EFFECT OF TERNARY ADDITIONS ON THE OXIDATION RESISTANCE OF Ti_5Si_3

Andrew J. Thom and Mufit Akinc

Ames Laboratory* and Department of Materials Science and Engineering
Iowa State University, Ames, IA 50011

ABSTRACT

Refractory intermetallic silicides are receiving increasing consideration for use as high temperature structural materials. Ti_5Si_3 -based compositions are attractive due to their ability to incorporate a variety of interstitial ternary additions. These ternary additions present a unique opportunity to potentially tailor physical properties. Previous experimental work has shown that these additions significantly increase the otherwise poor oxidation resistance of undoped Ti_5Si_3 above 700°C. Recent experimental work by the authors on the oxidation of small atom doped Ti_5Si_3 is discussed. Interstitial additions of boron, carbon, and oxygen substantially improve the isothermal oxidation resistance of Ti_5Si_3 at 1000°C. In contrast, added nitrogen does not provide significant improvement. Even up to 1306°C, interstitial oxygen imparts excellent oxidation resistance with a mass gain of 1.1 mg/cm² after 240 hours.

*Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract number W-7405-ENG-82. This research was supported by the Office of Basic Energy Science, Materials Science Division.

DISCLAIMER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED JR

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTRODUCTION

The need for better performing high temperature structural materials has generated considerable interest in the processing and properties of advanced intermetallics. The status of intermetallic research pertaining to high temperature structural applications has been summarized by several authors (1,2,3,4,5). Anton et al. have recommended several selection criteria for determining candidate material systems (1). Among these criteria is adequate oxidation resistance, and therefore silicon-bearing intermetallics are candidate materials since they are more likely to form protective scales. A_5Si_3 intermetallic silicides (A=transition metal) are particularly interesting since this phase is typically the highest melting compound in the respective A-Si binary phase diagram. The compound Ti_5Si_3 is particularly attractive because of its high melting point of 2130°C, adequate oxidation resistance, and low density of 4.32 g/cm³.

Liu et al. (6) produced alloys of Ti-29Si-8Cr, Ti-33Si-4Cr-4Zr, and Ti-36.5Si by arc melting and casting. Isothermal oxidation at 800°C in air showed parabolic oxidation for the last two alloys with a mass gain of 0.88 and 0.98 mg/cm² at 120 hours. The alloy of lowest silicon content showed linear oxidation with a mass gain of 1.8 mg/cm² at 120 hours. All three alloys formed adherent scales. Anton and Shah (7) performed cyclical oxidation testing of arc-cast Ti_5Si_3 at 1149°C. After 50 hours the mass gain was about 31 mg/cm². An external brown oxide was observed, and x-ray diffraction of the oxidation products indicated 75-80 vol. % TiO_2 (rutile), 20 vol. % hexagonal Ti_5Si_3 and less than 5 vol. % tetragonal SiO_2 (α -cristobalite).

While Ti_5Si_3 has adequate oxidation resistance up to about 800°C, envisioned use temperatures for new high temperature structural applications extend well in excess of 1000°C. The key to the potential usefulness of Ti_5Si_3 -based materials lies in the ability to vary stoichiometry by the incorporation of ternary interstitial additions. This property arises from the interesting Mn_5Si_3 -type structure of Ti_5Si_3 . The hexagonal Mn_5Si_3 structure can incorporate a wide variety and amount of atoms in the interstitial sites at the corners of the unit cell (8,9,10,11). This presents a unique opportunity to tailor properties such as oxidation resistance by the proper interstitial addition.

This work presents some very encouraging results on the improvement in oxidation resistance of Ti_5Si_3 resulting from ternary additions.

EXPERIMENTAL

Nominal compositions of $Ti_5Si_3Z_x$ ($x = 0.25, 0.50, 0.75$) were synthesized by the method of arc-melting. Table I shows the starting constituents for each of the various compositions synthesized. Materials were arc-melted under argon using a non-consumable tungsten electrode. Materials were triple melted to promote chemical homogenization.

