

Preparation of Ti₃SiC₂ by Electron-Beam-Ignited Solid-State Reaction

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This paper describes a novel way to prepare the ternary phase Ti_3SiC_2 in a single-step procedure that we call electron-beam-ignited solid-state reaction (EBI-SSR). The preparation route is discussed by means of an isothermal section of the Ti-Si-C phase diagram. Properties such as the Vickers hardness and the electrical resistivity of the resulting samples are presented. Our property data compare well to those that have been published. The main advantages of this preparation method are the controllability of process parameters such as heating rates, temperatures, and times, as well as the short duration of the overall sample preparation. However, a disadvantage is the presence of second phases (typically in amounts of <8%) that must be reduced via further optimization of the process.

I. Introduction

TITANIUM SILICON CARBIDE (Ti_3SiC_2) is an interesting compound in the Ti-Si-C ternary system for several reasons. Firstly, Ti_3SiC_2 is a machinable ceramic material with a low hardness¹ and good oxidation resistance.² Secondly, it can be found in titanium–SiC metal-matrix composites (MMCs) as a reaction phase between titanium and SiC.³ Thirdly, Ti_3SiC_2 is the boundary-layer phase that determines the electrical properties of a titanium contact on semiconducting single-crystal 6H-SiC.⁴

The purpose of this study was to investigate an inexpensive and simple way to prepare Ti_3SiC_2 ; we call this method electron-beam-ignited solid-state reaction (EBI-SSR).[‡] This study was undertaken so that this material could be available for bulk diffusion studies, because it is not available commercially.

Several methods to prepare the ternary phase Ti_3SiC_2 (τ) have been suggested. The first method, which was used by Jeitschko and Nowotny,⁵ was a solid-state reaction where the τ -phase crystals were formed inside cavities in bulk samples and selected by hand. From these specimens, the crystallographic structure was described for the first time. To prepare single-crystal Ti₃SiC₂, chemical vapor deposition (CVD) reac-tions were used.^{6,7} A solid-state combustion reaction from elemental powders was suggested by Pampuch et al.8 The resulting material contained τ -phase and a minor but unspecified quantity of TiC_{1-y}. High-purity powder (less than ~5% TiC_{1-v}) was produced via a solid-state reaction and subsequent tedious chemical removal of silicides and carbides by Racault et al.² A method to prepare mixtures of SiC and τ -phase from silicon and TiC_{1-y} via solid-state reaction was suggested by Radhakrishnan *et al.*⁹ Furthermore, the τ -phase was found in reaction zones between SiC and titanium.^{3,4} Arunajatesan et al.¹⁰ proposed a way to synthesize Ti₃SiC₂ via arc melting of compressed mixtures of elemental powders and subsequent annealing, which was difficult because of weight losses during preparation. Most recently, Barsoum and El-Raghy¹ demonstrated the possibility of producing very-high-purity τ -phase material via the hot isostatic pressing (HIP) of powder mixtures of titanium, SiC, and graphite. The samples showed no porosity and are the best material that has been produced in bulk form thus far.

II. Sample Preparation by Electron-Beam-Ignited Solid-State Reaction (EBI-SSR)

We prepared Ti₃SiC₂ using an electron-beam furnace that was initially designed as an evaporation source. This type of heating has the advantages of having an ultrahigh vacuum (UHV) environment and very fine power control, while the samples are constantly visible, which makes it ideal for optimizing the heating procedures with very good reproducibility. The samples were prepared from titanium (99.9%, 100 mesh, Johnson Matthey, Ward Hill, MA) and SiC of 3C modification (99%, SGL Carbon AG, Werk Ringsdorff, Bonn, Germany) powders, which were weighed so that the amounts of titanium and carbon corresponded to the required composition in the ternary phase. This procedure was followed for two reasons: (i) it is the preparation method that is most similar to our actual electrical contact formation, where a titanium film on SiC is annealed, and (ii) it gave the highest purity of the ternary phase. The silicon composition will be discussed later. The powder was mixed in a ball mill and cold-pressed into pellets of up to 500 mg in a hydraulic press using a pressure of 430 MPa. The green density of this unreacted pellet was 73% of the theoretical density of the Ti + SiC mixture, which is not high considering that it is a mixture of a ductile material (titanium) and hard grains (SiC). The actual reaction occurred in a high vacuum chamber (Model 306A, Edwards, Grand Island, NY), where the sample was heated in an electron-beam furnace (Model EB1, Edwards) using a graphite crucible. Graphite was the most readily available and promising candidate as crucible material, because we wanted to stay within the ternary system. The pellets did not stick, which indicated negligible reaction with the crucible. The pellets were heated, to make them glow homogeneously. At a temperature of ~900°C, they ignited and reacted while the temperature increased above 1700°C (which was the temperature at which the thermocouple was destroyed) but below 2617°C (where a small piece of molybdenum foil should have shown signs of melting). The reaction front moved through the pellet at a rate of ~ 1 cm/s. The pellets were heated further by the electron beam at ~1500°-1600°C after the reaction occurred, to evaporate excess silicon. The total heat treatment was completed in ~5 min.

