Fabrication of Ti_3SiC_2 by Mechanical Alloying Under Air Atmosphere

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Abstract

Ti_3SiC_2 is a member of the MAX phase material, which is a group of ternary compounds with the family formula of $M_{N+1}AX_N$. Ti_3SiC_2 has excellent properties such as machinability, low density, good damage tolerance, and high thermal stability due to the layered nature of its structure. Ti_3SiC_2 can be produced by many methods such as hot isostatic pressing (HIP), powder metallurgy, hot pressing, spark plasma sintering and mechanical alloying (MA). The result of synthesis of Ti_3SiC_2 by mechanical alloying was comparable to other process, even though additional phases, such as TiC, $TiSi_2$, or Ti_5Si_3 may still be present in the final products. The objective of the experiment is to produce Ti_3SiC_2 using mechanical alloying under air atmosphere. Ti_3SiC_2 was produced by mechanical alloying using high energy ball milling machine under air atmosphere. Elemental powders of Ti, Si, and C were used as raw materials for Ti_3SiC_2 fabrication. Various powder compositions based on molar ratio, ball to powder ratio (BPR), milling speed and milling time were introduced to the process. X-ray diffraction (XRD) and scanning electron microscope (SEM) is used to characterize as-milled powder. Afterwards, sintering was carried out to the selected powders in order to enhance the purity of the ternary carbide. The as-sintered products were also examined using XRD and SEM. Results showed that the amount of Ti_3SiC_2 in the as-milled powders was low. TiC was the major phases detected along with titanium silicides. Some of XRD pattern of as-milled powder exhibited amorphous pattern. The amount of Ti_3SiC_2 is increasing after sintering process. The formation of Ti_3SiC_2 involved mechanically induced self-propagating reaction (MSR). However, due to contamination during milling the amount of the ternary carbide was low. The amount of Ti_3SiC_2 was enhanced after sintering, indicating that crystallization and nucleation of ternary carbides occurred during the process.

Keywords: mechanical alloying, air atmosphere, elemental powders, mechanically induced self-propagating reaction (MSR), contamination.

Pendahuluan

Ti_3SiC_2 is a member of the MAX phase material, which is a group of ternary compounds with the family formula: $M_{N+1}AX_N$; where N is an integer 1, 2 or 3; M is a transition metal; A is an element from groups IIB to VIA in the periodic table of the elements; and X is either carbon or nitrogen. Structure of $M_{N+1}AX_N$ phase material is layered hexagonal with two formula units per unit cell.
Ti_3SiC_2 consists of layered structure with planar Si layer linked together by Ti_6C octahedral. The layered nature of Ti_3SiC_2 can readily be observed on its fracture surface (Li, J.F., 1999). Ti_3SiC_2 exhibits a combination of exceptional properties of both metal and ceramic. The layered nature of Ti_3SiC_2 influences the exceptional properties (Barsoum, 2001).
Excellent machinability, low density, good damage tolerance, high thermal stability, high oxidation resistance, good electrical and thermal conductivity, and high thermal shock resistance are among the promising properties (Barsoum, 2001). It is worth to note that particular properties, such as machinability, give this material a credit. The fact that it is very readily machinable using conventional tool and evidence of self lubricating is a great technological importance (Barsoum, 2001, 1996).
Many synthesis methods have been developed in order to produce high purity Ti_3SiC_2, namely sintering, hot isostatic pressing (HIP), hot pressing (HP), combustion synthesis or self propagating high temperature synthesis (SHS), pulse discharge sintering and spark plasma sintering (SPS) (Li, J.F., 1999, Li, H., 2004, Yeh, 2008, Zhou, 2005, Zhu, 2003). Apart from using elemental powder, the synthesis can also be done using combination of elemental powder with TiC, SiC, or Al_4C_3 as starting material. All the mentioned methods are performed at

high temperature and most of them require extensive soaking time. Recently, many efforts have been done to produce using mechanical alloying and the results were comparable to those using other synthesis methods (Jin, 2007, Li, S.-B.Zhai, 2005, Liang, B.Y.M.Z.Wang, 2009). It is considerably better than the methods mentioned previously in term of energy and time consumption.