Table I - Starting Materials for Synthesized $Ti_5Si_3Z_x$

Composition	Starting materials
$Ti_5Si_3B_x$	$Ti_5Si_3 + B$
$Ti_5Si_3C_x$	$Ti_5Si_3 + \text{graphite}$
$Ti_5Si_3N_x$	$Ti_5Si_3 + TiN + Si$
$Ti_5Si_3O_x$	$Ti_5Si_3 + TiO_2 + Si$

For each of the synthesized compositions, the starting Ti_5Si_3 was previously arc-melted from elemental Ti and Si. Because of the high melting point of boron, graphite, and TiN, prealloyed Ti_5Si_3 was used as a starting material to reduce the amount of silicon volatilization compared to using elemental silicon. Carbon, nitrogen, and oxygen content were analyzed by the technique of inert gas fusion and combustion analysis. Boron was analyzed by spark source laser mass spectroscopy. The arc-melt buttons were ground in an agate mortar and pestle and sieved to -325 mesh for x-ray diffraction. The powders were analyzed in a powder x-ray diffractometer using $\text{Cu K}\alpha$ radiation.

During powder processing of Ti_5Si_3 , powders must be handled under inert conditions. To accomplish this, a Spex Mixer-mill was placed inside a glovebox which contained an argon atmosphere and a recirculating purification system to maintain a low water and oxygen content, oxygen measured to be typically 0.5 parts per million (ppm). Atmospheric control is necessary because finely milled Ti_5Si_3 will visibly combust when exposed to ambient air.

Facilities are available to mill, sieve, cold-press, and encapsulate the unconsolidated pellets without exposure to ambient air. Powders were prepared by loading arc-melt material into a WC-lined mill container inside the atmosphere controlled glovebox and milling exclusively inside the glovebox for 90 minutes. About 2 wt.% grinding additive was used to reduce caking of the powders and increase grinding efficiency. The milled powder was sieved to -635 mesh (less than 20 μm). Pellets were cold-pressed in a 13 mm diameter die at 87 MPa, yielding typical green densities of about 62% of theoretical ($\rho_{\text{th}} = 4.32 \text{ g/cm}^3$). The pellets containing a grinding additive were slowly heated and pre-fired at 1000°C under flowing ultra-high purity (UHP) argon to burnout the grinding additive prior to hot isostatic pressing (HIPing).

The green bodies were then embedded within boron nitride powder and sealed in borosilicate tubes. Ti_5Si_3 was HIPed at 206 MPa and 1200°C for 10 hours. A slow cooling rate of 1-2°C/min. was used to minimize bulk thermal stresses and reduce cracking.

Specimens for isothermal oxidation studies were prepared by cutting coupons from HIPed specimens. A 0.5 mm diameter hole was EDM-drilled in the coupons from which to suspend the samples in a vertical tube thermogravimetric analyzer using 125 μm diameter sapphire fiber. Samples were heated at 20°C/min. in flowing air. Ti_5Si_3 coupons were polished through 0.05 μm Al_2O_3 abrasive and oxidized in synthetic 'zero' air (mixture of 79% N_2 -21% O_2 and water typically 3 ppm). Continuous isothermal oxidation was measured for up to 240 hours.

The oxidized sample surface was analyzed by x-ray diffraction. Cross-sections of selected oxidized samples were analyzed by optical and electron microscopy, including x-ray dot mapping and energy dispersive spectroscopy (EDS).

RESULTS AND DISCUSSION

Composition and Structure

The synthesis and characterization of arc-melted Ti_5Si_3 used in this study has been previously discussed (12). Some of the salient results of chemical analysis regarding materials used in this study are given below in Table II.

Table II - Chemical Analysis of Arc-Melted $\text{Ti}_5\text{Si}_3\text{Z}_x$

Nominal Composition	Carbon (x) wt%	Nitrogen (x) wt%	Oxygen (x) wt%	Boron (x) wt%
Ti_5Si_3	120 ppm	69 ppm	1100 ppm	*
$\text{Ti}_5\text{Si}_3\text{C}_{0.25}$	$x = 0.25$	56 ppm	674 ppm	*
$\text{Ti}_5\text{Si}_3\text{C}_{0.75}$	$x = 0.71$	58 ppm	186 ppm	*
$\text{Ti}_5\text{Si}_3\text{B}_{0.25}$	260 ppm	58 ppm	750 ppm	$x = 0.18$
$\text{Ti}_5\text{Si}_3\text{B}_{0.75}$	180 ppm	58 ppm	940 ppm	$x = 0.75$
$\text{Ti}_5\text{Si}_3\text{N}_{0.25}$	150 ppm	$x = 0.17$	910 ppm	*
$\text{Ti}_5\text{Si}_3\text{N}_{0.75}$	170 ppm	$x = 0.52$	1200 ppm	*
$\text{Ti}_5\text{Si}_3\text{O}_{0.25}$	290 ppm	120 ppm	$x = 0.27$	*
$\text{Ti}_5\text{Si}_3\text{O}_{0.75}$	250 ppm	200 ppm	$x = 0.65$	*

