

Preparation and Characterization of Mo_3Si and Mo_5Si_3

A. NØRLUND CHRISTENSEN

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

Crystals of Mo_3Si were grown from a melt using the travelling solvent method and crystals of Mo_5Si_3 were grown from the melt using the Czochralski growth method.

Mo_3Si was characterized by neutron single crystal diffractometry and Mo_5Si_3 by neutron powder diffraction methods. Mo_3Si is cubic, $Pm\bar{3}n$ (No. 223), $a=4.897(1)$ Å. Shortest Mo–Mo distance is 2.449(1) Å. Mo_5Si_3 is tetragonal, $I4/mcm$ (No. 140), $a=9.650(2)$, $c=4.911(1)$ Å. Shortest Mo–Mo distance is 2.456(2) Å.

A large number of intermetallic compounds with the nominal composition A_3B are isostructural with $\beta\text{-W}$ and have the so-called A15 structure. This structure belongs to the space group $Pm\bar{3}n$, and has the A-atoms in site 6c and the B-atoms in site 2a. However, a major fraction of these intermetallic compounds are not strictly stoichiometric but exist in broad composition ranges. Mo_3Si is one of the few A15 compounds that has the stoichiometric A_3B composition at room temperature according to the literature^{1–4} concerning the binary phase diagrams of the corresponding A–B system. Most of the intermetallic A15 compounds melt incongruently and this is also the case for Mo_3Si . In a project concerning development of crystal growth methods for incongruently melting compounds large single crystals of Mo_3Si were obtained. As Mo_3Si belongs to the stoichiometric A15 compounds it was decided to characterize the compound using neutron diffraction techniques.

Mo_5Si_3 is one of the congruently melting compounds in the Mo–Si systems. This compound was prepared as well and characterized by neutron diffraction technique.

EXPERIMENTAL

Crystal growth of Mo_3Si . The following compounds can be found in a zone melted rod of the composition Mo_3Si : The first part of the specimen contains a polycrystalline core of Mo_5Si_3 and Mo_3Si . The rest of the specimen is Mo_3Si and the frozen zone is a mixture of Mo_3Si and Mo. This shows without ambiguity that the phase diagram published for the Mo–Si system in Ref. 5 is in error. It demonstrates in addition that Mo_5Si_3 isostructural with W_5Si_3 ⁶ is formed instead of a compound with the composition Mo_3Si_2 .¹ The structure of that compound has not been confirmed. In Fig. 1 is shown a fraction of the Mo–Si phase diagram reproduced from literature data¹ and with Mo_5Si_3 as one of the solid phases. The hatched area represents a two phase temperature composition range where the melt is in equilibrium with solid Mo_3Si . Single crystals of Mo_3Si can be made by a modified floating zone growth procedure, the so-called travelling solvent method where the molten zone of solvent has the nominal composition Mo_4Si , indicated by an arrow, z, in Fig. 1. The feed rod and the grown crystal have the composition Mo_3Si . The volume of the molten zone of solvent must be kept

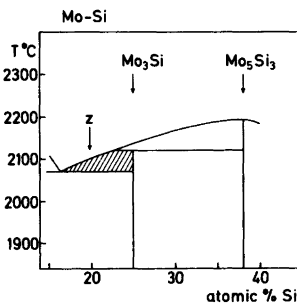


Fig. 1. Fraction of the phase diagram of the Mo–Si system (data from Ref. 1).

constant in the floating zone like growth procedure. The crystals of Mo_3Si were made in an ADL-MP crystal growth unit at an ambient He pressure of 2 MPa. With a typical growth rate of 1 mm h^{-1} single crystals of Mo_3Si with a volume of up to 1 cm^3 were obtained.

Crystal growth of Mo_5Si_3 . As can be seen from the phase diagram Fig. 1, the compound Mo_5Si_3 melts congruently and a normal Czochralski growth technique can be used in preparation of single crystals of Mo_5Si_3 . Crystals of volume of up to 1 cm^3 were pulled from the melt kept in a cold crucible. The pulling rate was 1 mm h^{-1} and an ambient He pressure of 1 MPa was used.

Diffraction experiments. X-Ray diffraction powder patterns of Mo_3Si and Mo_5Si_3 were recorded on a Guinier camera with silicon as an internal standard using $\text{CuK}\alpha_1$ radiation. From these measurements the following unit cell parameters were calculated: $a_{\text{Mo}_3\text{Si}}=4.897(1) \text{ \AA}$, $a_{\text{Mo}_5\text{Si}_3}=9.650(2) \text{ \AA}$, $c_{\text{Mo}_5\text{Si}_3}=4.911(1) \text{ \AA}$.

Mo_3Si was characterized by single crystal neutron diffractometry. A single crystal of dimensions $2 \times 2 \times 2 \text{ mm}$ was cut from a large crystal of Mo_3Si using spark erosion and this crystal was used in measuring neutron intensities using a four-circle neutron diffractometer at Risø. Neutrons of 0.8 \AA wave length were used, and the ω - 2θ scan technique was applied. Two standard reflections were measured for each 50 reflections, and a total of 1496 reflections were measured in a half sphere out to $\sin \theta/\lambda=1.16 \text{ \AA}^{-1}$. After correction for absorption ($\mu=0.065 \text{ cm}^{-1}$) and data reduction, the number of reflections with $I>3\sigma(I)$ was 154. However, 26 of these were weak and space group forbidden, but apparently present due to multiple scattering. These reflections were omitted in the structure factor calculations. The parameters refined and the values arrived at for these parameters are listed in Table 1. A list of observed and calculated structure factors is available on request.