Most of the works on synthesis of Ti_3SiC_2 by mechanical alloying used elemental powders as starting materials, and the results were comparable to other process, even though additional phases, such as TiC, $TiSi_2$, Ti_5Si_3 or Al_3Ti may still be present in the final products. Various reaction mechanisms for formation of Ti_3SiC_2 by MA have been proposed, however most of them involved mechanically induced self-propagating reaction (MSR) (Jin, 2007, Li, S.-B.Zhai, 2005). MSR is self sustaining reaction induced by ball milling, and has relation with self-propagating high-temperature synthesis (SHS) reaction (Takacs, 2002). Concisely, MSR is a combination of ball milling induced, mechanochemical or mechanical alloying with combustive, explosive, self-propagating reaction (SHS). The objective of the experiment is to produce Ti_3SiC_2 using mechanical alloying under air atmosphere.

Experimental Methods

Ti_3SiC_2 was produced by mechanical alloying using high energy ball milling machine under air atmosphere. Elemental powders were used in the milling, and weighed according to molar ratio based on the following stoichiometric reactions:

$$3Ti + Si + 2C \rightarrow Ti_3SiC_2 \quad (1)$$

Table 1. Parameters used in the milling process

Specimen	Composition (molar ratio)	BPR*	Milling Speed (RPM)	Milling Time (hour)
TSC-1	3Ti/1Si/2C	20:1	300	1.5
TSC-2	3Ti/1Si/2C	20:1	300	3
TSC-3	3Ti/1Si/2C	20:1	500	1.5
TSC-4	3Ti/1Si/2C	20:1	500	3
TSC-5	3Ti/1Si/2C/0.1Al	10:1	300	6
TSC-6	3Ti/1Si/2C/0.1Al	10:1	300	8
TSC-7	3Ti/1Si/2C/0.1Al	10:1	300	10

Ti (99.9% purity, <45μm), Si (99% purity, <44 μm), and C (99% purity, <45 μm) powders were used as raw materials for Ti_3SiC_2 fabrication. Small addition of Al powder (99% purity, <75 μm) was used to enhance the formation of Ti_3SiC_2 (Jin, 2007). Parameters that were used in the milling of Ti3SiC2 are shown in table 1. Stainless steel jar was used as a grinding jar. Chromium steel (AISI 52100) balls with diameter of 10 mm and 15 mm were used as grinding balls.

X-ray diffraction (XRD) was used to characterize as-milled powder. Afterwards, sintering was carried out to the selected powders in order to enhance the purity of the ternary carbide. The powders were cold pressed to form compacts with diameter of 30 mm and a height of about 5 mm, and then pressureless sintered in a vacuum furnace at 1000 °C for 1 hour. Afterwards, the sintered specimens were investigated by mean of XRD. The fracture surface of sintered specimens was examined using scanning electron microscope (SEM).