*Not analyzed

This analysis indicates the presence of the intended dopant at levels reasonably close to the intended nominal composition. Powder x-ray diffraction (XRD) indicates that each composition has the Mn_5Si_3 structure with only a few minor unidentified peaks. XRD when coupled with chemical analysis has shown that several at. % of boron, carbon, nitrogen, and oxygen can be added to Ti_5Si_3 without significant second phase formation or change in the Mn_5Si_3 -type crystal structure. This is consistent with available ternary phase diagrams which indicate that up to 10 at. % ($x \approx 1$) of carbon, nitrogen, and oxygen can be accommodated into the structure at 1000-1100°C (13,14,15).

Oxidation

Undoped Ti_5Si_3

The isothermal oxidation of Ti_5Si_3 has been previously investigated from 700-1000°C in dry synthetic air (16,17). In summary, material at 700°C showed mass gains of less than 0.1 mg/cm² after 120 hours. At 700°C, the external surface was slightly tarnished, indicating the presence of a thin film. ESCA indicated predominately TiO_2 on the surface plus a minor amount of SiO_2 . For temperatures from 800-1000°C, the samples showed initial transient oxidation followed by assumption of a higher rate of mass gain. This transition to a higher rate occurred at shorter times as temperature increased. Mass gain after 115 hours was about 6 mg/cm². At 900°C mass gain increased significantly to nearly 12 mg/cm² at 72 hours. Oxidation at 1000°C caused growth of a dense outer 10 μm layer of rutile with an underlying stratified scale morphology consisting of interspersed silica and a total thickness of several hundred microns. Mass gain further increased to nearly 14 mg/cm² after only 60 hours.

Doped Ti_5Si_3

A dramatic improvement in oxidation resistance results from the addition of carbon to Ti_5Si_3 (17). Figure 1 shows the oxidation behavior of carbon-doped material at 1000°C compared to fine-grained, undoped Ti_5Si_3 . Carbon doping promotes parabolic oxidation kinetics, 5.2×10^{-4} mg²/cm⁴/hr for $\text{Ti}_5\text{Si}_3\text{C}_{0.25}$, after an initial transient period of about 30 hours. The mass gain at 1000°C for carbon doped material varies from 0.15-0.3 mg/cm², almost two orders of magnitude lower than

undoped material. A duplex scale forms, about 2-4 μm thick. A thin silicon rich layer underlies an external rutile layer.

Figure 1 - Isothermal oxidation of $\text{Ti}_5\text{Si}_3\text{C}_x$ in zero air at 1000°C compared to undoped Ti_5Si_3 .

Figure 2 - Isothermal oxidation of $\text{Ti}_5\text{Si}_3\text{Z}_{0.25}$ ($\text{Z}=\text{B}, \text{C}, \text{N}, \text{O}$) in zero air at 1000°C compared to undoped Ti_5Si_3 .

The oxidation behavior of boron, nitrogen, and oxygen doped Ti_5Si_3 at the level of $x=0.25$ is shown in Figure 2. For comparative purposes, Ti_5Si_3 and $\text{Ti}_5\text{Si}_3\text{C}_{0.25}$ are also plotted. The addition of boron and oxygen significantly improve oxidation resistance. However, nitrogen doped material has about the same oxidative stability as the undoped material. Table III shows the mass gain at the conclusion of the run for all compositions tested. These results are consistent with the observed trends in Figure 2.

