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Synthesis of Titanium Silicon Carbide

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Synthesis of bulk titanium silicon carbide (Ti_3SiC_2) from the elemental Ti, Si, and C powders has been accomplished for the first time, using the arc-melting and annealing route. The effects of various parameters on the phase purity of the Ti_3SiC_2 have been examined, including the starting composition of the powders, compaction technique, arc-melting of the samples, and temperature and time of anneal. The best bulk samples, containing about 2 vol% TiC as the second phase, were made from Si-deficient and C-rich starting compositions. Based on electron probe microanalysis data from a number of bulk samples, it appears that Ti_3SiC_2 exists over a range of compositions; the Ti–Si–C ternary section has been modified to reflect this. The purest samples of the ternary phase were obtained by leaching powders of silicide-containing samples in diluted HF, and contained over 99 vol% Ti_3SiC_2.

I. Introduction

Ti–SiC is one example of a metal–ceramic system that is of technological interest for its high-temperature stability and workability. The properties of such systems are limited by the chemical interactions and formation of reaction products at the metal–ceramic interface. Consequently, the phase relationships in the Ti–Si–C system have been studied by several authors. The ternary section at 1200°C has been established under 1 atm pressure[1–3] and at pressures greater than 2400 atm.[4,5] The currently accepted version of the ternary section at 1200°C under 1 atm pressure was established by Ratliff and Powell[3] and is shown in Fig. 1.

Of the various reaction products within this ternary system, only the formation of the ternary phase Ti_3SiC_2 has been associated with an improvement in Ti–SiC interfacial mechanical properties.[6–8] This has motivated attempts to synthesize Ti_3SiC_2 and study its properties. To date, pure Ti_3SiC_2 has been synthesized only by CVD techniques, in small quantities.[9–11] Attempts to synthesize Ti_3SiC_2-based materials in bulk resulted in composites—one containing about 10–20 vol% TiC[12,13] and another containing some SiC.[14,15] Some of the properties of the CVD Ti_3SiC_2 and the composites have been measured; a reported melting point of 3000°C[12] combined with some indications of plastic behavior[10,11,13] would suggest that Ti_3SiC_2 has unusual characteristics and is a potentially useful transition material at the Ti/SiC interface. This report pertains to the bulk synthesis of Ti_3SiC_2 from Ti, Si, and C by reacting and annealing of elemental powders in an inert atmosphere or under vacuum.

II. Experimental Procedure

Commercially available Ti, Si, and C powders were used to make samples. Attempts were made to work with SiC and TiC, but the hard abrasive powders proved to be very difficult to compact and hence had to be abandoned. The powders were stored and weighed in a glove box in an argon atmosphere and hand-mixed using a mortar and pestle. Subsequent processing of the powders varied considerably and is described in detail below.

In one technique the powder mixture was transferred directly to an alumina boat. The boat containing the powder mixture was placed in a furnace containing an Ar atmosphere at temperatures of 1270° to 1375°C for periods up to 24 h. The partially sintered material was then crushed into powder for characterization.

In the second technique, the powder mixture was first compacted in a hardened steel die to make pellets. Some of these were arc-melted in an Ar atmosphere, using a nonconsumable tungsten electrode. A titanium pellet was first arc-melted just before melting each set of samples; the Ti was expected to act as a getter and pick up any residual oxygen in the arc-melting chamber. All samples were then placed individually in quartz tubes and heated under vacuum to drive off volatiles. For the samples that were not arc-melted, a piece of silica wool was placed between the sample and the open end of the tube to prevent the samples from falling apart. The tubes were sealed under a vacuum of better than 6×10^{-5} atm and annealed at 1400°C for 5 h, at 900°C for 24 h, or at 1200°C for 100 h. All tubes were furnace-cooled and subsequently broken to extract the samples for characterization.

After annealing, some of the samples were crushed by grinding with a mortar and pestle. The resulting powder was leached in a 1:5 (volume ratio) $HF:H_2O$ solution for different time

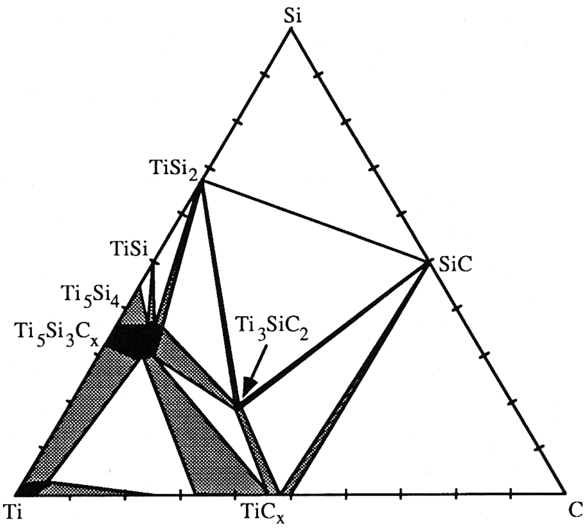

Fig. 1. Ti–Si–C ternary section at 1200°C, redrawn on a mole percent scale. (After Ratliff and Powell.[3])

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periods in an attempt to isolate the ternary phase. The powders were washed in acetone before being characterized.