The least-squares program LINUS⁷ was used in the structure factor calculations with the scattering lengths 0.695 and 0.4149 (in units of 10^{-12} cm),⁸ respectively, for molybdenum and silicon.

Mo_5Si_3 was characterized by neutron diffraction powder methods. Powder patterns were measured at room temperature on the D1B spectrometer at the Laue-Langevin Institute in Grenoble, using neutrons of wavelength $\lambda=2.5186 \text{ \AA}$. The pattern of Mo_5Si_3 was measured in the 2θ interval 10.0 to 89.8° in steps of 0.2° . Mo_5Si_3 was housed in a 12 mm vanadium container. The structure was refined using the Hewat version of the Rietveld profile refinement programme.^{9,10} The values of the scattering length used for the two elements were as reported above. A list of observed and calculated intensities is available on request.

RESULTS AND DISCUSSIONS

Mo_3Si . The A15 structure, space group $Pm\bar{3}n$ (No. 223), has the B-atoms placed in a body centered unit cell and the A-atoms in strings on the cubic faces of the unit cell. The direction of the strings are parallel to the axis of the unit cell and the interatomic distances between the metal atoms in the strings are approximately 10–15 % smaller than the interatomic distances in the corresponding pure metal.¹¹ For the A15 compounds the parameters of the thermal ellipsoid of the A-atoms have lower values in the direction of the strings than perpendicular to this direction, so in general U_{11} (Å) is smaller than U_{33} (Å). For compounds that are superconductors, the ratio U_{11}/U_{33} is smaller than the ratio $a/4r$ where a is the unit cell parameter and r the Goldschmidt radius of the A-atom. For Nb_3Al and V_3Si the values are $0.645 < 0.887$, and $0.792 < 0.881$,

Table 1. Mo_3Si , $Pm\bar{3}n$, Mo in site 6c, Si in site 2a. Standard deviations in parentheses.

$h^2+k^2+l^2 >$	No. of reflections	R %	Scale factor	Isotropic ext. parameters	Mo-atom U_{11} U_{33} $\times 10^4$	Si-atom U_{11} $\times 10^4$
1	128	2.1	54.6(5)	6.9(4)	15(1) 22(1)	27(1)
25	112	1.9	55.6(5)	7.2(4)	17(1) 24(1)	29(1)
50	92	1.9	57.3(7)	8.0(6)	20(1) 27(1)	34(2)
75	64	1.9	60.5(1.4)	8.6(9)	26(2) 32(2)	42(3)
85	56	1.9	64.1(1.8)	8.8(1.1)	32(3) 38(3)	50(3)
95	45	2.0	72.2(3.2)	11.2(1.6)	41(4) 47(4)	62(5)
100	41	1.9	72.9(3.3)	9.7(1.6)	43(4) 49(4)	64(5)

Table 2. Atomic coordinates of Mo₅Si₃ from neutron diffraction powder pattern, $R=10.1\%$. Standard deviations in parentheses.

Atom	Site	x	y	z	B (Å ²)
Mo 1	16k	0.0786(6)	0.2247(6)	0	0.9(2)
Mo 2	4b	0	1/2	1/4	0.9(2)
Si 1	8h	0.1710(10)	0.6710(10)	0	0.9(2)
Si 2	4a	0	0	1/4	0.9(2)

respectively.¹² For A15 compounds that show no superconductivity at moderately high temperatures, the values of the two ratios are close to each other. For Cr₃Si as an example, U_{11}/U_{33} is 0.879 and $a/4r$ is 0.876.¹² Mo₃Si belongs to this group of compounds and has $a/4r$ equal to 0.875 and U_{11}/U_{33} equal to 0.878. Table 1 lists the results of the least-squares refinement of the Mo₃Si structure, including all the 128 observed reflections and selections of high angle data. The isotropic extinction parameter used assumes a Nelmes-Thornly formalism.⁷

Refinement of the occupancy factor of the silicon atom showed that the composition did not deviate significantly from the stoichiometry of A₃B.

Mo₅Si₃. The compound was first reported to have the composition Mo₃Si₂,¹ but later Aronsson⁶ showed Mo₅Si₃ to be isostructural with tetragonal W₅Si₃. According to this, the space group of Mo₅Si₃ is $I4/mcm$ (No. 140) and the molybdenum atoms are placed in site 16k and 8b. The silicon atoms are placed in site 8h and 4a. The powder pattern of Mo₅Si₃ had fourteen resolved peaks and the profile refinement yielded the values of the parameters listed in Table 2. As starting parameters, the atomic coordinates for W₅Si₃ reported by Aronsson were used.⁶ The structure investigation of Mo₅Si₃ shows a good agreement between the atomic parameters of Mo₅Si₃ derived from a neutron diffraction powder pattern and the atomic parameters of W₅Si₃ obtained from a single crystal X-ray investigation.⁶

The following Mo–Mo distances are found in Mo₅Si₃: 2.456(2) Å in a string of atoms parallel to the c -axis, 2.684(5) Å in the ab -plane, and 3.023(5) and 3.163(5) Å between atoms placed in planes spaced $c/4$ and $c/2$, respectively, from each other. In Mo₃Si the Mo–Mo distances are 2.449(1) and in molybdenum the interatomic

distances are 2.725(1) Å.¹³ The Mo–Mo distances in Mo₃Si are thus 10% shorter than in pure molybdenum.

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