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Influence of small amounts of Fe and V on the synthesis and stability of Ti_3SiC_2

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Abstract

Polycrystalline bulk samples of $(Ti_{1-y}Me_y)_3SiC_2$, where Me = Fe or V and $y = 0.01$ to 0.1, were fabricated by reactive hot isostatic pressing of a mixture of Ti, C (graphite), SiC and Fe or V at 1450°C for 4 h under a pressure of 60 MPa. X-ray diffraction and scanning electron microscopy of the fully dense samples have shown that small amounts of Fe and V interfere with the reaction between Ti, C and SiC leading to the presence of SiC, TiC_x, as well as different Fe and V-containing phases in the final microstructures. The presence of these impurity phases also reduces the temperature at which Ti_3SiC_2 decomposes. The decomposition is manifested by the formation of a network of pores when the samples are annealed at 1600°C, a temperature at which pure Ti_3SiC_2 is thermally stable. The concentration threshold for this decomposition is as low as 1 at%. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carbides; Decomposition; Hot isostatic pressing; Microstructure-final; Porosity; Silicides; Ti_3SiC_2

1. Introduction

Jeitchko and Nowotny[1] were the first to synthesize Ti_3SiC_2 by a chemical reaction between TiH_2, Si and graphite at 2000°C. Prior to a series of papers by Barsoum et al.[2–5] all previous attempts [6–10] to produce single-phase bulk polycrystalline samples of Ti_3SiC_2 were unsuccessful. Some authors also reported that Ti_3SiC_2 became unstable at temperatures greater than 1400°C, by dissociating into Si and TiC_x.[7,10] However, we have shown that Ti_3SiC_2 was thermodynamically stable up to at least 1700°C in vacuum and Ar atmospheres.[2,5]

The initial purpose of this paper was to fabricate magnetic carbides by substituting for the Ti atoms, ones that had a magnetic moment such as Fe or V. However, in the course of this work it became apparent that these additions interfered with the reactions that form Ti_3SiC_2. In a previous paper[11] we have shown that when Ti, C and SiC react, the intermediate phases that form are TiC_x and $Ti_5Si_3C_x$. To eliminate these phases and obtain fully dense, essentially single phase samples required annealing in the 1450–1700°C temperature range for 1–8 h. Samples made by this technique were shown to be thermally stable for long times at elevated temperatures.

The purpose of this work is to report on the effect of small (< 10 at%) additions of Fe and V powders on the kinetics of formation and stability of Ti_3SiC_2 processed by reactively hot isostatic pressing (HIPing) of Ti, SiC and graphite powders.

2. Experimental

The processing details for fabricating bulk single-phase polycrystalline samples are the same as described earlier.[2] In summary, bulk polycrystalline samples ($30\times12\times7$ mm^3) were fabricated by mixing Ti, C, SiC and the metal — Fe or V — powders to yield the desired stoichiometry; viz. $(Ti_{1-y}Me_y)_3SiC_2$, where Me = Fe or V. The powders used and their sources are listed in Table 1. Three Fe compositions were produced, namely, $y = 0.01$, 0.03 and 0.05. For the V containing samples y was either 0.01 or 0.1. The powders were ball milled for about 24 h, uniaxially cold pressed in a die at 180 MPa and HIPed at 1450°C for 4 h at 60 MPa — conditions at which single-phase Ti_3SiC_2 sample have been prepared before. To further explore the stability of the samples

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Table 1
Purity, particle size and source of the powders, used in this work

Powder	Purity (%)	Particle size	Source
Ti	99.0	−325 mesh	Titanium Powder Specialist, Sandy, UT
C (graphite)	99.0	$d_m = 1$–2 μm	Aldrich Chemical, Milwaukee, WI
SiC	99.5	−325 mesh	Atlantic Engineering Equipment, Bergenfield, NJ
Fe	99.9	$d_m < 10$ μm	Johnson Matthey, MA
V	99.5	−325 mesh	Johnson Matthey, MA

some were annealed in a tube furnace under flowing Ar gas at 1600°C for 4 h.

X-ray diffraction, XRD, of powders taken from the sintered samples by drilling holes in them was performed on a Siemens 500D diffractometer after the HIPing and annealing steps. Si powder was used as an internal standard. Extra slow scans enabled us to determine minority peaks of additional phases in the samples.