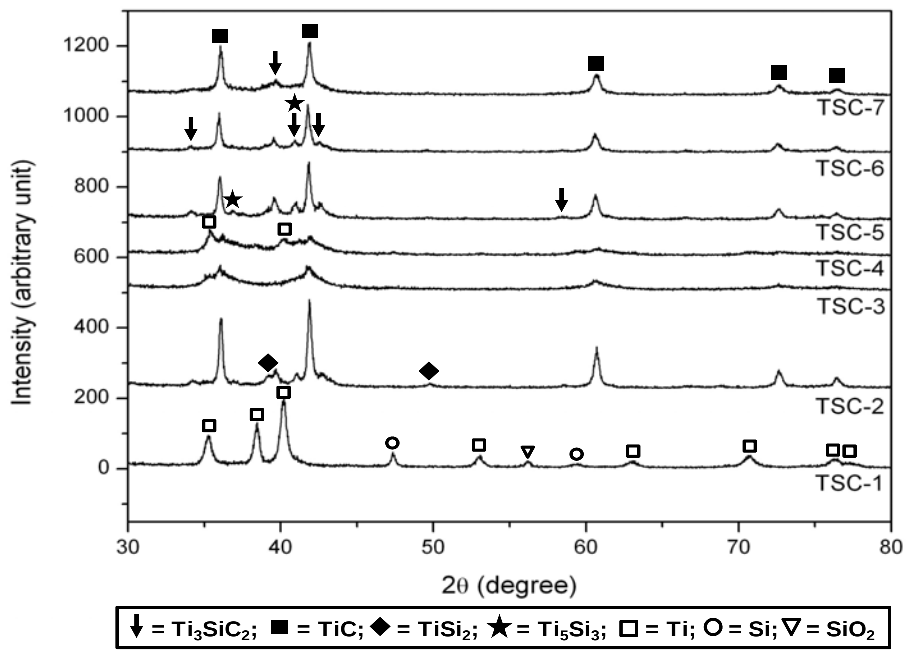

Figure 1. XRD patterns of as-milled Ti_3SiC_2 specimens

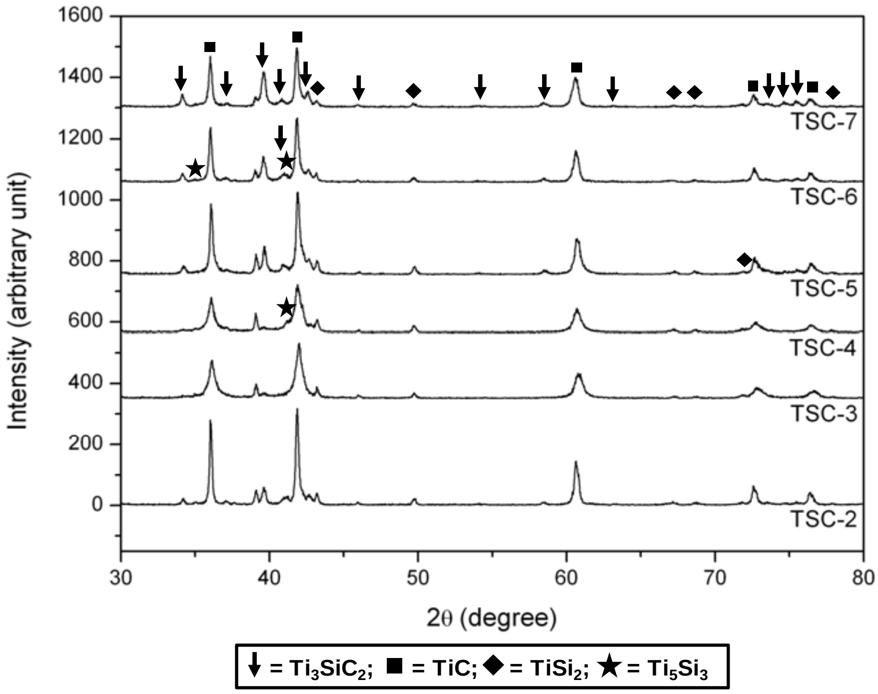

Figure 2. XRD patterns of as-sintered Ti_3SiC_2 specimens

Results and Discussion

Figure 1 shows the XRD patterns of as-milled Ti3SiC2. It can be seen that specimen TSC-1 exhibited only elemental phases Ti and Si. Carbon peaks could not be observed in all of the XRD patterns because of the formation of amorphous carbon or distribution of C in the grain boundaries of Ti or Si. Low intensity peaks of Ti_3SiC_2 could be seen in specimen TSC-2, indicating its small amount. TiC was the main phase in specimen TSC-2, as indicated by its high intensity. Two forms of titanium silicides, Ti_5Si_3 and $TiSi_2$, could also be observed in the specimen. In the XRD patterns of specimen TSC-3 and TSC-4, only TiC and Ti peaks were appeared. Both TiC and Ti peaks were broad and the intensity was very low, indicating the presence of nanocrystalline or amorphous phases.
Specimen TSC-5 to TSC-7 was added by Al powders. Ti_3SiC_2 peaks appeared in the XRD patterns of all three specimens however, the intensity was still lower. The low intensity indicated that the amount of Ti3SiC2 was small. TiC was still the main phase, and titanium silicides remained detectable in the entire specimen. By comparing the result of these three specimens to specimen TSC-2, it could be seen that there was low or no increase in the peaks of Ti_3SiC_2. A decrease in the intensity of $TiSi_2$ peaks due to the addition of Al was observable in specimen to specimen TSC-7.
