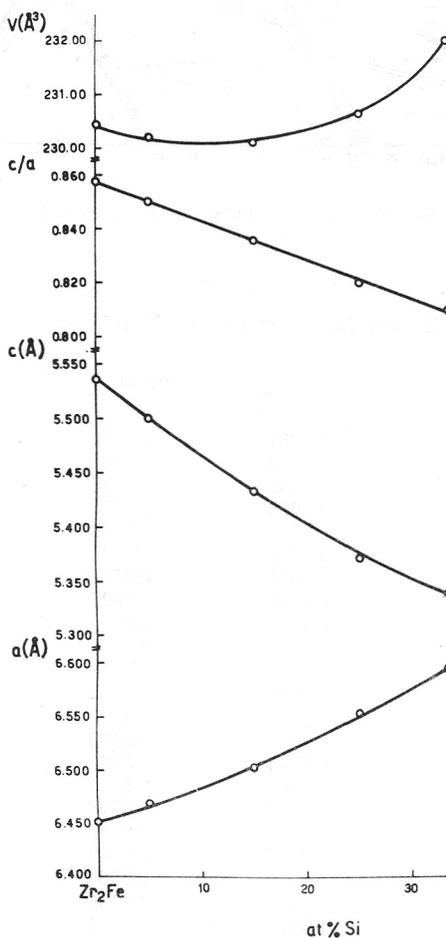
Fig. 2. Variation of the relevant crystalographical parameters for a series of solid solutions Zr_2Fe—Zr_2Si.

a continuous series of solid solutions $Zr_2($ (Fe, Si) resulted in a decrease of the cell volume (deviation from linearity). This fact allows to draw the conclusion that one is in fact dealing with an ordered ternary system ($CuAl_2$-type) which is analogous to those described earlier (Nb_4FeSi, Nb_4CoSi and Nb_4NiSi).[20] The variation of the lattice parameters of the phase $ZrFe_2$ show that the maximum solubility of the third component (Si) is appr. 5 $p. c.$ The solubility of iron in other zirconium silicides and zirconium in silicides of iron at 800^0 C is negligible.

The comparison between different ternary system M-X-Si (M = Ti, Zr and Hf; X = Fe, Co and Ni) shows that, from the crystallographical point of view, they belong to the same family, with the exception of Ti-Fe-Si. In all of these systems phases V, E an T were found. The T-phase ($Zr_6Fe_{16}Si_7$) is a unique one because there are no related phases in the systems M-X-Si if X stands for iron. As expected, the system Ti-Fe-Si differs from Zr-X-Si and Hf-X-Si systems because instead of V, E and T phases a number of other compounds exist. By increasing the atomic number of both the M and X transition metals, the number of ternary phases in these particular systems is increased.

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IZVOD

Istraživanje sistema Zr-Fe-Si

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Rendgenografskom i metalografskom analizom 110 uzoraka u ternarnom sistemu Zr-Fe-Si postavljen je izotermni presjek kod 800^0 C. Osim već poznatih faza ZrFeSi (E), $ZrFe_2Si_2$, Zr_2Fe_3Si (λ) i $Zr_4Fe_4Si_7$ (V), utvrđeno je postojanje novog inter-metalnog spoja $Zr_6Fe_{16}Si_7$ strukturnog tipa $Mg_6Cu_{16}Si_7$ kubične strukture ($a = 11,53 \pm 0.01$ Å). Također je nađeno da cirkonij stabilizira fazu Fe_5Si_3 koja ispod 825^0 C nije stabilna, a iznad 1090^0 C se raspada. Na izokoncentracionoj liniji kod 66,7 at. % Zr postoji neprekinuti niz čvrstih otopina dvaju izostrukturnih spojeva (Zr_2Fe i Zr_2Si). Primjećena je kontrakcija parametara elementarne ćelije koja ukazuje na pojavu sređivanja pojedinih atomskih vrsta. Također je ispitana topljivost treće komponente u većini binarnih spojeva. U slučaju $ZrFe_2$ ona iznosi cca 5 at. %, dok je kod ostalih zanemarljiva.

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