X-ray diffraction (XRD) and electron probe microanalysis (EPMA) were the primary characterization tools used for phase identification. Powders of the annealed samples were used for XRD which was performed on a Rigaku diffractometer using Cu$K\alpha$ radiation with a wavelength of 1.54 Å. A Cameca SX 50 electron probe was used to observe secondary electron and backscattered electron images of the polished samples, and to analyze the compositions of the different phases present in the samples using wavelength dispersive spectroscopy (WDS). The probe was operated at an acceleration potential of 15 kV and a current of 12 nA. For the WDS, pure metallic Ti was used as a standard for Ti and uncoated SiC for Si and C. Charging was evident for some samples; carbon was coated onto these to alleviate the problem, and the C was analyzed by difference. The $K\alpha$ intensity ratios for the Ti and Si were generated using a pentaerythritol (PET) crystal, while the ratio for C was determined using a W/Si layered synthetic microstructure. Oxygen analyses were done at random on the interiors of some samples prepared by each technique (e.g., with and without arc melting) and no oxygen was detected; furthermore, the XRD patterns were checked against the various oxides of Ti and no match was obtained.

III. Results and Discussion

XRD of the uncompacted powder mixtures annealed in an argon atmosphere did not indicate the formation of any Ti_3SiC_2. The main constituents of the annealed samples were TiC and C, suggesting a loss of Si. Small amounts of $Ti_5Si_3C_x$ also appear to have formed. At any rate, since detectable amounts of Ti_3SiC_2 did not form, this method was not pursued further. All further samples were die-compacted prior to arc-melting and/or annealing. (A summary of the phases present in the samples discussed in this report is given in Table I.)

(1) *Effect of Temperature*

Because our initial interest was in phase formation in brazed ceramic joints, the first set of compacted samples was annealed at 900°C. It was found that even after annealing for 24 h, no Ti_3SiC_2 formed; the sample contained $Ti_5Si_3C_x$, $TiSi_2$, and TiC. Not surprisingly, equilibrium does not appear to be achieved under these conditions because diffusion is not sufficiently rapid. The annealing temperature of the samples was then raised to 1400°C and the annealing time reduced to 5 h. XRD performed on the annealed samples showed the presence of significant amounts of Ti_3SiC_2. However, the quartz tubes in which the samples were encapsulated were found to collapse on the sample under these conditions. Although the samples did not react with the collapsed tube in every case, they did react in some cases and it was not possible to foresee which samples would react and which would not. The unpredictability was probably due to small compositional variations in the commercial quartz tube. In order to obtain equilibrium Ti_3SiC_2-containing samples without interactions with the tube, the remaining samples were annealed for 100 h at 1200°C. This time period was considered to be appropriate for reaching equilibrium by comparison with prior studies of the Ti–Si–C system; Brukl's conclusions[2] were based on samples that were hot-pressed for 50 to 87 h at 1200°C, whereas Ratliff *et al.*[3] assumed equilibrium for samples that were annealed for only 8 h at 1200°C. As described further below, in most cases extraneous phases were eliminated after 100 h and thus it appears that near-equilibrium conditions were achieved.

(2) *Effect of Arc-Melting*

Arc-melting was done to improve chemical homogeneity of the samples. It was also found that the samples that were only arc-melted (without subsequent annealing) had not reached equilibrium. Figure 2 is a backscattered electron image of a sample made with a starting composition $Ti_3Si_{1.5}C_2$, obtained just after arc-melting. It can be seen from the ternary section (Fig. 1) that the coexistence of the three observed phases—Ti_3SiC_2, TiC, and $TiSi_2$—is not consistent with the expected thermodynamic equilibrium at 1200°C. This result may indicate that equilibrium was not attained, or that the equilibrium at the very high temperature corresponding to arc-melting includes a mixture of solid phases (presumably Ti_3SiC_2 and TiC) and a liquid alloy. On annealing, the sample contains the equilibrated phase assemblage of Ti_3SiC_2, $TiSi_2$, and SiC.