The samples were polished and their microstructure observed under both optical (Olympus PMG 3) and scanning electron (AMRAY 1830) microscopes. Energy dispersive spectroscopy, EDS, in the SEM was used to determine the chemical composition of some of the phases observed. There is little contrast difference between Ti_3SiC_2 and TiC in the SEM and it thus difficult to accurately determine the volume fraction of the latter. We have previously shown that the most accurate technique to differentiate between the various phases is to combine SEM with optical microscopy on etched samples. Samples exposed to the etchant, (a mixture of concentrated HF, HNO_3 and H_2O in a 1:1:1 volume ratio) for several seconds will color the Ti_3SiC_2, dissolve the silicides, and render the TiC_x phase a bright white.[2] It is by etching and sometime over-etching, together with image analysis software, that the volume fractions of TiC_x is most accurately measured.

3. Results and discussion

3.1. Fe-containing samples

XRD spectra of $(Ti_{1-y}Fe_y)_3SiC_2$ ($Y=0$, 0.01, 0.03, 0.05) samples after HIPing are shown in Fig. 1, in which peaks due to Ti_3SiC_2 are denoted with asterisks, and those due to TiC_x by inverted triangles. In Fig. 1 some low intensity peaks, denoted by question marks appear in the XRD spectra of the samples with $y=0.03$ and

