SYNTHESIS OF Ti₃SiC₂ BY REACTION OF TiC AND Si POWDERS

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SYNTHESIS OF Ti_3SiC_2 BY REACTION OF TiC AND Si POWDERSIda Kero^{1*}, Marta-Lena Antti¹, and Magnus Odén²¹Luleå University of Technology, Department of Applied Physics and Mechanical Engineering, Division of Engineering Materials, 971 87 Luleå, Sweden²Linköping University, Division of Nanostructured Materials, 581 83, Sweden

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ABSTRACT

The MAX phase Ti_3SiC_2 has been synthesized from starting powder mixtures which do not include pure titanium. The presence of pure titanium in a powder is problematic because of its oxidizing, and in the form of a finely divided powder, explosive nature. The aim of this study was to evaluate the synthesis of bulk polycrystalline samples of Ti_3SiC_2 from a starting powder mixture which is more suited for large scale production.

Titanium silicon carbide MAX phase was synthesized by pressureless sintering of ball milled TiC and Si powders of six different compositions. The sintering reactions were evaluated in situ by dilatometer analysis under flowing argon gas. The as-sintered samples were evaluated using mainly x-ray diffraction (XRD) analysis. This study showed that titanium carbide, silicon carbide and titanium disilicide were present as intermediate or secondary phases in the samples.

Our results indicate that TiSi_2 is an intermediate phase to the formation of Ti_3SiC_2 when excess Si is present. The excess of silicon also proved beneficial for the synthesis of the MAX phase and there is a Si content which is optimal with respect to the maximum MAX phase content of the final product. The Ti_3SiC_2 was found to decompose into TiC and gaseous Si at high temperatures.

INTRODUCTION

Ti_3SiC_2 is a ceramic material which has received increased attention over the past decade because of its attractive combination of properties. It belongs to a group of ternary layered nitrides and carbides known as the MAX phases; with general formula $\text{M}_{n+1}\text{AX}_n$, where M is an early transition metal, A is an element from groups 12-16 in the periodic table of the elements, X is either nitrogen or carbon and n is an integer 1-3. Titanium silicon carbide is the most well known of the MAX phases and it combines some of the most appreciated qualities of ceramics with those of metals, e.g. it is refractory, light weight and stiff but also damage tolerant, machinable with conventional tools and not susceptible to thermal shock.¹⁻⁵

Ti_3SiC_2 is most often prepared from starting powder mixtures including pure titanium, such as Ti/Si/C ⁶⁻¹¹, Ti/C/SiC ^{2,12-15} and Ti/Si/TiC ¹⁶⁻¹⁸ by use of different powder metallurgical synthesis methods, e.g. hot pressing,^{2,8,10} hot isostatic pressing,^{12,17} vacuum sintering,^{7,11,15,18} pressureless sintering,^{6,9,13,14,16} mechanical alloying¹⁹⁻²¹ and self-propagation high-temperature synthesis.²² Pure titanium powder is highly oxidizing and thus has to be handled with great care under strict safety precautions.²³

Monolithic Ti_3SiC_2 has been reported by a handful of authors^{2,12,16,18} but secondary phases such as titanium carbides, silicon carbides and/or titanium silicides are still common in the final products. Different intermediate phases and reactions have been proposed for the formation of Ti_3SiC_2 .

El-Raghy and Barsoum¹² worked with Ti/C/SiC powders and reported that Ti_3SiC_2 nucleated and grew within $\text{Ti}_5\text{Si}_3\text{C}_x$ grains. They proposed a series of reactions where $\text{TiC}_{0.5}$ and $\text{Ti}_5\text{Si}_3\text{C}$ would serve as intermediate phases. Wu et al. initially confirmed¹³ the observations of El-Raghy and Barsoum and later added¹⁴ that the reactions took place simultaneously. Istomin et al.¹⁵ proposed in 2006 a different set of reactions where TiC and Si would be the first intermediate phases to

form. These would then react to form Ti_5Si_3 and TiSi_2 which would in turn consume more TiC and Si to produce Ti_3SiC_2 .