In order to understand the role of arc-melting in the formation of Ti_3SiC_2, a pellet formed from elemental powders with

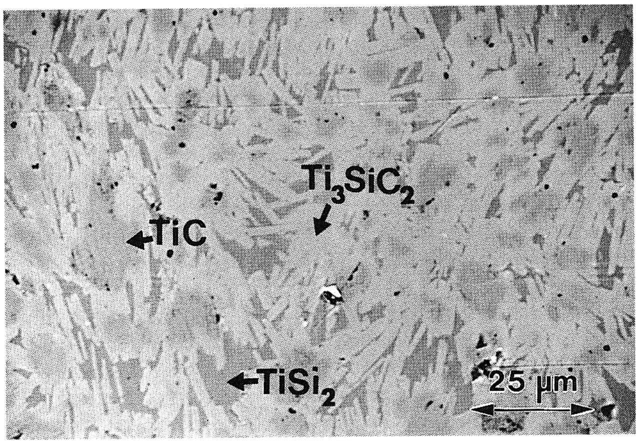

Fig. 2. Backscattered electron image of a sample with nominal composition $Ti_3Si_{1.5}C_2$ after arc-melting only. A nonequilibrium mixture of phases is present.

Table I. Phases Present after Various Treatments, as Described in the Text*

Processing and nominal stoichiometry	Anneal, ambient temperature, time	Phases present (by XRD and EPMA)
Uncompacted powder mixtures; Ti_3SiC_2 and $Ti_3Si_{1.5}C_2$	Ar, 1270–1375°C, up to 24 h	TiC, C, small amounts of $Ti_5Si_3C_x$
Arc-melted; $Ti_3Si_{1.5}C_2$	Vacuum, 900°C, 24 h	TiC, $TiSi_2$, $Ti_5Si_3C_x$
Arc-melted; Ti_3SiC_2 and $Ti_3Si_{1.5}C_2$	Vacuum, 1400°C, 5 h	(Varied; often reacted with quartz tubes)
Arc-melted; $Ti_3Si_{1.5}C_2$	(Not annealed)	Ti_3SiC_2, TiC, $TiSi_2$
Arc-melted; $Ti_3Si_{1.5}C_2$	Vacuum, 1200°C, 100 h	Ti_3SiC_2, SiC, $TiSi_2$, occasionally some $Ti_5Si_3C_x$
Arc-melted; Ti_3SiC_2	(Not annealed)	Ti_3SiC_2, TiC
Arc-melted; Ti_3SiC_2	Vacuum, 1200°C, 100 h	Ti_3SiC_2, TiC, $Ti_5Si_3C_x$
Not arc-melted; $Ti_3Si_{1.5}C_2$	Vacuum, 1400°C, 5 h	(Tube burst)
Not arc-melted; $Ti_3Si_{1.5}C_2$	Vacuum, 1200°C, 100 h	(Tube burst)
Arc-melted; $Ti_3Si_{1.1}C_2$	Vacuum, 1200°C, 100 h	Ti_3SiC_2, TiC, $Ti_5Si_3C_x$
Arc-melted; $Ti_3Si_{0.95}C_{2.15}$	Vacuum, 1200°C, 100 h	~98% Ti_3SiC_2 (+TiC_x, very little $Ti_5Si_3C_x$)
Arc-melted; $Ti_3Si_{1.8}C_{1.2}$	Vacuum, 1200°C, 100 h	Ti_3SiC_2, $TiSi_2$, $Ti_5Si_3C_x$; after leaching: ~99.6% Ti_3SiC_2, remainder TiC
Arc-melted; $Ti_3Si_{2.2}C_{0.8}$	Vacuum, 1200°C, 100 h	Ti_3SiC_2, $TiSi_2$, $Ti_5Si_3C_x$; after leaching: ~98.4% Ti_3SiC_2, remainder TiC

*All samples made from die-compacted powders except where indicated otherwise.