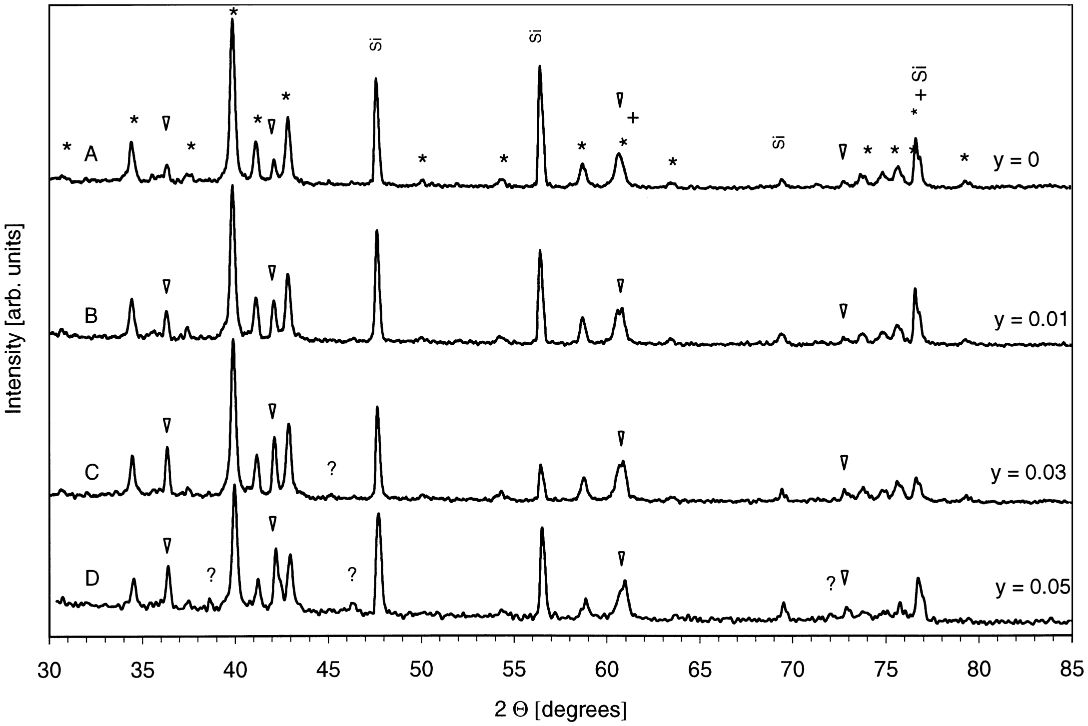


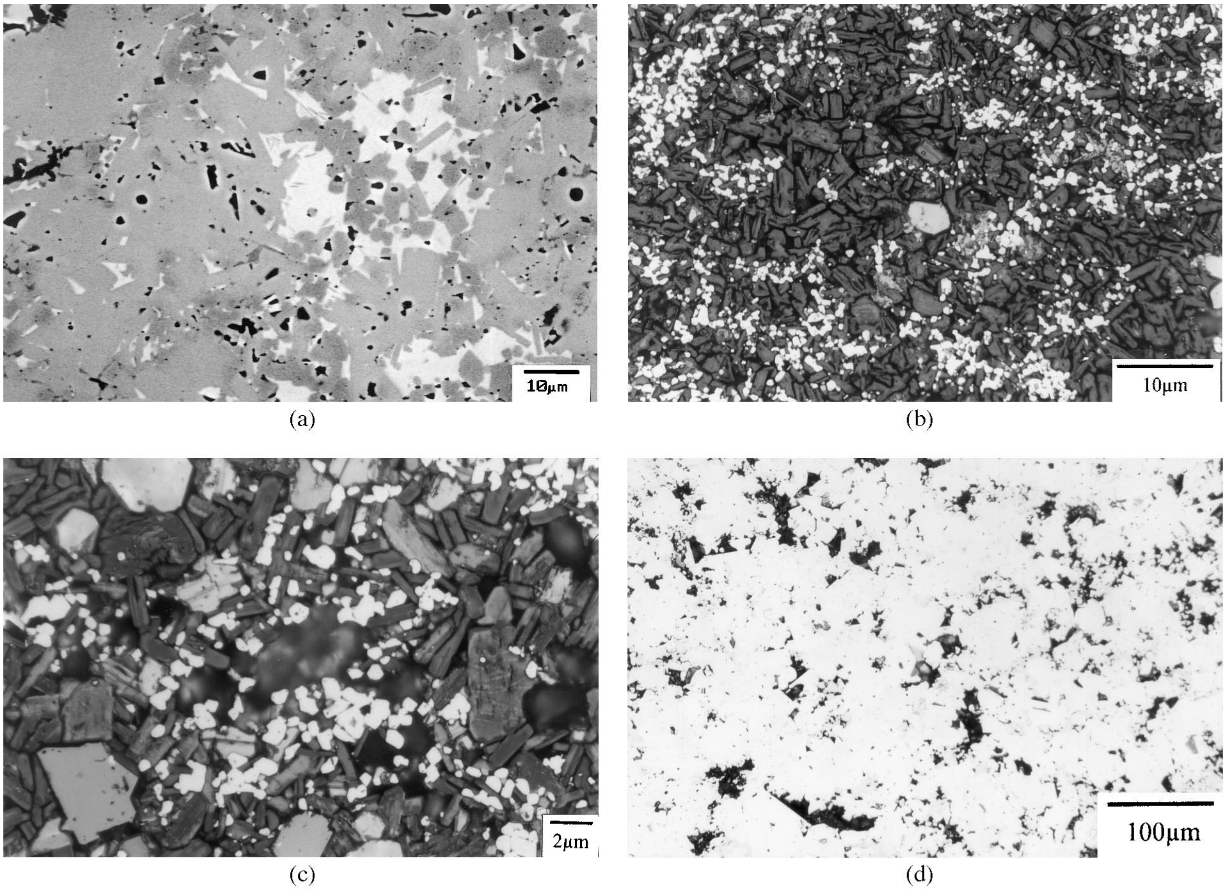
Fig. 1. X-ray diffraction spectra of HIPed samples of $(Ti_{1-y}Fe_y)_3$ SiC_2 with different Fe contents; from top to bottom, $y=0$; $y=0.01$; $y=0.03$, $y=0.05$. The peaks due to Ti_3SiC_2 are denoted with asterisks, those due to TiC_x by inverted triangles and the un-indexed peaks by question marks. Si was used as an internal standard.

$y=0.05$. These peaks, at $2\Theta=38.7°$, $45.3°$, $46.4°$ and $72°$, have not been indexed and their origin is unknown. As discussed below however, these peaks are most probably due to a Ti-rich phase observed in the SEM. As clearly seen from the Fig. 1, and confirmed below, the volume fraction of TiC_x increases with Fe content.