Li et al.¹⁰ found TiC , Ti_5Si_3 and TiSi_2 in their samples made from elemental starting powders. They stated that the starting powder composition, especially with regards to the silicon content, determined the phase composition of the final product. Yang et al.¹⁸ reported comparable observations to the effect of varying silicon content to Ti/Si/TiC powders and concluded that the optimum silicon content was 10 % excess to the stoichiometric composition. They stated that excess silicon would compensate for Si loss by evaporation whereas too much added Si would promote TiSi_2 formation over Ti_3SiC_2 .

Attempts have also been made to synthesize Ti_3SiC_2 from TiC/Si powder mixtures, thus avoiding the pure titanium. Radhakrishnan et al.²⁴ reported that a reaction of $3\text{TiC}/2\text{Si}$ powders would first generate the intermediate phase TiSi_2 at a temperature of 1170°C . In a second step the silicide would be consumed as Ti_3SiC_2 and SiC would form. Li et al.²⁵ published in 2004 a differential scanning calorimetry (DSC) study, suggesting that the reaction between $3\text{TiC}/2\text{Si}$ powders would start at 1340°C . They found SiC and TiC to be present as secondary phases in their final products.

Racault et al.⁷ were first to report the decomposition of Ti_3SiC_2 into TiC_x and gaseous Si . Wu et al.¹³ who observed that the presence of titanium carbide in the sample was deleterious to the thermochemical stability of Ti_3SiC_2 . Gao et al.¹⁷ stated that the stability was related to the vapor pressure of silicon in the furnace. Li et al.²⁵ suggested another reaction formula for the decomposition of Ti_3SiC_2 by carburization where SiC instead of Si would be produced. We have previously reported observations of MAX phase formation via the intermediate phase of TiSi_2 and a decomposition of the MAX phase into TiC and gaseous Si .²⁶ The aim of this study was to evaluate the influence of excess silicon in the starting powders on the amount of MAX phase obtained in the final products as well as the reaction mechanisms governing its formation.

EXPERIMENTAL

The powders used were TiC (Aldrich, -325 mesh) and Si (Aldrich, -325 mesh); they were mixed at six different ratios. The B composition with the smallest amount of silicon had a TiC/Si ratio of 3:1 and the G composition with the largest amount of silicon had a TiC/Si ratio of 3:2.8. The different starting powder compositions are summarized in Table 1. The powders were mixed and milled in a ball mill and then compacted by uniaxial pressing to 10 MPa, and cold isostatic pressing to 300 MPa. The samples were sintered in a dilatometer with graphite heating elements and sample holder, under flowing argon gas. Sintering was also performed in a furnace with graphite heating elements in which the samples were embedded in boron nitride. Here the sintering took place at a temperature of 1250°C and with 2.5 hour holding time, under a vacuum of approximately 0.02 mbar. The samples were crushed into a powder, and analyzed by x-ray diffractometry (XRD) using Cu radiation and a proportional detector. The phase fractions were determined using the direct comparison method²⁷. Here, the integrated intensity for a minimum of three diffraction lines of each phase were summed and the volume fraction of the individual phases was calculated by:

$$V_i = \frac{\frac{1}{n} \sum_{j=1}^n \frac{I_i^j}{R_i^j}}{\frac{1}{n} \sum_{j=1}^n \frac{I_\alpha^j}{R_\alpha^j} + \frac{1}{n} \sum_{j=1}^n \frac{I_\beta^j}{R_\beta^j} + \frac{1}{n} \sum_{j=1}^n \frac{I_\gamma^j}{R_\gamma^j} + \dots} \quad (1)$$

Where n is the number of hkl peaks for a given phase, V is the volume fraction, I is the integrated intensity and R is the calculated theoretical intensity. The validity of this procedure has been demonstrated for highly anisotropic, two-phase steels by Dickson²⁸.