Table III- Mass Gain for Oxidized $\text{Ti}_5\text{Si}_3\text{Z}_x$ ($Z=\text{B,C,N,O}$)

Nominal Composition	Mass Gain (mg/cm^2)	Temperature ($^{\circ}\text{C}$)	Time (hrs)
Ti_5Si_3	14	1000	60
$\text{Ti}_5\text{Si}_3\text{C}_{0.25}$	0.22	1000	115
$\text{Ti}_5\text{Si}_3\text{C}_{0.75}$	0.36	1000	130
$\text{Ti}_5\text{Si}_3\text{B}_{0.25}$	0.50	1000	130
$\text{Ti}_5\text{Si}_3\text{B}_{0.75}$	0.53	1079	130
$\text{Ti}_5\text{Si}_3\text{O}_{0.25}$	0.45	1000	240
$\text{Ti}_5\text{Si}_3\text{O}_{0.75}$	0.82	1079	130
$\text{Ti}_5\text{Si}_3\text{N}_{0.25}$	5.5	1000	48
$\text{Ti}_5\text{Si}_3\text{N}_{0.75}$	10	1000	48

Figure 3 shows a compositional backscattered electron (BSE) image of the scale which develops on $\text{Ti}_5\text{Si}_3\text{B}_{0.75}$ oxidized at 1079°C . Due to the fine nature of the scale, EDS spot analysis and x-ray dot mapping were inconclusive. XRD of the scale exterior indicates presence of rutile (JCPDS Card #21-1276) and α -cristobalite (JCPDS Card #39-1425). Coupled with the BSE image contrast observed in the duplex phase assemblage, this information indicates that the scale consists of a crystalline silica matrix forming a thin continuous layer with a substantial volume fraction of titania particles. The total scale thickness is $2\text{-}3\text{ }\mu\text{m}$ with $1\text{ }\mu\text{m}$ -sized irregular-shaped titania particles.

Figure 3 - Backscattered electron image of $\text{Ti}_5\text{Si}_3\text{B}_{0.75}$ oxidized at 1079°C .

The high temperature oxidative stability of these compositions is indicated by their isothermal oxidation at 1306°C. These results are given in Figure 4. $\text{Ti}_5\text{Si}_3\text{C}_{0.25}$ was only tested up to 1191°C, and so it has been included in the plot for comparative purposes only. There is a general loss of protective behavior with a few notable exceptions. $\text{Ti}_5\text{Si}_3\text{B}_{0.75}$ undergoes rapid transient oxidation, but assumes a linear mass gain after about ten hours. The linear rate constant, $1.9 \times 10^{-2} \text{ mg/cm}^2/\text{hr}$, is about an order of magnitude lower than the linear rate constant of undoped Ti_5Si_3 at 1000°C.

The most notable feature of Figure 4 is that $\text{Ti}_5\text{Si}_3\text{O}_{0.25}$ maintains protective behavior at the test temperature of 1306°C. Mass gain after 240 hours is about 1.1 mg/cm^2 . Figure 5 shows a compositional backscattered electron (BSE) image of the scale which developed on $\text{Ti}_5\text{Si}_3\text{O}_{0.25}$ oxidized at 1306°C. The small bright spots correspond to residual polishing media. EDS spot analysis and x-ray dot mapping indicate the scale is composed of Ti-rich, Si-deficient particles in a matrix phase which is Si-rich and Ti-deficient. XRD of the scale exterior indicates presence of rutile and α -cristobalite. Based on these data, the scale consists of crystalline silica matrix forming a continuous layer containing titania particles. The total scale thickness is 5-10 μm with 3-8 μm regularly shaped titania particles. Apparently the continuous silica layer is imparting protective behavior to the material.

The increased oxidation resistance of interstitially doped Ti_5Si_3 is likely related to the effect of ternary atom on the local bonding nature of titanium atoms within the Mn_5Si_3 structure of Ti_5Si_3 . Single crystal x-ray diffraction data indicate a contraction of the interstitial cavity in response to the presence of a Z interstitial atom (12). Additionally, increases are observed in Ti-Si bond lengths. The bonding which develops between Ti and Z atoms likely decreases Ti activity while the increase in Ti-Si bond lengths increases Si activity. The overall net effect should be an increase in Si mobility relative to Ti, providing for sufficient mobility of Si to form a continuous silica layer. This is an obviously oversimplified description which requires further research and modeling.

Figure 4 - Isothermal oxidation of $\text{Ti}_5\text{Si}_3\text{Z}_x$ oxidized at 1306°C.

Figure 5 - Backscattered electron image of $\text{Ti}_5\text{Si}_3\text{O}_{0.25}$ oxidized at 1306°C .