The XRD results are in accord with observations made under the SEM and optical microscopes. Fig. 2(a) shows a backscattered SEM image of a polished surface of a sample with $y=0.05$ in which four phases are identifiable — a dark phase which is SiC, a white phase, a gray matrix phase which is Ti_3SiC_2 and a slightly darker gray phase. EDS of the white phase indicates that it is a Ti-rich phase, in which the Ti:Si:Fe elemental ratio is ~5:3:2, for an approximate chemistry: $Ti_5Si_3Fe_2$. This phase probably also contains some C — the latter could not be detected by our EDS. No ternary compounds with such a stoichiometry exist in that system. The darker gray areas are TiC_x. As noted above in order to quantify the TiC_x content polished and etched surfaces are used instead [Figs. 2(b) and (c)]. Fig. 2(b) is an optical micrograph of the over-etched surface of a sample with $y=0.05$, showing the distribution of the TiC_x, which is not uniform, but appears to occur in a loose network. Image analysis of this, and similar micrographs, shows that the TiC_x content increases from about 4 to 8 vol % as the y increases from 0 to 0.05.

As shown in Fig. 2(c), which is an etched surface of the sample with $y=0.05$, the TiC_x forms in the vicinity of the Ti-rich phase. In this micrograph, the Ti-rich phase [i.e. the brightest phase in Fig. 2(a)]) dissolves, leaving behind the TiC_x that had formed in its vicinity. The power of etching to distinguish the TiC_x is clear upon comparing Fig. 2(a) and (b) or (c).

It is important to note that based on its morphology the Ti-rich phase must have been a liquid at the processing temperature. With increasing Fe content a third phase identified as SiC is present. In the optical micrographs this phase is gray [see lower left-hand corner in Fig. 2(c)]). This SiC is not unreacted SiC, but a phase that precipitates out during the reaction because: (i) the SiC particles are typically surrounded by the Ti-rich liquid phase, and, (ii) the likelihood of having unreacted SiC



(a) (b) (c) (d)

Fig. 2. (a) Backscattered SEM image of polished surface of $(Ti_{0.95}Fe_{0.05})_3SiC_2$ — the darkest phase is SiC; the dark gray phase is TiC_x; the light gray matrix phase is Ti_3SiC_2 and the lightest phase is a Ti-rich Fe-containing phase; (b) Optical image of over-etched surface of same sample as a; white phase is TiC_x, darker phase is Ti_3SiC_2; (c) Optical image of etched $(Ti_{0.95}Fe_{0.05})_3SiC_2$ sample. Void at center of micrograph is where the Fe-containing light phase used to be. d) Optical image of sample with $(Ti_{0.99}Fe_{0.01})_3SiC_2$ after annealing at 1600°C for 4 h in Ar. Note development of porosity, where none existed before.

Table 2
Summary of EDS results on bright phases seen in the microstructures (atomic ratios)

Sample	After HIPing			After annealing		
	Si	Ti	Fe	Si	Ti	Fe
Fe; $y=0.01$	38	43.5	19	48	27	25
Fe; $y=0.03$	40	40	20	48	29	24
Fe; $y=0.05$	32	51	17	48	28	24
Fe; $y=0.1$	36	46	18	37	43	19

particles should decrease with increasing liquid content, i.e. with increasing y, rather than increase as observed, since the presence of a liquid should, if anything, enhance the reaction rate rather than suppress it.

Based on the aforementioned observations the most likely reaction occurring in this system upon the addition of Fe is:

$$(3 - Y\,\mathrm{Ti} + \mathrm{SiC} + \mathrm{C} + y\,\mathrm{Fe} \Rightarrow \mathrm{a\,Ti_3SiC_2} + \mathrm{b\,TiC}_x + \mathrm{c\,Ti_5Si_3Fe_2\,(liquid)} + \mathrm{d\,SiC}$$

By having some of the Ti atoms form a Ti-rich liquid phase implies that they are not available for the formation of Ti_3SiC_2. In other words the addition of Fe shifts the overall chemistry into the Ti_3SiC_2–SiC–TiC_x compatibility triangle. Assuming equilibrium, which is a good assumption especially in the presence of larger amounts of liquid, implies that the composition of the liquid phase should be more or less constant in all microstructures irrespective of Fe content. The EDS analysis of the bright phases, shown in Fig. 2(a) and others, and summarized in Table 2, for the most part confirm that prediction.

As discussed below, the presence of Fe in the final microstructure not only shifts the equilibrium into the Ti_3SiC_2–SiC–TiC_x compatibility triangle, but also reduces the decomposition temperature of Ti_3SiC_2.