Table I. Starting powder compositions

Sample name	TiC/Si ratio of the starting powder	Expected phases	Phases present
B	3:1	TiC, Ti ₃ SiC ₂ & SiC	TiC & Ti ₃ SiC ₂
C	3:2	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC
D	3:2.2	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC
E	3:2.4	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC
F	3:2.6	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC
G	3:2.8	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC

RESULTS

Figure 1 shows a typical thermal expansion curve for the samples analyzed in this study. Up to 1142°C the thermal expansion is linear and the rate is constant. At 1142°C the curve increases and 1276°C is the onset of a peak. The peak reaches a maximum at 1457°C, after which the sample shrinks abruptly and considerable amounts of silicon is given off. In order to avoid excessive silicon evaporation and instrument contamination, the heating segment was limited to 1500°C for most samples.

The only sample which differs from this behavior is the B sample with the lowest amount of silicon. It is represented by a dotted line in Figure 1 and it has an earlier onset of the peak. As can be seen from the figure the peak begins with a much less distinct “shoulder” at a temperature of about 1238°C. The curve peaks at 1382°C, which is 75° lower than the other samples.

Figure 1: Dilatometer curves of samples B and C with a TiC/Si ratio of 3:1 and 3:2 respectively. The curves of all other samples analyzed followed the same typical pattern as sample C.

Figure 2 is a scanning electron micrograph of the F sample showing a typical microstructure. Backscattered electron mode revealed different chemical compositions of the matrix and the different grains within the matrix. TiC, TiSi₂ and SiC phases occur in separate grains distributed in a Ti₃SiC₂ matrix. A closer look at the TiC grains revealed two types of grains with different morphologies, indicating that TiC is not only a reactant phase but also a product of the decomposition of the MAX phase.⁷

Figure 2: Scanning electron micrograph of the F sample showing a microstructure consisting of grains of TiC, SiC and TiSi₂ and a matrix of Ti₃SiC₂. TiC grains are present in two different morphologies.

Figure 3 shows x-ray diffractograms of the samples sintered under vacuum for 2 hours and 30 min in 1250°C. The B sample with the lowest amount of silicon in the starting powder differs from the other samples. It is the only sample which does not contain silicon carbide (SiC) and titanium disilicide (TiSi₂). All samples contained titanium silicon carbide MAX phase (Ti₃SiC₂) and titanium carbide (TiC).

The relative phase amounts of Ti₃SiC₂ and TiC are shown for the different starting powders in Figure 4. Most MAX phase was obtained for the 3TiC/2.6Si starting powder composition. The relative amount of TiC is decreasing while the amount of Ti₃SiC₂ increases, but when the decomposition of Ti₃SiC₂ causes the MAX phase amount to drop, the TiC content is raised again. This suggests that the TiC is both a reactant, consumed in the MAX phase forming reaction, and a product of the decomposition reaction.

Figure 3: X-ray diffractograms of samples B to G after sintering for 2.5 hours in 1250°C.

Figure 4: Effect of initial silicon content on the amount of titanium silicon carbide MAX phase (Ti_3SiC_2) and titanium carbide (TiC) obtained in the final product after sintering for 2.5 hours at 1250°C .

DISCUSSION

The 1200°C isothermal section of the ternary phase equilibrium diagram of the Ti-Si-C system is shown in Figure 5. The composition of sample B is represented in the figure by a circle and the compositions of the other samples are found within the marked rectangle. The B sample had an initial composition within the Ti_3SiC_2 -SiC-TiC three phase area. The sample was found to contain TiC and small amounts of Ti_3SiC_2 . Though the x-ray diffractograms do not indicate any SiC in the samples its presence in small amounts cannot be completely ruled out as the main peaks of SiC can be overlapped by those of the other two phases. The evaporation of silicon has been observed for other samples in this investigation and is commonly reported in the literature^{16,18,22,29-33}, which may explain the very low amounts of MAX phase and SiC obtained in sample B. As silicon is lost by evaporation, the composition of the samples will shift along the marked line in the figure towards the Ti-C base line of the diagram. Moving towards the TiC corner of the three phase area will deplete the samples of the other two phases.