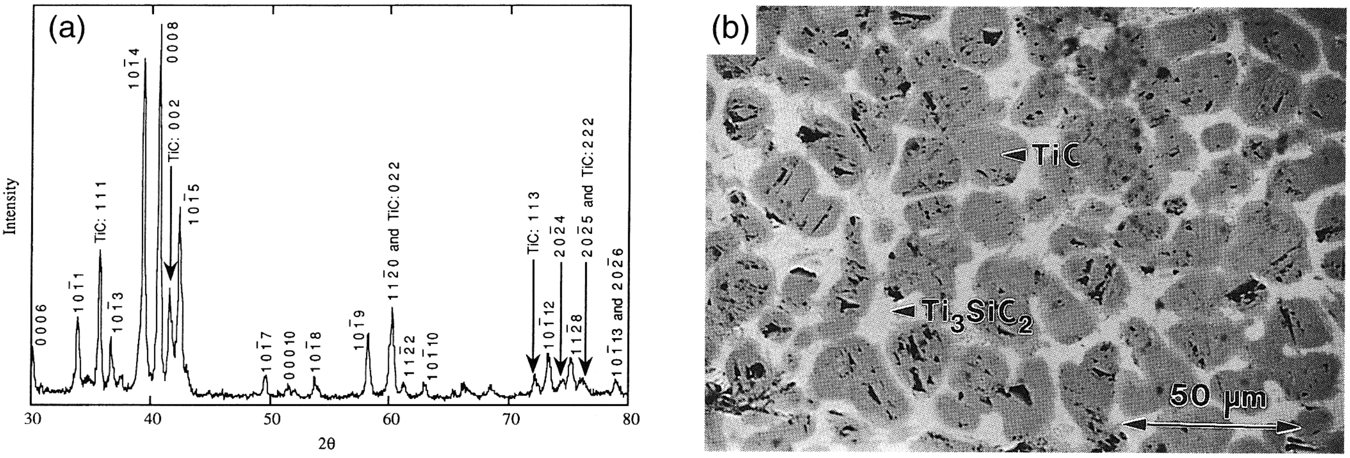

Fig. 3. (a) XRD pattern and (b) backscattered electron image, both obtained after arc-melting only, of a sample with a nominal starting composition of Ti_3SiC_2. Peaks are indexed for Ti_3SiC_2 except where indicated otherwise.

starting composition Ti_3SiC_2 was arc-melted and, with no further annealing, examined by EPMA and XRD. Figures 3(a) and (b) are the XRD pattern of the sample right after arc-melting and the corresponding backscattered electron image of the microstructure. The sample shows a "droplet"-type microstructure of TiC in a Ti_3SiC_2 matrix. A sample with the same starting composition was arc-melted and then annealed at 1200°C for 100 h and the resulting diffraction data and microstructure are shown in Fig. 4. It is interesting to note that on annealing, the sample contains Ti_3SiC_2, $Ti_5Si_3C_x$, and TiC; i.e., it lies in a three-phase region. As can be seen from the ternary section at 1200°C (Fig. 1), this would be the case if there is a loss of Si and/or C during the processing stages. During arc-melting, the temperatures are high enough for the Si to vaporize (the boiling point of Si is 2355°C) and this could result in the loss of Si in the arc-melter. The loss of C could occur due to the turbulent nature of the arc-melting process, at the start of which some powder was seen to be thrown out of some of the compacted pellets.

An attempt was made to investigate the role of arc-melting in the loss of Si and/or C by annealing some samples without arc-melting them. These samples, encapsulated in evacuated quartz tubes, were annealed either at 1400°C for 5 h or at 1200°C for 100 h. In every case it was found that the quartz tubes burst open while in the furnace and the samples, exposed to atmospheric oxygen, were oxidized. This never occurred with samples that were arc-melted, which indicates that in the case of samples that were not arc-melted, a pressure buildup occurs in the quartz tube during annealing and that this problem is averted by arc-melting of the samples.

The equilibrium pressure within the quartz tube at 1200°C, with 3 mol of Ti, 1 mol of Si, and 2 mol of C as the system components, was calculated using the commercially available thermodynamic software Chemsage. The calculated equilibrium pressure is several orders of magnitude less than atmospheric pressure and hence cannot account for the bursting of the tube. However, on including even 0.1 mol of water as an additional component in the system, the equilibrium pressure is about 8.5 atm—which would cause rupture of the quartz tube.

To detect any significant quantities of water in the Si and/or C powder, especially in light of the three-phase microstructure observed, thermogravimetric analysis (TGA) was performed on both the Si and C powder in argon atmospheres. No loss of weight was detected in either case. The detection limit of the TGA is about 1 wt%, which implies that the H_2O contents associated with the Si and C powders are less than about 1.5 and 0.7 mol%, respectively.