Figure 2 represents the XRD patterns of specimen Ti_3SiC_2 after being sintered at 1000°C for 1 hour in vacuum condition. Specimen TSC-1 was not sintered due to the presence of elemental phases Ti and Si. It can be seen that there was a considerable increase in the intensity and number of peaks of Ti_3SiC_2 phase compared to as-milled specimens. Having the highest intensity, TiC was still the main phase in all specimens. Some peaks of $TiSi_2$ remained in the sintered specimens. Sintered specimen TSC-7 displayed an increase of the intensity of $TiSi_2$ in 2θ range of 38.5°-39.5°. Ti_5Si_3 phase was also detected in sintered specimens; however, the intensity was low, indicating the amount being small. Addition of Al in specimen TSC-5 to specimen TSC-7 created significant effect on phase formation of Ti_3SiC_2 and suppressing the formation of titanium silicides.
The figure reveals that the intensity of Ti_3SiC_2 peaks in specimen TSC-5 to TSC-7 are higher than in specimen TSC-2 to TSC-4. More peaks of Ti_3SiC_2 could also be found in specimen with Al addition. Suppression of $TiSi_2$ and promotion of Ti_3SiC_2 could be observed clearly in 2θ degree of 38°-40° in specimen TSC-5 and TSC-6. Both of them were milled with same milling parameter, except that specimen TSC-6 had Al addition. In specimen without Al (TSC-2 to TSC-4), the intensity of $TiSi_2$ was higher than the intensity of Ti_3SiC_2. The opposite condition occurs in specimen with Al addition (TSC-5 to TSC-7) where the intensity of Ti_3SiC_2 was higher than that of $TiSi_2$.
The fracture surface of a sintered specimen (specimen TSC-7) is shown in Figure 3. It can be seen that the sintering did not produce fully dense morphology. Most of the powder is still in individual particle and having particle size of less than 1 µm. Hence, the intensity of Ti_3SiC_2 did not increase significantly after sintering.

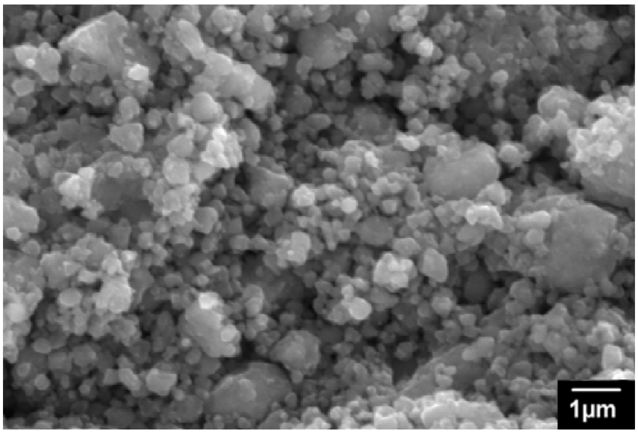

Figure 3. SEM micrograph of the fracture surface of as-sinteredTi_3SiC_2.