The initial composition of samples C to G is situated within the TiSi_2 -SiC- Ti_3SiC_2 three phase area. These three phases were indeed observed in the samples along with some TiC. The presence of TiC may have more than one reason: it may, of course, be residual, unreacted starting powder or it may be a product of the decomposition of the MAX phase. The two different morphologies observed by SEM suggest that the TiC phase may have more than one origin in which case both of these reasons may be valid. The evaporation of silicon from these samples will shift the phase composition towards the Ti_3SiC_2 -SiC line of the diagram. If the line is traversed due to silicon evaporation TiC will form as a result of an equilibrium phase reaction.

Much more MAX phase was achieved in these samples with excess silicon and most MAX phase was obtained with the $3\text{TiC}/2.6\text{Si}$ starting powder. This amount of silicon is likely to compensate for a certain amount of evaporation in such a way that the sample composition is shifted most closely to the Ti_3SiC_2 phase area.

Samples analyzed in the dilatometer up to temperatures above 1500°C lost considerable amounts of silicon through evaporation that was deposited on the graphite sample holder in the dilatometer. These samples consisted mostly of TiC. Since carbon was present in the furnaces through the graphite heating elements and sample holder/crucible, the decomposition of Ti_3SiC_2 is likely to follow the reaction initially proposed by Racault et al.⁷:

As no intermediate phases or unexpected secondary phases were observed in sample B, with no excess silicon, the MAX phase forming reaction is assumed to be a direct displacement reaction as proposed by Radhakrishnan et al.²⁴:

The silicide forming reaction of samples C to G is assumed to follow equation 3 as theoretical computations by Li et al.²⁵ has pointed this reaction out as the thermodynamically most favourable of the plausible reactions.

As the sample holders and the crucibles used in this study were made of graphite, carbon was readily available during the sintering reactions. All samples with excess silicon had comparable and relatively low amounts of TiSi_2 . Previous results³⁴ have shown that the silicide is an intermediate phase to MAX phase formation from these powders. TiSi_2 is then likely consumed in a second, Ti_3SiC_2 forming reaction:

Alternatively, more than one reaction may occur simultaneously in the samples with excess silicon, in which case concurrent reactions according to equations 2 and 3 may compete.

Figure 5: 1200°C isothermal section of the ternary phase equilibrium diagram of the Ti-Si-C system. Illustration by Arunajatesan and Carim²⁹, original after Ratcliff and Powell³⁵. The starting powder compositions used in this study are situated along the marked line; sample B at the marked circle and samples C to G within the marked rectangle.

CONCLUSIONS

- Excess silicon is beneficial for the production of Ti_3SiC_2 . The largest amount of the MAX phase was achieved in the samples with a TiC/Si ratio of 3:2.6, i.e. about 46% Si. The excess silicon is likely to compensate for losses due to evaporation.
- In the samples with excess silicon, TiSi_2 and SiC were observed. These are secondary equilibrium phases but the silicide may also take part in a Ti_3SiC_2 forming reaction.
- In the samples without excess silicon, Ti_3SiC_2 is assumed to form via a direct solid state displacement reaction.
- The MAX phase decomposes into TiC and gaseous Si at temperatures above 1500°C.

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EXPERIMENTAL

The powders used were TiC (Aldrich, -325 mesh) and Si (Aldrich, -325 mesh); they were mixed at six different ratios. The B composition with the smallest amount of silicon had a TiC/Si ratio of 3:1 and the G composition with the largest amount of silicon had a TiC/Si ratio of 3:2.8. The different starting powder compositions are summarized in Table 1. The powders were mixed and milled in a ball mill and then compacted by uniaxial pressing to 10 MPa, and cold isostatic pressing to 300 MPa. The samples were sintered in a dilatometer with graphite heating elements and sample holder, under flowing argon gas. Sintering was also performed in a furnace with graphite heating elements in which the samples were embedded in boron nitride. Here the sintering took place at a temperature of 1250°C and with 2.5 hour holding time, under a vacuum of approximately 0.02 mbar. The samples were crushed into a powder, and analyzed by x-ray diffractometry (XRD) using Cu radiation and a proportional detector. The phase fractions were determined using the direct comparison method²⁷. Here, the integrated intensity for a minimum of three diffraction lines of each phase were summed and the volume fraction of the individual phases was calculated by:

$$V_i = \frac{\frac{1}{n} \sum_{j=1}^n \frac{I_i^j}{R_i^j}}{\frac{1}{n} \sum_{j=1}^n \frac{I_\alpha^j}{R_\alpha^j} + \frac{1}{n} \sum_{j=1}^n \frac{I_\beta^j}{R_\beta^j} + \frac{1}{n} \sum_{j=1}^n \frac{I_\gamma^j}{R_\gamma^j} + \dots} \quad (1)$$