SUMMARY

Transition metal intermetallic silicides have been demonstrated to be potential high temperature structural materials. Ti_5Si_3 possesses attractive properties, but cannot be used in pure monolithic form due to poor oxidation resistance above 700°C . The addition of interstitial atoms, including boron, carbon, and oxygen, dramatically improves oxidation resistance. It is anticipated that these interstitial additions may also have similar beneficial effects on the mechanical properties.

REFERENCES

1. D. L. Anton, D. M. Shah, D. N. Duhl, and A. F. Giamei, "Selecting High-Temperature Structural Intermetallic Compounds: The Engineering Approach," Journal of Metals, Sept. (1989), 12-17.
2. A. I. Taub and R. L. Fleischer, "Intermetallic Compounds for High-Temperature Structural Use," Science, 243 (1989), 616-621.
3. P. J. Meschter and D. S. Schwartz, "Silicide-Matrix Materials for High-Temperature Applications," Journal of Metals, Nov. (1989), 52-55.
4. D. M. Shah, D. Berczik, D. L. Anton, and R. Hecht, "Appraisal of other Silicides as Structural Materials," Mat. Sci. Eng., A155 (1992), 45-57.
5. K. S. Kumar and C. T. Liu, "Ordered Intermetallic Alloys, Part II: Silicides, Trialuminides, and Others," J. Metals, June (1993), 28-34.
6. C.T. Liu, E. H. Lee, and T. J. Henson, "Initial Development of High Temperature Titanium Silicide Alloys," (Report ORNL-6435; Order No. DE88007860, 1988).
7. D. M. Shah, Private communication with author, Pratt and Whitney, 15 September 1992.

8. E. Garcia and J. D. Corbett, "Chemistry of Polar Intermetallic Compounds. Study of Two Zr_5Sb_3 Phases, Hosts for a Diverse Interstitial Chemistry," Inorganic Chem., 27 (1988), 2353-2359.
9. Y. Kwon, M. A. Rzeznik, A. Guloy, and J. D. Corbett, "Impurity Stabilization of Phases with the Mn_5Si_3 -Type Structure. Questions Regarding La_5Sn_3 and Zr_5Si_3 ," Chem. Mater., 2 (1990), 546-550.
10. E. Garcia and J. D. Corbett, "Chemistry in the Polar Intermetallic Host Zr_5Sb_3 . Fifteen Interstitial Compounds," Inorganic Chem., 29 (1990), 3274-3282.
11. Y. Kwon and J. D. Corbett, "Chemistry in Polar Intermetallic Compounds. The Interstitial Chemistry of Zr_5Sn_3 ," Chem. Mater., 4 (1992), 1348-1355.
12. A. J. Thom, V. Young, and M. Akinc, "Single Crystal Studies of $Ti_5Si_3Z_x$," to be published.
13. J. I. Goldstein, S. K. Choi, F. J. J. Van Loo, G. F. Bastin, and R. Metselaar, "Solid State Reactions and Phase Relations in the Ti-Si-O System at 1373K", Journal Amer. Ceram. Soc., 78 [2] (1995), 313-322.
14. S. Arunajatesan and A. H. Carim, "Synthesis of Titanium Silicon Carbide," Journal Amer. Ceram. Soc., 78 [3] (1995) 667-672.
15. S. Sambasivan and W. T. Petuskey, "Phase Chemistry in the Ti-Si-N System: Thermochemical Review with Phase Stability Diagrams", Journal Mater. Res., 9 [9] (1994), 2362-2369.
16. A.J. Thom, Y. Kim, and M. Akinc, "Effect of Processing on Oxidation of Ti_5Si_3 ," Mat. Res. Soc. Symp. Proc., vol. 288, edited by Baker, Darolia, Whittenberger, and Yoo (Pittsburgh, PA: Materials Research Society, (1993), 1037-1042.
17. A. J. Thom, M. K. Meyer, Y. Kim, and M. Akinc, "Evaluation of $A_5Si_3Z_x$ Intermetallics for Use as High Temperature Structural Materials," Min. Met. Mater. Soc. Symp. Proc., edited by T. S. Srivatsan and V. A. Ravi, Processing and Fabrication of Advanced Materials for High-Temperature Applications - III, (1994) 413-439.