

The Intermediate Phase Zr_2Si

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A zirconium-rich phase has been found in the binary system zirconium-silicon. The crystal structure of this intermediate phase, Zr_2Si , has been determined by powder X-ray diffraction methods. The unit cell, which is tetragonal, has parameters $a = 6.6120 \pm 0.0004$ Å and $c = 5.2943 \pm 0.0003$ Å. There are eight zirconium atoms in (*h*) with $x = 0.156 \pm 0.001$ and four silicon atoms in (*a*) of space group $D_{4h}^{18}-I4/mcm$. Least-squares methods were used to determine the lattice constants, position parameter, and errors associated with these measurements. Zr_2Si is structurally isomorphous with $CuAl_2$ (*C16* type).

Introduction

At the time this investigation was being conducted there was little information available pertaining to phase equilibria and crystal structures in the zirconium-silicon system. Náray-Szabó (1937) determined the crystal structure of zirconium disilicide, *C49* type. Robertson & Hayes (unpublished work, International Metals Congress, 1951) found that a 3 wt. % silicon alloy contained approximately 50% of an intermediate phase and suggested Zr_4Si (7.1 wt. % silicon) as the formula of the first zirconium-rich phase in this system. More recently, Lundin, McPherson & Hansen (1953) have presented a constitution diagram for the zirconium-silicon system, and while the present paper was being reviewed for publication an investigation of the crystal structures of Zr_2Si and Zr_5Si_3 by Schachner, Nowotny & Machenschalk (1953) was brought to the author's attention.

Experimental methods

Zirconium metal used in this investigation was acquired from the Foote Mineral Company. It had been produced by the iodide reduction process. Silicon powder was obtained from Charles Hardy, Inc. of New York. The purity of this constituent was given as 97% minimum.

Alloying was achieved with an inert atmosphere electric arc furnace; this method of alloy preparation has been described in the literature by Schramm, Gordon & Kaufmann (1950). The weight loss during the alloying process amounted to less than 1%. For this reason the cast ingots were not chemically analyzed, and calculated compositions were accepted as a fair measure of the actual compositions of the various alloys. Isothermal heat treatments were performed after the ingots had been sealed in quartz ampoules. Specimens were rapidly quenched in water from the homogenization temperature. Powders of the alloys

were then placed in thin walled quartz vials, sealed, annealed at the homogenization temperature, and quenched into liquid argon.

Data for lattice parameters and intensity calculations were obtained from a 143.2 mm. diameter Debye-Scherrer powder camera. For the latter purpose a multiple-film technique was employed; intensities of diffraction maxima recorded in this manner were estimated with the assistance of external standards. The camera employed to collect the X-ray data was also used for preparing linear intensity scales. A properly constructed camera, in which the film is located on the outside of a cylindrical drum, may be easily adapted to such usage in the manner to be described. A phosphorus bronze strip was placed on the periphery of the Debye-Scherrer camera in the position normally occupied by the film. From this mask a window 2 mm. by 3 mm. was cut; a small cam-type locking device allowed the adjustment of the bronze mask so as to permit a selected maximum of the diffraction pattern to pass through this slit uninterrupted. Calculations to determine the position of the window are unnecessary if a powder diffraction film of the sample is available, as is usually the case. Behind the slit in the bronze strip is placed a curved film cassette actuated by a rack and pinion; a graduated dial, each division of which advanced the multiple-film holder one window width, aided in spacing the timed sequence of exposures. By permitting the simultaneous exposure of a pack of film strips in the cassette, the film factor 3.7 was checked for copper $K\alpha$ radiation. Coupons selected for this purpose were taken from the same sheet of Eastman Kodak Duplitized No-Screen film which was used to record the entire diffraction pattern.

Conventional methods were used to prepare the alloys for examination with the optical microscope. Hand grinding on papers from 0 to 4/0 was followed by mechanical polishing on a cloth-covered lap, which was impregnated with diamond dust. The etchant was a solution consisting of one part 48% hydrofluoric

acid, one part concentrated nitric acid, and two parts glycerine.