Some of the reacted pellets were polished metallographically and examined via optical microscopy as well as scanning electron microscopy (SEM); others were ball milled to produce material for X-ray diffractometry (XRD) study. In addition, chemical analysis and measurements of electrical resistivity and hardness were performed.

Attempts that began with elemental powders, similar to the approach used by Pampuch *et al.*,⁸ led to very vigorous reactions that left behind the ternary phase and >10% TiC_{1-y}, almost regardless of the amount of excess silicon used in the pellet preparation. Starting with TiSi₂, TiC_{1-y}, and SiC led to reaction products that contained more than two phases.

The reactions can be depicted in an isothermal section of the

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Ti-Si-C phase diagram; this section basically has been taken from Goesmann et al.4 and has been modified here by the inclusion of a solution range of τ -phase. Figure 1(a) shows this section for 1000°C; Fig. 1(b) is an enlarged view of this section. This figure is discussed in detail in Section III(5). The solid-state equilibria is assumed to remain mainly constant over the temperature range that has been used in the preparation. The dotted line in the figure from Ti to SiC is the range of possible starting compositions if only titanium and SiC are used. The solid square in the figure indicates the actual starting composition of the pellets. The dotted line from Si through τ toward TiC_{1-y} is the possible shift in composition, provided that only silicon evaporates. We have started from the solid square and intend to reach the stoichiometric τ -phase, which is located at the left end of the broad line, via reaction and annealing.

III. Analytical Results and Discussion

(1) Ignition Conditions

The ignition temperature of 900°C correlates well with earlier investigations. The ternary phase was only found in titanium/SiC bulk-diffusion couples annealed at temperatures \geq 850°C in these earlier studies.⁴



Fig. 1. (a) Isothermal section of the Ti-Si-C phase diagram at 1000°C. (b) Enlarged view of Fig. 1(a), showing the details of the sample compositions and the minimum extent of a proposed homogeneity range of the ternary phase Ti_3SiC_2 toward SiC, as well as the resulting two-phase regions $\tau + TiC_{1-y}$, $\tau + TiS_2$, and $\tau + Ti_5Si_3$; the stoichiometric composition of the ternary phase is at the left end of the broad line.

(2) Weight Loss

If the excess silicon completely evaporates, a 12.5% loss in weight is expected, to attain the stoichiometric τ -phase composition. On average, the pellets lost 4% of weight during the heating procedure, which indicates that the silicon bakeout was incomplete. The total weight loss is low for a UHV environment; because of the fine powder control and the ability to observe the samples during preparation, such results can be achieved.

(3) Chemical Analysis

For the chemical analysis, samples were prepared by omitting the final heating step, to have an intermediate product to prove the assumption of silicon loss. Hence, the weight loss was smaller (only 1.2%).

Carbon content was analyzed in a carbon–sulfur analyzer (Model CSA 2003, Leybold–Heraeus, Cologne, Germany), whereas silicon content was analyzed via solution in sodium potassium peroxide and precipitation of SiO₂. Titanium content was analyzed via atomic absorption spectroscopy.

The solid triangle shown in Figs. 1(a) and (b) is the composition as determined by chemical analysis of the samples after the ignition step (that is, without annealing for an additional 5 min). The composition results are as follows (in at.%): titanium, 46.2; silicon, 21.7; and carbon, 32.1. The composition apparently has shifted from the starting values along the direction of silicon loss only. The open circle in Fig. 1(a), which is half-covered by the solid square, is the theoretical composition of the ignited samples calculated from the 1.2% weight loss, which is assumed to be due to silicon loss only.

