	Experiment title: *In situ* thermodynamic measurements of *C54* titanium disilicide, TiSi$_2$	**Experiment number:** ME 247
Beamline: ID30	**Date of experiment:** from: 5 May 2001 to: 9 May 2001	**Date of report:** February 26, 2002
Shifts: 12	**Local contact(s):** Mohamed Mezouar	*Received at ESRF:*

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Report:

The behaviour of the most technically practical prototype C54 *form of TiSi$_2$ has been studied at high pressures and temperatures by angle dispersive XRD. From these x-ray data we report the decomposition of TiSi$_2$ to an unquenchable osbornite (TiN)-like phase accompanied by a primary melt of pure Si that is found in recovered samples included in recrystallised Ti$_3$Si$_7$. This is in turn surrounded by a matrix of Si$_9$Ti composition. We cannot, at this point, rule out the possibility of of these compositions being Si-deficient TiSi$_{2-x}$ and TiSi$_{1-x}$.*

Somewhat contrary to thin-film experience and calculation, we did not encounter any other stable phase of TiSi$_2$ in our investigation to pressures above 5 GPa and temperatures >1300K. The C49 *phase, in particular, is most notable in its absence. Through unit-cell volume data collected in this study, we also report the compressibility and thermal expansivity of the* C54 *phase. Each of these are in very good agreement with recent calculations of Iannuzzi [1].*

1 Introduction

A review of recent literature reveals an abundance of theoretical calculations and experiments on thin-film titanium disilicides. In particular, on the stability of the *C54* form compared to metastable *C49* and other encountered structural forms of TiSi$_2$. This is primarily due to the high desirability of *C54* in the IC industry, due to its low resistivity in use as a contact to Si in electronic devices. However, the main drawbacks in the production of thin film *C54* are linked to the growth from the *C49* phase and the lattice mismatch with Si and other substrates that may lead to degradation of *C54* to, or preferred growth of primarily, the *C49* (other structures are reported for various compositions of Ti$_X$Si$_Y$; e.g. *C11b*, *C40*) phases during processing. We undertook tests of the stability of bulk TiSi$_2$ in order to elucidate any possible stable phase relationships between the *C54* and other silicide structures commonly occuring in both thin-film processing and *ab initio* experience. We have found that no other previously reported titanium disilicide phases were formed through stable transition within the p, T range investigated. The data collected have afforded analysis of unit-cell volumes in p, T space and we present the results of these thermal expansivity and compressibility in addition to data obtained of the crystallisation of the osbornite-like phase from the observed decomposition.

2 Results

2.1 Thermal Expansivity and Compressibility

Diffraction data were collected for $C54$ from room temperature to 1500K. The results of Rietveld fits of all $P - V$ data above the Debye region (estimated at 510K to 600K [2]) give:

$$lnV = 1.506(7) \times 10^{-8}T^2 + 1.78(13) \times 10^{-5}T + 5.8207(6), \text{ therefore,}$$
$$\alpha = \partial lnV/\partial T = 3.012 \times 10^{-8}T + 1.782 \times 10^{-5} \text{ and } \alpha = 2.680 \times 10^{-5} \text{ K}^{-1}$$

The average thermal expansivity of all data is $\overline{\alpha} = 4.35(13) \times 10^{-5}$. Fitting of a second-order Birch-Murnaghan EoS to 13 data from room pressure to 4.5 GPa result in a $V_0 = 340.74(20)\text{Å}^3$ with $K_0 = 131.7 \pm 3.8$GPa. The low upper pressure limit achieved obtained relative to the incompressibility and imprecision in pressure estimation (± 0.1 GPa, χ^2 of fit = 1.4) under non-hydrostatic conditions does not warrant fitting to a higher order EoS. Nevertheless, our data are in very good agreement with those of Iannuzzi [1], who obtain 2.52×10^{-5} for the linear extrapolation at 600K and of tabulated values of the thermal expansivity in [3].

2.2 Decomposition and Formation of TiSi

The possible formation of TiSi has previously been observed by Muraka and Fraser [4] as a part of two-stage reaction to form $TiSi_2$ by diffusing Si through a Ti substrate in order to first form the monosilicide. This was however re-evaluated as $C49$ by [5] and the XRD lines observed for the TiSi according to [4] do not occur in our pattern.
Our pattern appears to form:

- Decomposition of $TiSi_2$ into Si + Si- deficient TiSi + tentative AlB_2-type ($C32$) phase

- Si melts

- AlB_2 dissolves into the melt, leaving,

- TiSi as TiN, which later melts

3 Conclusions

We have identified that:

1. apart from decomposition, TiSi2 as a bulk material undergoes no stable transition to any other disilicide phase

2. we confirm themal expansivity and produce new data on the compressibility of $C54$

3. we have evidence of a non-quenchable TiN-type monosilicide akin to TiC and also for a $C32$-type phase

4. we are therefore sure that the phase relations occuring in thin-film experience are due only lattice-mismatch-induced strain.

Careful analysis of Ti-Si bond length behaviour at p, T may lead to selection of more appropriate conditions for synthesis of disilicide films without the need for $MoSi_2$ or other mitigating layer.

1. Iannuzzi, M., Miglio, L. and M. Celino (2000) *Phys. Rev. B* **61** 14405

2. Affronte, M. Labourde, J. C., Lasjaunias, U., Gottlieb, U. and R. Madar (1996) *Phys. Rev. B* **54** 7799

3. *Properties of Metal Silicides*, edited by K. Maex and M. Van Rossum (INSPEC, London, 1995)

4. Muraka and Fraser (1980) *J. Appl. Phys.* **51** 342

5. Beyers, R. and R. Sinclair (1985) *J. Appl. Phys.* **57** 5240