Results

Metallographic observations were made on as-cast alloys containing less than 45 at. % silicon. An alloy containing 8 at. % silicon was over 90% eutectic mixture, the remainder being primary crystals of the phase which Robertson & Hayes probably had referred to and which Lundin *et al.* conclude to be Zr_4Si . Alloys with increasing amounts of silicon revealed that a phase richer in silicon than Zr_4Si was undergoing a peritectic reaction with the melt. A rapidly cooled 25 at. % silicon alloy was comprised of primary crystals (Zr_2Si), whose form was quite unlike Zr_4Si , and a eutectic mixture. With increasing silicon content (35 at. % silicon), a primary crystal of hexagonal habit, unlike Zr_4Si or Zr_2Si , was observed. This phase had also entered into a peritectic reaction with the melt. The matrix of this alloy contained small primary crystals of Zr_2Si and residual eutectic. From these observations it was concluded that Zr_2Si was formed by the peritectic reaction of a silicon-rich phase with the melt. Homogenization at 1100° C. for 11 days failed to produce a single-phase micro-structure of Zr_2Si . An alloy containing 33½ at. % silicon was over 95% Zr_2Si , and no specimen in this region of the phase diagram gave evidence of containing greater amounts of this phase.

X-ray diffraction data obtained from filings of a homogenized alloy of ideal composition were indexed on the basis of a body-centered tetragonal lattice with the following expression for the square of the reciprocal interplanar spacings:

$$1/d^2 = 0.02291\alpha + 0.03571\beta \text{ \AA}^{-2},$$

where $\alpha = h^2 + k^2$ and $\beta = l^2$. Calculated values of $1/d^2$ obtained with this expression are presented in Table 1. The lattice parameters were determined in a manner similar to that devised by Cohen (1936). Thirty-four weighted observations of resolved $K\alpha_1$, $K\alpha_2$ were used for this calculation; the observational equation for the *i*th reflection was written:

$$\sqrt{w_i} \cdot \sin^2 \theta_i = \sqrt{w_i} \cdot A_0 \alpha_i + \sqrt{w_i} \cdot B_0 \beta_i + \sqrt{w_i} \cdot D \delta_i.$$

The function $\delta_i = \delta(\theta_i)$ was obtained from the data given by Nelson & Riley (1945). Weights were assigned in a manner described by Shoemaker, Marsh, Ewing & Pauling (1952). An auxiliary weight function w_i' was arbitrarily assigned values of 1, 2, 3, or 4, depending on factors which would influence the physical appearance of the diffraction line, such as broadening due to partial $K\alpha_1$, $K\alpha_2$ separation and near coincidence of reflections of different *hkl*. Equations of observations were written in a conventional manner and reduced to three normal equations, which were solved for the parameters $A_0 = (\lambda/2a)^2$, $B_0 = (\lambda/2c)^2$, and D . The errors to be expected in the lattice constants were obtained from the residuals and

Table 1. X-ray powder diffraction data for Zr_2Si

$1/d^2$ (\AA^{-2})		<i>hkl</i>	F_o	F_c
Obs.	Calc.			
0.0457	0.0458	110	56	— 48
0.0920	0.0916	200	75	— 61
0.1429	0.1428	002	197	213
0.1496	0.1503	211	208	192
0.1820	0.1833	220	78	72
0.1866	0.1886	112	98	—111
0.2280	0.2291	310	109	161
0.2347	0.2345	202	129	—122
0.3328	0.3336	321	38	— 39
0.3658	0.3665	400	71	— 89
0.3749	0.3719	312	117	— 80
0.4145	0.4123	330	148	—160
0.4255	0.4252	411	111	—116
0.4368	0.4359	213	159	152
0.4583	0.4581	420	77	84
0.5118	0.5093	402	137	—141
0.5556	0.5552	332	182	—207
0.5699	0.5713	004	224	212
0.7022	0.7001	521	123	157
0.7129	0.7108	413	107	—100
0.7997	0.8004	314	109	116
0.8262	0.8247	600	199	177
0.9407	0.9378	404	63	— 68
0.9706	0.9675	602	112	121
0.9763	0.9749	541	108	—110
1.0064	1.0072	215	111	121
1.0294	1.0294	424	64	66
1.0603	1.0591	622	77	— 58
1.2509	1.2497	721	94	— 75
1.2616	1.2606	543	112	—101
1.2822	1.2821	415	98	— 85
1.3047	1.3043	444	80	95
1.3302	1.3286	730	148	139
1.3359	1.3340	642	104	—115
1.3508	1.3501	534	51	48
1.3962	1.3960	604	138	151
1.4340	1.4330	651	52	54
1.4733	1.4714	732	84	94
1.5135	1.5145	316	53	55
1.5556	1.5570	525	123	124
1.6505	1.6519	406	109	— 97

appropriate coefficients of the determinant, as described by Whittaker & Robinson (1937). Wavelengths used for calculations are those suggested by Lonsdale (1950).

