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STRUCTURE OF Ti_3SiC_2

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ABSTRACT

Earlier high temperature structure analysis by neutron powder diffraction suggested that Si vacancies were created when Ti_3SiC_2 was heated. A specimen that was heated to 906 °C overnight was later examined at room temperature. For this subsequent room temperature data set refinement of the Si site occupancies in the Ti_3SiC_2 structure did not support the hypothesis that Si vacancies were being created when the sample was held at elevated temperatures in a vacuum furnace.

INTRODUCTION

Ti_3SiC_2 has a number of exceptional properties including high electrical and thermal conductivity, oxidation resistance up to 1400 °C, resistance to thermal shock, and mechanical properties that include good compressive strength, high Young's modulus, low hardness, easy machinability, and plastic behavior at high temperatures, making it attractive as a structural ceramic for high temperature applications. Bruckl first identified the ternary carbide Ti_3SiC_2 as " Ti_2SiC " and gave an unindexed powder x-ray pattern, noting that the superposition of diffraction peaks from many of the binary compounds added to the difficulties for identification [1]. Jeitschko and Nowotny determined the "312" structure to be hexagonal, space group $P6_3/mmc$ with lattice parameters, $a = 3.06 \text{ \AA}$ and $c = 17.66 \text{ \AA}$ [2]. The structure is comprised of layers of Ti and C atoms, forming octahedra where the carbon atoms occupy all the octahedral sites, interleaved with layers of Si atoms. Recent neutron diffraction studies of Ti_3SiC_2 [3,4] confirmed this structure.

Recently we reported the thermal expansion of Ti_3SiC_2 calculated from the lattice parameters determined from high temperature neutron diffraction data [4]. The thermal expansion coefficients of the a - and c -axes and the volume are, respectively $8.6 (\pm 0.1) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, $9.7 (\pm 0.1) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, and

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$8.9 (\pm 0.1) \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ which were in good agreement with the bulk thermal expansion coefficient measured by dilatometry of $9.1 (\pm 0.2) \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. Due to the strong anisotropy of the mechanical properties and plate like microstructure it was surprising that only a small thermal expansion anisotropy was observed.

All of the atoms in the structure are on special positions and the site symmetry restricts the atomic displacement parameters. For the refinement at room temperature [4] the equivalent isotropic atomic displacement parameter, U_{eq} , of the Ti atom (Ti_I) adjacent to the Si layer was greater than the Ti atom (Ti_{II}) sandwiched between the C layers. The atomic displacements for the Ti and C atoms were larger along the c -direction ($U_{33} > U_{11}$) while the atomic displacement for the Si atoms was primarily isotropic. These results and the large Si-Si bond lengths supported the hypothesis that the Si atom were weakly bonded in the structure and that vacancies might develop in the Si layers at high temperatures. Refinements of data sets collected at elevated temperatures showed a small decrease of Si occupancy as the temperature increased, given in Table 1; however, these results were within 4σ of full occupation, and given the high correlation between atomic displacement parameters and site occupancies, these results were not considered conclusive. Once cooled from $906 \text{ }^{\circ}\text{C}$ to room temperature the sample was removed from the neutron beam; however, due to the indication that Si vacancies were possibly created, the same sample was subsequently remounted and a second room temperature data set was collected to explore this possibility. This paper gives the results of the Rietveld refinement of data collected from this thermally aged specimen.

Table 1. Si site occupancy as a function of temperature.

Temperature ($^{\circ}\text{C}$)	% occupied
355	95(2)
531	93(2)
714	97(2)
906	93(2)

EXPERIMENTAL

Polycrystalline samples were fabricated by reactive hot pressing of a stoichiometric mixture of Ti, SiC, and graphite powders at 1600°C for 4 hours under a pressure of 40 MPa. Microstructural analysis indicated that TiC_x was the most common impurity and was present as less than 3 vol. %. Details of the powder processing and resulting microstructures have been presented elsewhere [5,6]. The neutron diffraction measurements were conducted at the High Flux Isotope Reactor (HFIR) on the HB-4, high-resolution neutron powder diffractometer. HB-4 is equipped with a Ge(115) monochromator, 32 equally spaced ^3He detectors. The powder for the original neutron diffraction study was put through a 325 mesh sieve and 4.65 g of this powder was contained in a cylindrical V can suspended in the vacuum furnace. Data were collected at room temperature in the range of 11 to

135 °2 θ at a step size of 0.05 °2 θ , and the data collection time was at least 8 hours for each scan. For the Rietveld refinements the General Structure Analysis System (GSAS) software was used [7]. The structures were drawn using ATOMS software [8].

RESULTS AND DISCUSSION

Figure 1 is a structure projection based on the refined lattice parameters, atomic positions, and atomic displacement parameters (99% probability) that resulted from the room temperature neutron data collection following the heat treatment. The graphical fit to the data is shown in Figure 2 and the profile agreement factors for the Rietveld refinement are $wR_p = 7.30\%$, $\chi^2 = 1.484$, and $R_{exp} = 6.02\%$, where wR_p is the weighted pattern index and χ^2 , the goodness of fit, is the ratio of the weighted pattern wR_p to the expected R_{exp} index. The refined lattice parameters are $a = 3.0654(1)$, $c = 17.635(1)$ Å, and the cell volume = 143.51(1) Å³, where the reported estimated standard deviations, given as 3σ , are in excellent agreement with prior measurements [3,4]. Table 2 gives the refined atomic coordinates and atomic displacement parameters. Refinement of the occupancy factor for the Si site did not reveal any vacancies (fraction occupied = 1.00(2)). Likely what appears as a trend of increasing Si vacancies in the high temperature data sets was related to thermally induced exaggerated atomic displacement parameters and/or the material experiencing grain growth and introducing preferred orientation at higher temperatures. Preferred orientation, atomic displacement parameters, and site occupation all influence the intensity as a function of 2 θ and are therefore all highly correlated, making it difficult to separate one effect from the others in a refinement.

Table 2. Refined atomic coordinates and atomic displacement parameters^{a,b} ($U \cdot 100$) for the room temperature neutron powder diffraction data set following thermal aging.

Atom	multiplicity	symmetry	x	y	z	$U_{11}=U_{22}$ $U_{11}=\frac{1}{2}U_{12}$	U_{33}	U_{eq}
Ti _I	4	$3m$	1/3	2/3	0.1348(2)	0.6(1)	1.3(2)	0.73(6)
Ti _{II}	2	$\bar{3}m$	0	0	0	0.4(1)	0.7(3)	0.46(8)
Si	2	$\bar{6}m2$	0	0	1/4	1.0(1)	1.5(3)	1.00(8)
C	4	$3m$	1/3	2/3	0.57244(8)	0.32(5)	1.3(1)	0.61(3)

^aFor these site symmetries the Debye-Waller factor (T) simplifies to:

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*c^*)] \quad (1)$$

For the hexagonal crystal system anisotropic U_{ij} 's are converted to U_{eq} by:

$$U_{eq} = 1/3(U_{11} + U_{22} + U_{33} - U_{12}) \quad (2).$$

^bThe standard deviation of U_{eq} was calculated as outlined by Schomaker and Marsh [9].

Figure 1. Structure drawn from the refined lattice parameters, atomic positions, and atomic displacement parameters (99% probability) that resulted from the room temperature neutron data collection following the heat treatment.

Figure 2. Graphical fit of the Rietveld refinement.

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