Where n is the number of hkl peaks for a given phase, V is the volume fraction, I is the integrated intensity and R is the calculated theoretical intensity. The validity of this procedure has been demonstrated for highly anisotropic, two-phase steels by Dickson²⁸.

Table I. Starting powder compositions

Sample name	TiC/Si ratio of the starting powder	Expected phases	Phases present
B	3:1	TiC, Ti ₃ SiC ₂ & SiC	TiC & Ti ₃ SiC ₂
C	3:2	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC
D	3:2.2	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC
E	3:2.4	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC
F	3:2.6	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC
G	3:2.8	TiSi ₂ , Ti ₃ SiC ₂ & SiC	TiC, TiSi ₂ , Ti ₃ SiC ₂ & SiC

RESULTS

Figure 1 shows a typical thermal expansion curve for the samples analyzed in this study. Up to 1142°C the thermal expansion is linear and the rate is constant. At 1142°C the curve increases and 1276°C is the onset of a peak. The peak reaches a maximum at 1457°C, after which the sample shrinks abruptly and a considerable amount of silicon is given off. In order to avoid excessive silicon evaporation and instrument contamination, the heating segment was limited to 1500°C for most samples.

The only sample which differs from this behavior is the B sample with the lowest amount of silicon. It is represented by a dotted line in Figure 1 and it has an earlier onset of the peak. As can be seen from the figure the peak begins with a much less distinct “shoulder” at a temperature of about 1238°C. The curve peaks at 1382°C, which is 75° lower than the other samples.

Figure 1: Dilatometer curves of samples B and C with a TiC/Si ratio of 3:1 and 3:2 respectively. The curves of all other samples analyzed followed the same typical pattern as sample C.

Figure 2 is a scanning electron micrograph of the F sample showing a typical microstructure. Backscattered electron mode revealed different chemical compositions of the matrix and the different grains within the matrix. TiC, TiSi₂ and SiC phases occur in separate grains distributed in a Ti₃SiC₂ matrix. A closer look at the TiC grains revealed two types of grains with different morphologies, indicating that TiC is not only a reactant phase but also a product of the decomposition of the MAX phase.⁷

Figure 2: Scanning electron micrograph of the F sample showing a microstructure with grains of TiC and SiC in a matrix primarily consisting of Ti_3SiC_2 . TiC grains are present in two different morphologies.

Figure 3 shows x-ray diffractograms of the samples sintered under vacuum for 2 hours and 30 min in 1250°C . The B sample with the lowest amount of silicon in the starting powder differs from the other samples. It is the only sample which does not contain silicon carbide (SiC) and titanium disilicide (TiSi_2). All samples contained titanium silicon carbide MAX phase (Ti_3SiC_2) and titanium carbide (TiC).

The relative phase amounts of Ti_3SiC_2 and TiC are shown for the different starting powders in Figure 4. Most MAX phase was obtained for the 3TiC/2.6Si starting powder composition. The relative amount of TiC is decreasing while the amount of Ti_3SiC_2 increases, but when the decomposition of Ti_3SiC_2 causes the MAX phase amount to drop, the TiC content is raised again. This suggests that the TiC is both a reactant, consumed in the MAX phase forming reaction, and a product of the decomposition reaction.

Figure 3: X-ray diffractograms of samples B to G after sintering for 2.5 hours in 1250°C.

Figure 4: Effect of initial silicon content on the amount of titanium silicon carbide MAX phase (Ti_3SiC_2) and titanium carbide (TiC) obtained in the final product after sintering for 2.5 hours at 1250°C.