3.2. V-containing samples

A typical XRD spectrum of the $(Ti_{0.9}V_{0.1})_3SiC_2$ samples is shown in Fig. 3 (bottom curve, curve B). In addition to the presence of TiC_x and Ti_3SiC_2, peaks possibly corresponding to $(Ti,V)_5Si_3C_x$, which are denoted by question marks, are also present. Despite our best efforts we were not able to unambiguously assign the unknown peaks to $(Ti,V)_5Si_3C_x$ because of the weakness of the signal and the lack of reliable data on XRD of the $(Ti,V)_5Si_3C_x$ solid solutions. A typical backscattered SEM image of a $(Ti_{0.9}V_{0.1})_3SiC_2$ sample is shown in Fig. 4(a), where in addition to the Ti_3SiC_2 matrix which appears as a gray phase, two other phases are clearly obvious: a darker and a lighter phase. The darker phase is once again TiC_x. EDS of the lighter phase shows the elemental ratios of Ti:V:Si to be,

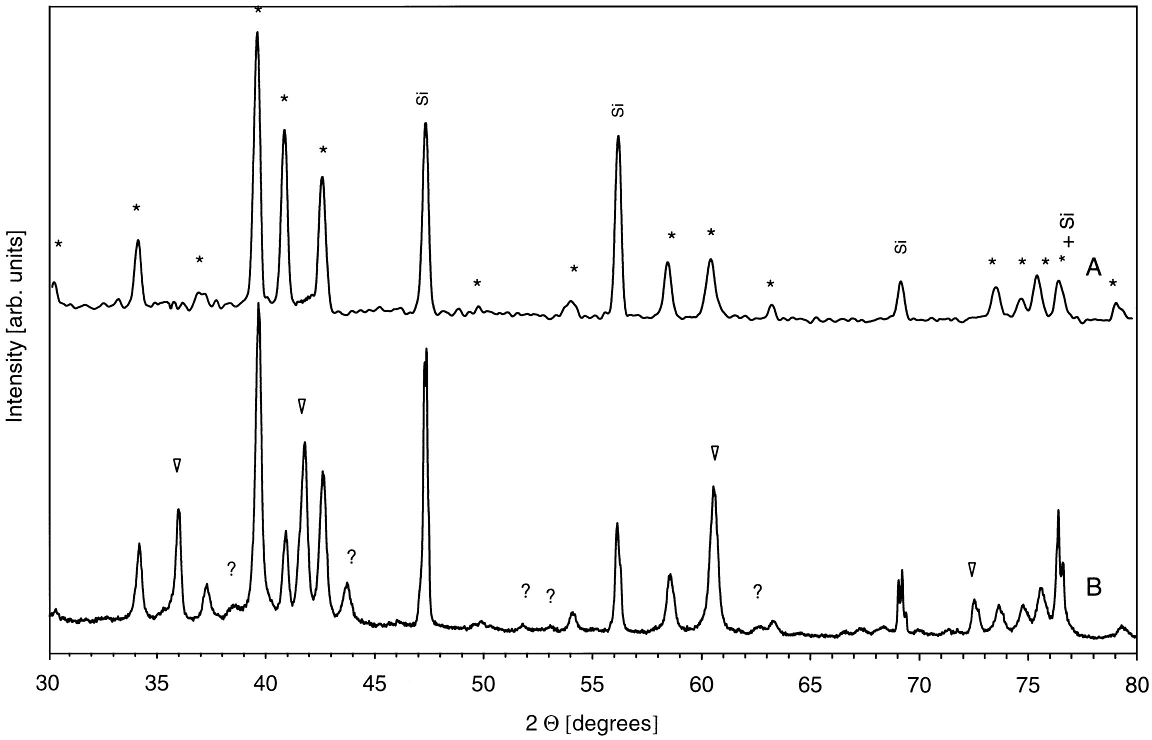


Fig. 3. X-ray diffraction spectra of Ti_3SiC_2 samples, prepared with high purity Ti powders and annealed at 1600°C for 4 h (curve A) and HIPed samples of $(Ti_{0.9}V_{0.1})_3SiC_2$ (curve B). The peaks due to Ti_3SiC_2 are denoted with asterisks, those due to TiC_x by inverted triangles and the unindexed peaks by question marks. Si was used as an internal standard.