Although such quantities are small, that amount of water could arise from absorption of atmospheric H_2O during storage and/or processing and would account for the bursting of the quartz tubes (containing samples that were not arc-melted) during annealing. The encapsulation process apparently was not sufficient to drive off all water vapor or other gases adsorbed on the powder particles in the compact. However, the amount of water is not large enough to explain the off-stoichiometric microstructure observed in the annealed samples. This would

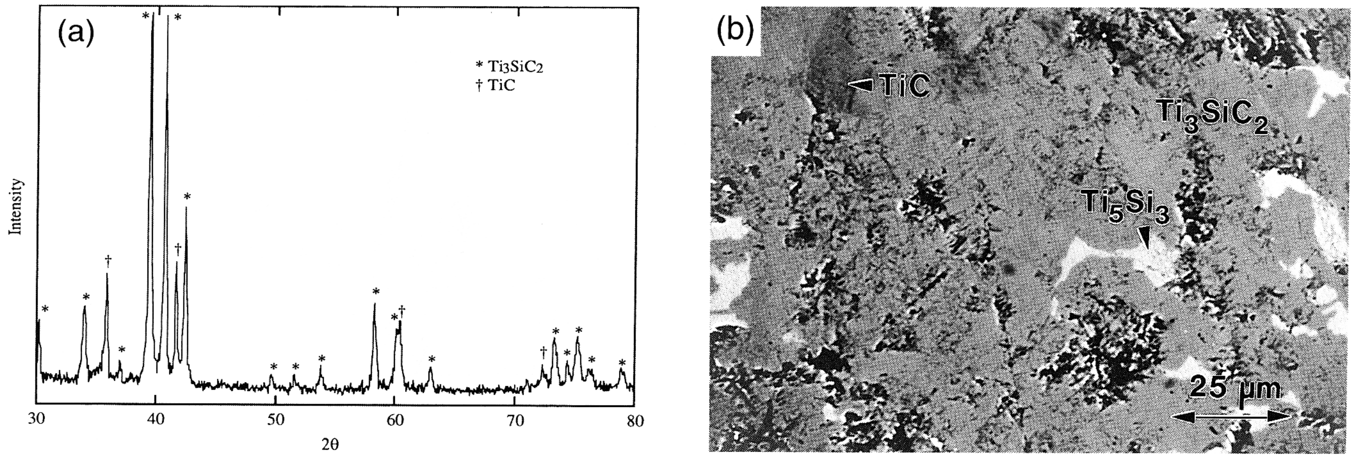

Fig. 4. (a) XRD pattern and (b) backscattered electron image of a sample with a starting composition Ti_3SiC_2 after both arc-melting and annealing at 1200°C for 100 h.

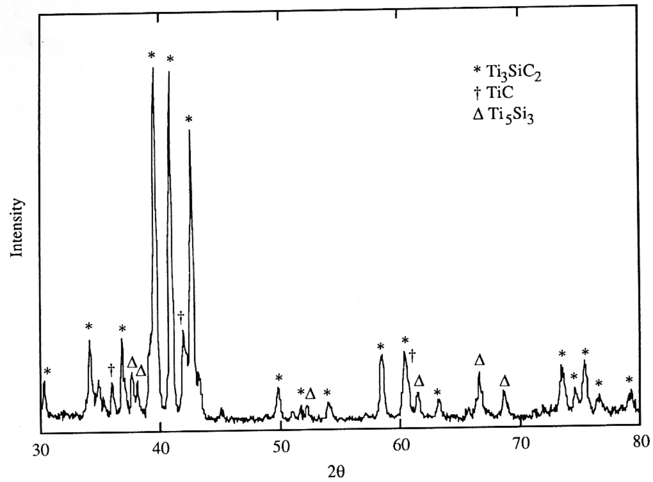

Fig. 5. XRD pattern of a sample with a starting composition that was about 10 mol% Si-rich.

indicate that during arc-melting, along with the expulsion of any H_2O present in the powders, there is also a minor loss of Si and/or C.

(3) *Effect of Composition*

Since it appeared that the arc-melting process resulted in a small loss of Si and/or C, but it was not possible to reliably quantify this loss, a number of different starting compositions were used to make the samples. Varying amounts of Si and C were introduced in the starting powders. Excess Si was introduced into the starting compositions and samples with starting compositions of about 10 and 20 mol% excess Si were made. These samples, on annealing, revealed a microstructure of Ti_3SiC_2 and TiC with small amounts of $Ti_5Si_3C_x$ (Fig. 5). Since this phase-field is still Si-poor relative to Ti_3SiC_2, other samples that were even richer in Si were then made. The latter were found to consist of Ti_3SiC_2 and $TiSi_2$ with some SiC (Fig. 6). EPMA analysis of samples that were made with slightly different C contents suggested that, while the phase field to which the sample finally belonged was more sensitive to variations in the amount of Si in the starting composition, the actual stoichiometry of the phases formed was affected by the C content.