DISCUSSION

The 1200°C isothermal section of the ternary phase equilibrium diagram of the Ti-Si-C system is shown in Figure 5. The composition of sample B is represented in the figure by a circle and the compositions of the other samples are found within the marked rectangle. The B sample had an initial composition within the Ti_3SiC_2 -SiC-TiC three phase area. The sample was found to contain TiC and small amounts of Ti_3SiC_2 . Though the x-ray diffractograms do not indicate any SiC in the samples its presence in small amounts cannot be completely ruled out as the main peaks of SiC can be overlapped by those of the other two phases. The evaporation of silicon has been observed for other samples in this investigation and is commonly reported in the literature^{16,18,22,29-33}, which may explain the very low amounts of MAX phase and SiC obtained in sample B. As silicon is lost by evaporation, the composition of the samples will shift along the marked line in the figure towards the Ti-C base line of the diagram. Moving towards the TiC corner of the three phase area will deplete the samples of the other two phases.

The initial composition of samples C to G is situated within the TiSi_2 -SiC- Ti_3SiC_2 three phase area. These three phases were indeed observed in the samples along with some TiC. The presence of TiC may have more than one reason: it may, of course, be residual, unreacted starting powder or it may be a product of the decomposition of the MAX phase. The two different morphologies observed by SEM suggest that the TiC phase may have more than one origin in which case both of these reasons may be valid. The evaporation of silicon from these samples will shift the phase composition towards the Ti_3SiC_2 -SiC line of the diagram. If the line is traversed due to silicon evaporation TiC will form as a result of an equilibrium phase reaction.

Much more MAX phase was achieved in these samples with excess silicon and most MAX phase was obtained with the 3TiC/2.6Si starting powder. This amount of silicon is likely to compensate for a certain amount of evaporation in such a way that the sample composition is shifted most closely to the Ti_3SiC_2 phase area.

Samples analyzed in the dilatometer up to temperatures above 1500°C lost considerable amounts of silicon through evaporation that was deposited on the graphite sample holder in the dilatometer. These samples consisted mostly of TiC. Since carbon was present in the furnaces through the graphite heating elements and sample holder/crucible, the decomposition of Ti_3SiC_2 is likely to follow the reaction initially proposed by Racault et al.⁷:

As no intermediate phases or unexpected secondary phases were observed in sample B, with no excess silicon, the MAX phase forming reaction is assumed to be a direct displacement reaction as proposed by Radhakrishnan et al.²⁴:

The silicide forming reaction of samples C to G is assumed to follow equation 3 as theoretical computations by Li et al.²⁵ has pointed this reaction out as the thermodynamically most favourable of the plausible reactions.

As the sample holders and the crucibles used in this study were made of graphite, carbon was readily available during the sintering reactions. All samples with excess silicon had comparable

and relatively low amounts of TiSi_2 . Previous results³⁴ have shown that the silicide is an intermediate phase to MAX phase formation from these powders. TiSi_2 is then likely consumed in a second, Ti_3SiC_2 forming reaction:

Alternatively, more than one reaction may occur simultaneously in the samples with excess silicon, in which case concurrent reactions according to equations 2 and 3 may compete.

Figure 5: 1200°C isothermal section of the ternary phase equilibrium diagram of the Ti-Si-C system. Illustration by Arunajatesan and Carim²⁹, original after Ratcliff and Powell³⁵. The starting powder compositions used in this study are situated along the marked line; sample B at the marked circle and samples C to G within the marked rectangle.

CONCLUSIONS

- Excess silicon is beneficial for the production of Ti_3SiC_2 . The largest amount of the MAX phase was achieved in the samples with a TiC/Si ratio of 3:2.6, i.e. about 46% Si. The excess silicon is likely to compensate for losses due to evaporation.
- In the samples with excess silicon, TiSi_2 and SiC were observed. These are secondary equilibrium phases but the silicide may also take part in a Ti_3SiC_2 forming reaction.
- In the samples without excess silicon, Ti_3SiC_2 is assumed to form via a direct solid state displacement reaction.
- The MAX phase decomposes into TiC and gaseous Si at temperatures above 1500°C.

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