respectively, 0.43:0.19:0.37, for a (Ti + V)/Si ratio of ~5/3. This fact corroborates the XRD spectra and is strong evidence that the lighter phase could be $(Ti,V)_5Si_3C_x$. Since both $Ti_5Si_3C_x$ and $V_5Si_3C_x$ exist, it is reasonable to expect them to have some mutual solubility. The corresponding optical micrograph, i.e. image of over-etched surface, is shown in Fig. 4(b), where again it is clear that the TiC_x is present in a network. In this micrograph the brighter phase in Fig. 4(a), has dissolved leaving behind pores in which Ti_3SiC_2 grains are suspended. This is more clearly shown in Fig. 4(c), which is the same as Fig. 4(b), but at higher magnification.

Based on these results we propose the following reaction:

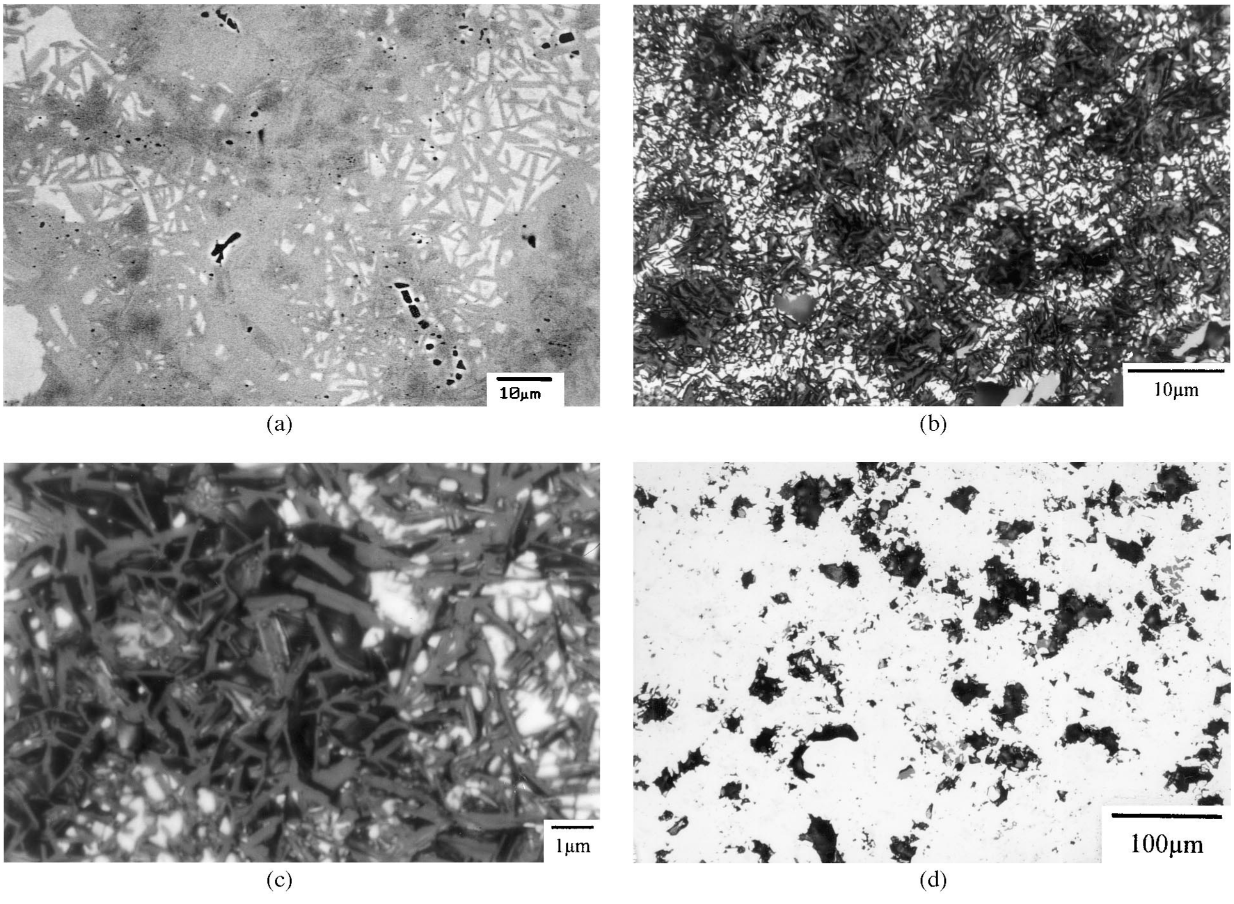
$$(3-y)\mathrm{Ti} + \mathrm{SiC} + \mathrm{C} + y\mathrm{V} \Rightarrow a\mathrm{Ti_3SiC_2} + b\mathrm{TiC} + c(\mathrm{Ti,V})_5\mathrm{Si_3C}_x + d\mathrm{SiC}$$