(4) X-ray Diffractometry

The reaction products of the completely heat-treated samples were verified by XRD using CoK α radiation and an iron filter in an X-ray diffractometer (Model D5000, Siemens, Karlsruhe, Germany). The samples consisted of Ti₃SiC₂ with small amounts of TiSi₂ or sometimes TiC_{1-y}. A typical diffraction pattern is shown in Fig. 2, which shows the diffraction intensity plotted against the 2 θ angle. Most of the peaks are of the τ -phase and are marked by chevrons ("^"). All peaks in the 2 θ



Fig. 2. XRD pattern of the prepared material. Most of the peaks are from Ti_3SiC_2 ; these peaks are marked by chevrons ("^^'). The position of the tallest TiC_{1-y} peak is marked by a plus ("+"), and the most prominent $TiSi_2$ peaks are marked by asterisks ("*"). The best samples, which were obtained in 5 min, resulted in an almost-XRD-"pure" τ -phase that contained no TiC_{1-y} and very little $TiSi_2$.

range of $20^{\circ}-120^{\circ}$ were identified. A range from 30° to 80° was selected in Fig. 2 to show possible traces of TiC_{1-y} and TiSi₂ most clearly. This pattern is meant to serve as an example; it was not the only source of information. Additional scans at higher resolutions and wider ranges were performed to be sure about the respective phases.

No SiC was detected in the XRD patterns of the samples. The starting material (SiC powder and titanium powder, SiC + Ti) was investigated via XRD, and the 20 ranges of the respective peaks were individually and clearly identified. By comparing these patterns with the reacted samples, the presence of SiC could be excluded. SiC and TiC show very similar XRD patterns; however, two peaks outside the depicted range allow for a proper distinction: the (311) TiC peak, at 86.52° 20 (33% relative height), and the (311) SiC peak, at 85.80° 20 (37% relative height). Because SiC is strictly stoichiometric, its peaks are not shifted at all.

Analysis of TiC_{1-y} can be performed provided that SiC is absent. The position of the TiC_{1-y} peak that is used (the (200) peak, at 48.82° 2 θ) is marked by a plus sign (''+'') below the diffraction curve in Fig. 2. The amount of TiC_{1-y} in this sample is estimated to be <1%, because no peak is visible. The additional complication of TiC_{1-y} not being a stoichiometric phase was addressed by using several samples of pure TiC_{1-y} with varying values of y. The spectra were almost identical, with only slight shifts in the *d*-values.

A similar procedure can be performed for TiSi₂. The three tallest peaks are marked by asterisks (''*''). The peaks are as follows: the (311) peak, at 46.06° 2 θ (100%); the (004) peak, at 49.47° 2 θ (40%); and the (022) peak, at 50.61° 2 θ (74%). Comparison of the third TiSi₂ peak with the 100% τ -phase peak ((104), at 46.06° 2 θ) leads to a TiSi₂ concentration of <8%, assuming perfect isotropy, which is justified for a ball-milled sample. The other two TiSi₂ peaks are less suitable, because they are on the shoulders of the τ -phase peaks. The presence of amorphous carbon or even graphite in small amounts cannot be excluded, judging by the XRD spectra alone. However, because such a phase would appear as being of very low order number in a backscattered electron (BSE) image and nothing of that sort was observed, we have concluded that such phases are absent.

The final composition of the sample, as determined by XRD, is dependent on the heating procedure. If the silicon bakeout step is omitted, the amount of silicide increases; if the temperature is too high or the bake is too long, the TiC_{1-y} amount increases as expected, according to Gottselig *et al.*³ In both cases, the reduction of one phase occurs at the expense of the growth of the other; in some samples, traces of both phases were found.