$$a = 6.6120 \pm 0.0004 \text{ \AA}, \quad c = 5.2943 \pm 0.0003 \text{ \AA}.$$

The density of a solid specimen of homogenized Zr_2Si was measured with a pycnometer and found to be $6.22 \pm 0.02 \text{ g.cm.}^{-3}$; the number of molecules per unit cell is calculated to be 4.10 (i.e. 4). Indices assigned to the observed maxima in Table 1 indicate that *hkl* reflections are present only if $h+k+l = 2n$, and *h0l* are observed if $h = 2n$ and $l = 2n$. In the tetragonal system the space group of highest symmetry which would explain these observations is $D_{4h}^{18} - I4/mcm$.

To explain the general reflections with the space group of highest symmetry the eight zirconium atoms were placed in position (*h*) of the *International Tables for X-ray Crystallography* (1952). When the one variable parameter of this set of equivalent positions is equal to 0.146 or 0.854, the zirconium atoms may

arrange themselves in a square Archimedean antiprism. The only fourfold position which would give reasonable Si-Si and Zr-Si distances with the zirconium atoms so disposed is (*a*). With the unit-cell content arranged in this way, it was evident that the crystal structure could be analogous to that of Al_2Cu , determined by Friauf (1927), in which the positional parameter is 0.158. Intensity calculations for the 81 spectra which are possible when a copper anticathode is used were made with the expression

$$\text{Intensity} \propto PLpF_c^2,$$

where PL represents the polarization and Lorentz factors, p the multiplicity of the particular form of hkl , and F_c the structure factor. Relative intensities of adjacent observed maxima were found to be in good agreement and those reflections too weak to be observed were also explained by the calculations.

The method of Hughes (1941) was chosen for the parameter refinement. Of the 46 observed maxima, only five are degenerate in the sense that they represent the coincidence or near coincidence of diffractions from different hkl . Three of these five lines were broadened considerably and would have received a very low weight had the refinement been carried out with respect to a quantity proportional to $\sum pF_o^2$. Since there were 41 non-degenerate maxima, the parameter refinement was made with regard to the F_o of these observations. Visually measured intensities were corrected for Lorentz and polarization factors, multiplicity, absorption, and an exponential temperature factor of the form $-B \sin^2 \theta / \lambda^2$. The powder specimen was mounted on a glass rod selected for size so that the resulting radii quotient $r_{\text{core}}/r_{\text{specimen}}$ was 0.5. Absorption corrections for $\mu r = 4.0$ were obtained from Møller & Jensen (1952). A least-squares analysis relating the linearity between $\log_e F_o/F_c$ and $\sin^2 \theta_i / \lambda^2$ was used to obtain a scale factor and the temperature factor parameter, $B = 1.65 \text{ \AA}^2$. Observed structure factors so obtained were weighted by the following procedure:

$$w_i = w_i''/nF^2 \quad \text{for } nF''s > 4nF_{\text{min.}},$$

$$w_i = w_i''/16nF_{\text{min.}}^2 \quad \text{for } nF''s < 4nF_{\text{min.}}.$$

A weighting function w_i'' , similar in purpose to w_i' (see Shoemaker *et al.*, 1952) was used. The 41 weighted equations of observation were handled by least-squares, from which Δx was determined to be -0.0019 and the error to be expected in the positional parameter was ± 0.001 . Thus the parameter for the eight zirconium atoms in (*h*) is 0.156 ± 0.001 . Structure factors calculated with this refined value are given in Table 1; spectra too weak to be observed were omitted to conserve space. The change in parameter due to this refinement resulted in decreasing the reliability factor,

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

from 0.112 to 0.097. Distances between adjacent atoms in Table 2 have been calculated with consideration of

Table 2. *Interatomic distances in Zr_2Si*

Atom	Neighbors	Distance (\AA)
Zr	(4) Si	2.827 ± 0.016
	(1) Zr	2.917 ± 0.019
	(2) Zr	3.178 ± 0.011
	(4) Zr	3.356 ± 0.009
	(4) Zr	3.532 ± 0.017
Si	(2) Si	2.6472 ± 0.0003
	(8) Zr	2.827 ± 0.016

the uncertainties as determined by the least-squares analyses.