Starting compositions with slightly deficient, stoichiometric, or slightly excess Si contents resulted in Ti_3SiC_2, TiC, and $Ti_5Si_3C_x$. The Si content of the Ti_3SiC_2 was always less than suggested by stoichiometry; it ranged from 0.85 to 0.97 atom%. Within these Si contents, as the number of moles of C in the starting composition was increased from 1.8 to 2.15, the number of moles of C in Ti_3SiC_2 correspondingly increased from about 1.85 to 2.7. The $Ti_5Si_3C_x$ had varying amounts of C, and TiC_x was always substoichiometric.

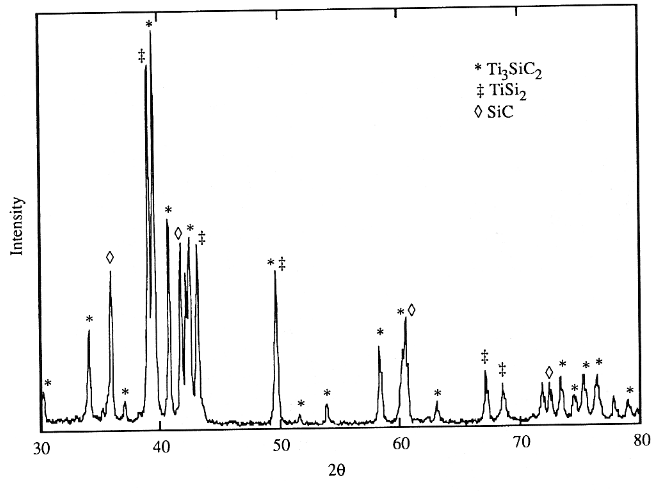

Fig. 6. XRD pattern of a sample with a starting composition that was about 50 mol% Si-rich.

Starting compositions with more excess Si primarily contained Ti_3SiC_2, SiC, and $TiSi_2$. Small amounts of $Ti_5Si_3C_x$ in some of the samples indicated that thermodynamic equilibrium was not always achieved. The composition of Ti_3SiC_2 in these samples was stoichiometric with respect to Si; the carbon content ranged from 1.8 to 2.8. It would appear from these observations that Ti_3SiC_2 has a single-phase field extending into the Si-deficient, C-deficient, and C-rich regions. The slightly Si-deficient Ti_3SiC_2 is in equilibrium with $Ti_5Si_3C_x$, in which the Ti:Si ratio appears to remain close to 5:3. $TiSi_2$ and SiC are in equilibrium with Ti_3SiC_2 over a range of carbon contents, and the extremely C-rich Ti_3SiC_2 is in equilibrium with C-deficient TiC_x. Based on these observations, the modified Ti–Si–C phase diagram reflecting the Ti_3SiC_2 phase field is presented in Fig. 7, on the same scale as Fig. 1.

Most of the earlier authors who have attempted the synthesis of Ti_3SiC_2 have identified the presence of Ti_3SiC_2 using only XRD techniques and hence there has been no mention of nonstoichiometric Ti_3SiC_2.[9–14] Sambasivan, in his investigations on the Ti–Si–C system,[4] has reported a small range of C content from 1.78 to 1.99 in Ti_3SiC_2 which was in equilibrium with TiC and SiC. This three-phase region was not studied in our investigations; however, there appears to be some disagreement with our results, suggesting a more C-rich Ti_3SiC_2 phase under these circumstances. A range of C-deficient compositions was found by Sambasivan in the Ti_3SiC_2–$TiSi_2$–SiC equilibrium. That work suggested that the C deficiency in the observed Ti_3SiC_2 was due to the presence of vacancies. It is also possible that since C resides in interstitial-type positions in the structure of Ti_3SiC_2, excess C stabilizes the structure.

The direct comparison method[16] was used for a quantitative compositional analysis of the samples that predominantly contained Ti_3SiC_2, based on three XRD patterns from each one. Since the XRD patterns indicated the presence of Ti_3SiC_2 and TiC_x only, the samples were assumed to be essentially two-phase. The best samples contained only about 2 vol% TiC_x as the second phase (Fig. 8).