In our previous work, we have shown that the $Ti_5Si_3C_x$ phase was a precursor to Ti_3SiC_2 and that 4 h at 1450°C was sufficient to obtain single phase samples of Ti_3SiC_2.[11] We have also shown that Ti_3SiC_2 nucleated and formed within the $Ti_5Si_3C_x$ grains. Based on the aforementioned results, it appears that the major role of the V is to dissolve in the $Ti_5Si_3C_x$ phase stabilizing it and preventing the reaction from going to completion.

3.3. *Effect of transition metals on thermal stability of Ti_3SiC_2*

As noted above, there is little doubt that pure Ti_3SiC_2 is thermodynamically stable up to at least 1700°C.[2,5] This is clearly shown in Fig. 3 (top curve). It is a XRD pattern of Ti_3SiC_2 sample, prepared with high purity Ti and SiC powders, and annealed at 1600°C for 4 h; no TiC_x is detected. Optical micrograph (not shown) of the cross-section of that sample after annealing shows no porosity, indicating stability.

In contradistinction, all the samples fabricated in this work developed a network of pores when subjected to the aforementioned annealing treatment. Figs. 2(d) and 4(d) are optical micrographs of polished cross-sectional surfaces of Fe- and V-containing samples, respectively, with $y = 0.01$. In other words, additions as low as 1 at%



(a) (b)

(c) (d)

Fig. 4. (a) Backscattered SEM image of polished and HIPed $(Ti_{0.9}V_{0.1})_3SiC_2$ sample — the gray phase is Ti_3SiC_2, the darker phase is TiC_x; and the lighter phase is most probably $(Ti,V)_5Si_3C_x$; (b) optical image of over-etched surface of same sample — white phase is TiC_x; (c) same as (b), but at higher magnification; (d) optical image of $(Ti_{0.99}V_{0.01})_3SiC_2$ sample after annealing at 1600°C for 4 h in Ar. Note development of porosity, where none existed before.

are sufficient to cause noticeable dissociation, which is more pronounced for the V-containing sample. Furthermore, the higher the Fe- and V- content the more extensive the porosity network. The exact mechanism for the formation of these pores, and concomitant decomposition, is not understood at this time and is beyond the scope of this paper. Surprisingly, for the Fe-containing samples the TiC_x content decreased slightly after annealing, and the composition of the liquid phase became more Si-rich (Table 2). We currently have no explanation for these trends. Annealing of the V-containing samples, however, neither alters the Ti:V:Si elemental ratio, nor significantly alters the TiC_x content..

Finally, the results of this work could help explain the discrepancies in the decomposition temperatures of Ti_3SiC_2 reported in the literature.[7,10] From this work it is obvious that Ti_3SiC_2 is sensitive to the presence of minor amounts of transition metals, some of which are common impurities in Ti. This can best be seen in Fig. 1, top curve, which is that of Ti_3SiC_2 fabricated with the less pure powders listed in Table 1. A small amount of TiC is observed, and more important these samples were not stable at 1600°C.

4. Conclusions

The presence of small amounts of Fe or V during the reaction synthesis of Ti_3SiC_2, interfere with, and destabilize the latter. The presence of Fe results in the formation of a liquid at temperatures as low as 1450°C. The V goes into solution forming, most probably, $(Ti,V)_5Si_3C_x$ and stabilizing it. The threshold of Fe or V needed to destabilize the Ti_3SiC_2 is not high (<1 at%). The destabilization is manifest in the formation of an extensive network of pores when the samples are heated to temperature over 1600°C; a temperature at which pure Ti_3SiC_2 is stable. It is possible that the decomposition of Ti_3SiC_2 at elevated temperatures reported by others could have been due to the presence of trace impurities in the powders they started with.

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