Discussion

Zr_2Si is isomorphous with the Al_2Cu , *C16*-type structure, determined by Friauf. The variable parameter for the eight large atoms in the structure, calculated to be 0.156 ± 0.001 by this investigation, is in good agreement with the value of 0.158 reported by Friauf for intensity data obtained from Laue photographs. Silicon atoms form straight chains which are parallel to the *c* axis of the lattice; each silicon is surrounded by eight equi-distant zirconium atoms whose spatial configuration is similar to a square Archimedean antiprism. If the structure is considered as the packing of large and small spheres the atomic quotient for the regular coordination polyhedra just described is 1.55. In the space group selected the ideal positional parameter for the large spheres would be 0.146 or 0.854 and the axial ratio for the crystal lattice 0.91. Isomorphous crystal structures reported in the literature (for a summary see Wallbaum (1943)) have axial ratios which vary from Na_2Au (0.75) to Pb_2Rh (0.88). The atomic radii quotient R_A/R_B , coordination number 12, varies from Ge_2Fe (1.09) to that of Fe_2B (1.34). Extensive information relating the change in axial ratio to the positional parameter is not available since many of the reported A_2B -type alloys were determined from qualitative intensity measurements and 0.158 was accepted as the parameter of the large atoms. On the basis of a geometrical study of these A_2B -type structures, Wallbaum arrives at an optimum radii quotient $R_A/R_B \sim 1.20$ (C.N. 12). This is very close to the value obtained for Zr_2Si , which is 1.22.

Since the X-ray data for the structure determination had been collected from a specimen which was not 100% Zr_2Si , the influence of the second constituent present is of importance. X-ray powder diffraction patterns of the phase which was relatively rich in zirconium, Zr_4Si , and the relatively silicon-rich phase Zr_3Si_2 (after Lundin *et al.*, 1953), indicated that no Zr_3Si_2 was present in the filings used for diffraction. Maxima corresponding to the strongest reflections of this phase were not observed. Small amounts of Zr_4Si could have been present; if this were the case, the observed intensities from (211), (220), and (112) of Zr_2Si would have been influenced by this superposition of X-ray spectra. The data of Table 1 indicate that if such a possibility did occur, the magnitude of the

error so introduced is small. It is possible, since there is a considerable difference in ductility between Zr_4Si and Zr_2Si , that the minor constituent may have been separated preferentially by the filing process.

Although the exact location of Zr_2Si in the constitution diagram was not determined, 'lever rule' considerations would indicate that this intermediate phase must exist over a narrow range of composition near the ideal chemical composition. This is in agreement with the observations of Lundin and coworkers. Lattice parameter measurements of Zr_2Si in the adjacent zirconium-rich and silicon-rich two-phase regions, wherein cell constants should remain invariant, do not show a change in cell dimensions within the accuracy of the measurements, thus adding credence to the previous observation.

The crystal-structure type reported for Zr_2Si by Schachner *et al.* (1953) is in agreement with the author's results; differences in the positional parameter of the zirconium atoms, about 1/100th of the cell edge, are to be understood since the previous investigators used qualitative intensity measurements. Part of the large discrepancy in lattice parameters can be attributed to the method of specimen preparation; the high chemical reactivity of zirconium makes it unwise to compare data from alloys which were sintered with data from similar alloys prepared by the electric arc-inert atmosphere method used in this investigation. Other influencing factors, such as the sintering atmosphere, crucible material, homogenization procedure, and type of zirconium metal which was used, are not discussed

in sufficient detail by Schachner and coworkers to warrant a comparison of lattice parameters.

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On the Structure of the Heteropoly Anion in Ammonium 9-Molybdomanganate, $(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$.*

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A structure proposed for the complex anion in the heteropoly salt ammonium 9-molybdomanganate, $(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$, has been verified by use of single-crystal X-ray diffraction data. The rhombohedral crystal has space group D_3^5-R32 , $a_{rh.} = 10.08 \pm 0.01$ Å, $\alpha = 104^\circ 24' \pm 3'$. Approximate positional parameters have been determined.

Introduction

The molybdomanganates have been extensively investigated by Friedheim & Samuelson (1900) and Rosenheim (1920), and more recently by Schaal & Souchay (1949). As is the case with most heteropoly

salts, these compounds are stable and very soluble, and crystallize well from aqueous solutions. On making a survey of the crystallography of the heteropoly molybdates, we decided to investigate ammonium 9-molybdomanganate, as a representative of the important series of 9-compounds, which on Rosenheim's classification are intermediate between the two limiting series of 6-compounds and 12-compounds.

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