It was found that the samples containing the maximum amounts of the single-phase Ti_3SiC_2 were those with a

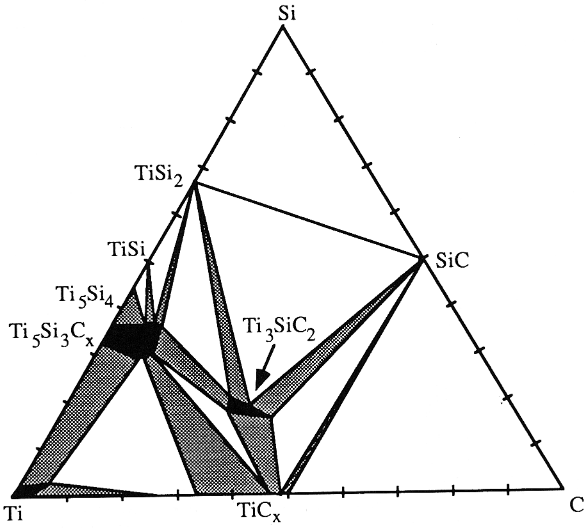

Fig. 7. Modified version of the 1200°C isothermal section of the Ti–Si–C ternary phase diagram, showing the extent of the single-phase region of Ti_3SiC_2 as determined in this work.

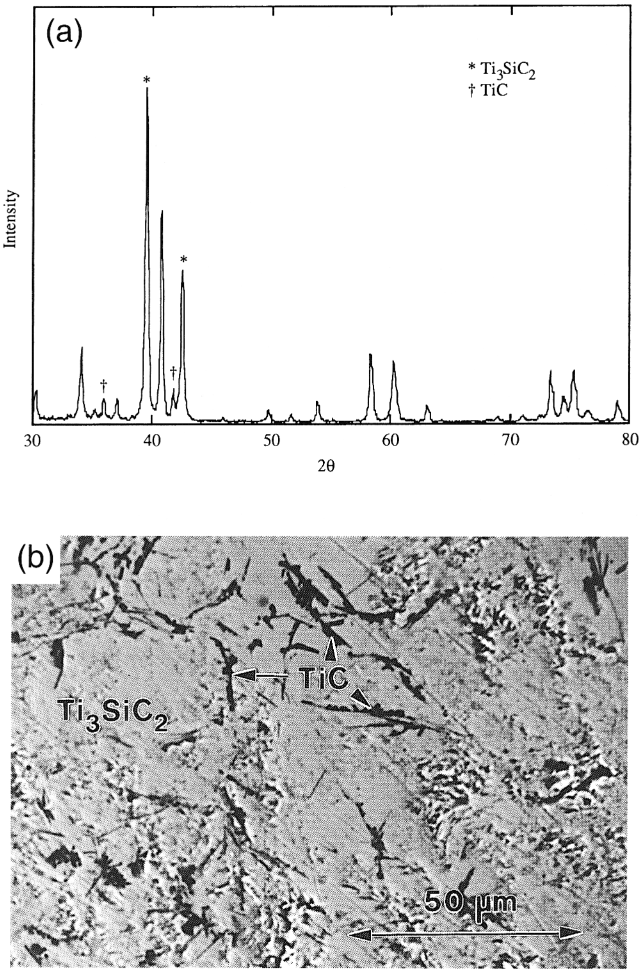

Fig. 8. (a) XRD pattern and (b) backscattered electron image of an as-produced sample containing about 98 vol% Ti_3SiC_2, with about 2 vol% TiC as the second phase. The labeled peaks are those that were used for quantitative analysis by the direct comparison method.

Si-deficient, C-rich starting composition. The composition of the ternary phase in these samples was correspondingly Si-deficient and C-rich. Based on Fig. 7, this would be expected since the single-phase region extends into the Si-deficient, C-rich compositions and is in equilibrium with substoichiometric TiC_x.

(4) Effects of Hydrofluoric Acid Leaching

Since 100% pure single-phase Ti_3SiC_2 could not be synthesized using the arc-melting and annealing route, another technique was attempted. From the available literature on Ti_3SiC_2, it is known that the titanium silicides are leached by hydrofluoric acid, but TiC, SiC, and Ti_3SiC_2 are not.[12] An attempt was made to leach out the titanium silicides from samples containing a mixture of the silicides and Ti_3SiC_2.

A solution containing HF and H_2O in the arbitrarily chosen ratio of 1:5 (by volume) was chosen for the leaching experiments. Powder samples were used in order to maximize leaching efficiency, and XRD was used to characterize the samples after leaching. To ensure thorough leaching of the samples, 30 min was chosen as the leaching time; preliminary tests indicated that samples treated for 15 min were almost completely leached while a period of 1 h resulted in additional decomposition.