(5) Phase Diagram

Obviously, definitive conclusions about thermodynamic equilibrium properties in the Ti-Si-C system cannot be made from our experiments, because our samples were not allowed to equilibrate properly. However, the results still cause some tentative changes of the simple phase diagram,⁴ where τ is assumed to be a stoichiometric line compound. We are aware of more-recent publications¹⁰ where a more-elaborate homogeneity range of the ternary phase has been proposed. However, because we did not perform extended investigations on this topic, our conclusions are an attempt to describe the minimum deviations from a stoichiometric compound suggested by our experimental results. The absence of SiC in the ignited sample (the open circle in Fig. 1(b)) indicates a homogeneity range of the ternary phase. The sample points in Fig. 1 are clearly located in a three-phase region (SiC + TiSi₂ + τ) if the τ -phase is stoichiometric. Because only the τ -phase and TiSi₂ were found in the sample, the homogeneity range of τ must have a component perpendicular to the original τ -TiSi₂ tieline. One option to achieve this relation is an extension of τ as a line compound along an existing tieline toward SiC, so that the open circle is within a two-phase region. The minimum extent $\tau + TiC_{1-y}$ and $\tau + TiSi_2$ are marked by dashed lines. As is evident from Fig. 1, there is no $\tau + TiSi_2 + TiC_{1-y}$ three-phase equilibrium, and one would expect either $\tau + TiSi_2$ or $\tau + TiC_{1-y}$ only. The best samples obtained—that is, the ones with the lowest overall content of non- τ phases—had traces of both TiC_{1-y} and TiSi_2, which indicates that the samples cannot be fully equilibrated in such a short processing time.

No Ti_3Si_5 was observed. For the sample composition to reach the $\tau + TiC_{1-y} + Ti_3Si_5$ three-phase field, a greater weight loss than that which has been observed would be necessary.

There may be several reasons why TiC_{1-y} was found in the samples, which contradicts the assumption of silicon loss only. First, energy-dispersive X-ray (EDX) analysis via electron microscopy gave the result that TiC_{1-y} grains were always surrounded by pure τ -phase, never by Ti_3Si_5 ; these may be locally overheated areas that are not in equilibrium with the rest of the sample. Secondly, an incorporation of carbon from the crucible may have occurred.

(6) Microstructure

The pellets contain the τ -phase in the form of interlocked needles that are ~3 μ m in diameter and 10–20 μ m long. Figure 3 shows a BSE image where crystallites of the τ -phase are clearly visible. The slightly darker material between the grains is TiSi₂. This statement is confirmed by EDX analysis (spot and map analysis) of various samples. The volume fraction of TiSi₂, as determined by image analysis, is 6%–8%, which is in agreement with the XRD results. The structure is much finer than that observed by Barsoum and El-Raghy.¹ If TiC_{1-y} grains occur in "overbaked" samples, they are surrounded by τ -phase. The material is porous (not shown in Fig. 3), and it is conceivable that using higher pressures at the pelleting step would help to reduce the porosity of the finer material.

(7) Electrical Resistivity

The electrical resistivity of the ternary phase was measured on a bar cut from a pellet using a four-point probe technique. The resistivity is <100 $\mu\Omega$ ·cm; however, this value is only an upper limit, because of the pores in the material. This value is a factor of ~4 greater than that cited in the literature.¹ The resistivity for pure titanium is ~50 $\mu\Omega$ ·cm, and that of TiC_{1-y} is ~60 $\mu\Omega$ ·cm. We agree with Barsoum and El-Raghy¹ in that pure and dense τ -phase is likely to have a lower resistivity than TiC_{1-y} and titanium.



Fig. 3. BSE image of the microstructure of the sample; the lighter areas are Ti_3SiC_2 , and the darker areas are $TiSi_2$.

(8) Hardness

The Vickers hardness (H_v) , as measured on our single-phase grains, was 570. Reported H_v values include 400 for highpurity HIPed material,¹ 600 for single crystals,⁷ and 750 in less-pure form.⁸ Our values agree well with the literature data that was obtained for pure material.

IV. Conclusion

Preparing Ti₃SiC₂ that contains <8% of secondary phases via electron-beam-ignited solid-state reaction (EBI-SSR) is possible. Three temperature levels are essential in the procedure: the preanneal (for homogeneous glowing), at 800°C; ignition, at ~900°C; and the final silicon evaporation reaction, at ~1500°-1600°C. It is conceivable that our preparation method works in a simple furnace under vacuum or maybe in a protective atmosphere too, because only three temperature levels are required. The process could be increased in scale easily and, therefore, may be applicable for the production of inexpensive bulk quantities; this condition would foster its use as refractory material, because this production method is faster than the hot isostatic pressing process that has been suggested in the literature.1 For low-porosity and high-purity applications, use of the HIPed material would be more likely.

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