Since HF does not strongly leach any of the carbides in the Ti–Si–C system, samples that contained only Ti_3SiC_2 and the silicides of Ti were required in order to attempt to isolate the ternary phase. A number of samples were made with moderately Si-rich, C-deficient compositions, but after annealing, they all contained considerable TiC or SiC. The carbides may form due to kinetic driving forces even though they are not stable in this ternary composition range. Two additional samples with the considerably off-stoichiometric compositions $Ti_3Si_{1.8}C_{1.2}$ and $Ti_3Si_{2.2}C_{0.8}$ were then made and the crushed powders leached in HF solution. Figures 9(a) and (b) are XRD patterns from the two leached powder samples, respectively. In both cases, nearly pure Ti_3SiC_2 is obtained. Very small TiC peaks remain at $2\theta \approx 41.8°$ for $\{002\}_{TiC}$ and $2\theta \approx 36.0°$ for $\{111\}_{TiC}$.

The near-background intensity of the $\{111\}_{TiC}$ signal in both cases makes it difficult to calculate the volume fraction of the carbide using the direct comparison technique, in which two peaks from each phase are used.[16] However, based on approximate correlations between the peak intensities and the volume percentages in the other samples, the observed signal corresponds to about 0.4 and 1.6 vol% TiC in the two cases. These preliminary leaching experiments indicate that nearly single-phase Ti_3SiC_2 powders can be obtained, and suggest that the amount of metastable carbide that forms is dependent upon the exact starting composition of the samples within the Ti_3SiC_2–$TiSi_2$–Ti_5Si_3 ternary region.

IV. Conclusions

The synthesis of Ti_3SiC_2 from powders of the elements and binary compounds in the Ti–Si–C system has been attempted. Because of the loss of Si and/or C during arc-melting, a variety of starting compositions containing different amounts of Si and C were tried. The best (closest to phase-pure) samples were

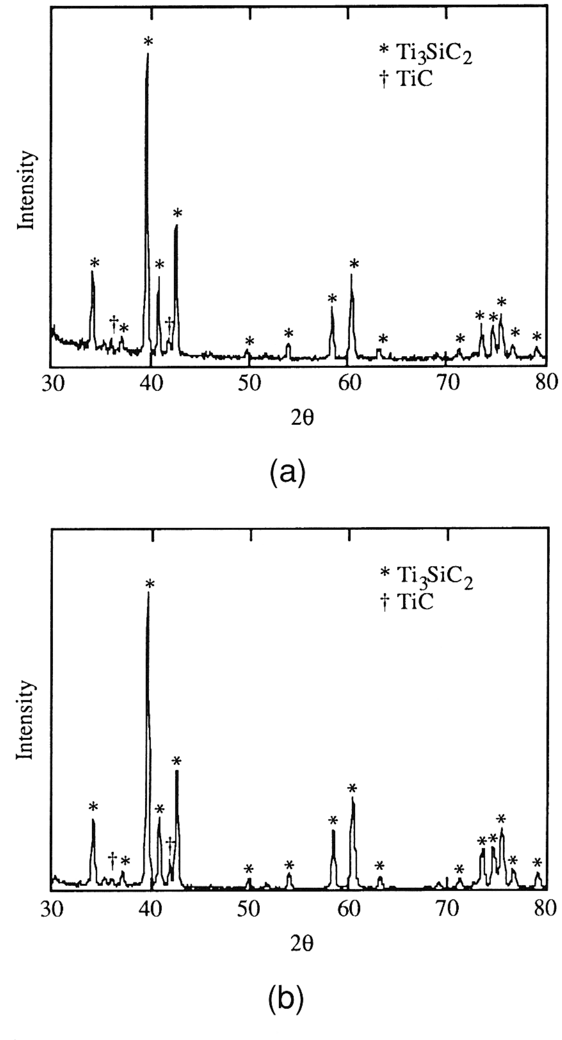

Fig. 9. XRD patterns from nearly single-phase Ti_3SiC_2 powder samples, obtained from arc-melted and annealed material with starting compositions of (a) $Ti_3Si_{1.8}C_{1.2}$ and (b) $Ti_3Si_{2.2}C_{0.8}$, after leaching in 1:5 $HF:H_2O$.

made from slightly Si-deficient and C-rich starting compositions and contained about 2 vol% TiC along with Ti_3SiC_2. However, the stoichiometry of the ternary phase was Si-deficient and C-rich. Based on the stoichiometry of Ti_3SiC_2 in this and other samples, the presence of a single-phase region of Ti_3SiC_2 that extends into the C-deficient, C-rich, and Si-deficient regions of the ternary section is suggested. The X-ray diffraction peaks of this ternary compound have remained unaltered in the range of stoichiometries encountered, confirming that it is a single phase. Leaching of the annealed samples in diluted HF, which does not affect any of the carbides in the Ti–Si–C system, was also investigated. By starting with a composition in a three-phase region containing only Ti_3SiC_2 and silicides, final powders with over 99% phase-pure Ti_3SiC_2 have been obtained.

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