Results of as-milled Ti_3SiC_2 specimen suggested that the amount of corresponding phases i.e. Ti_3SiC_2 were low. XRD patterns of as-milled Ti_3SiC_2 exhibit low intensity of Ti_3SiC_2 peaks accompanied by high intensity of TiC peaks and some small peaks of the titanium silicides, i.e. Ti_5S_3 and $TiSi_2$. Some of the Ti_3SiC_2 specimens exhibit amorphous-like XRD pattern with TiC as dominant phase. The presence of both TiC and titanium silicides, i.e. $TiSi_2$ and Ti_5Si_3 are unavoidable since the formation of Ti3SiC2 involves those phases.

The formation of Ti_3SiC_2 during milling may occur according to the following reactions as proposed by Li and Zhai (Li, S.-B.Zhai, 2005), and Jin et al (Jin, 2007):

$$Ti + C \rightarrow TiC \quad (1)$$
$$Ti + 2Si \rightarrow TiSi_2 \quad (2)$$
$$5Ti + 3Si \rightarrow Ti_5Si_3 \quad (3)$$
$$TiC + Ti\text{-}Si \text{ liquid} \rightarrow Ti_3SiC_2 \quad (4)$$

During the milling, Ti, Si and C powder undergo repeated impact, which leads to the refinement of their particle size. When the powders achieve a critical particle size, Ti and C react first and form TiC. The formation of TiC involves the mechanism so called mechanically induced self-propagation reaction (MSR), as suggested by numbers of work (Jin, 2007, Li, S.-B.ZhaiZhou, 2005, Jia, 2009). The formation of TiC releases a large amount of heat that leads to the formation of titanium silicides and Ti_3SiC_2. The heat released during the formation of TiC is high enough to induce the melting of Ti-Si system (Li, S.-B.Zhai, 2005). Then, TiC reacts with Ti-Si liquid to form Ti_3SiC_2. The addition of Al into Ti-Si-C system promotes the formation of Ti_3SiC_2 by affecting the reactions mentioned previously (reaction 1-3) as proposed by Jin et al (Jin, 2007). Jin proposed that Al might react with TiC, $TiSi_2$, and Ti_5Si_3, inducing the formation of Ti_3SiC_2.

Figure 4 shows the fracture surface of specimen TSC-7 in another location. It can be seen that there is a localized melting region as indicated by the arrow. EDX examination, depicted in Figure 5 revealed the the melted-like region is Ti_3SiC_2. Therefore, it is clear that the formation of Ti_3SiC_2 in this experiment is also governed by the MSR. The EDX examination also revealed the presence of oxygen, even though the quantity was low.

Though the formation of Ti_3SiC_2 this work is based on MSR, the amount of corresponding phases obtained in the as-milled specimen is surprisingly low. The specimens of Ti_3SiC_2 which was added by Al powders which were fabricated based on particular references (Jin, 2007, Liang, B.Y.M.Z.Wang, 2009) yielded different result than the result of references. Those specimens yielded lower purity of corresponding phases than the results of references. The condition was not changing even after sintering process.

Final Ti_3SiC_2 specimen displays a purity that is similar to the result of the work of Li et al (Li, S.-B.ZhaiZhou, 2005) and Liang et al (Liang, B.Han, 2009). However, it should be noted that the results of the final specimens was obtained after sintering, while in the references mentioned earlier was obtained from as-milled specimens in powder form. The bulk form of the references shows better purity than the result of final specimens. It is obvious that the results obtained in this work are influenced by few mechanisms. It is likely that the air atmosphere that was used in the fabrication is responsible for such results. The possible mechanisms related to the event are discussed in the following paragraphs.

Particle size is decreasing in a faster rate when the milling is performed under air atmosphere (Saji, 1994). As stated in the second chapter, the MSR occurs when the milled powder reaches a particular critical size. Therefore, it is possible that the condition for the MSR in this work, i.e. critical particle size, is achieved faster than in the reference works. The phases obtained by the MSR are decreased in size with further milling time, yielding

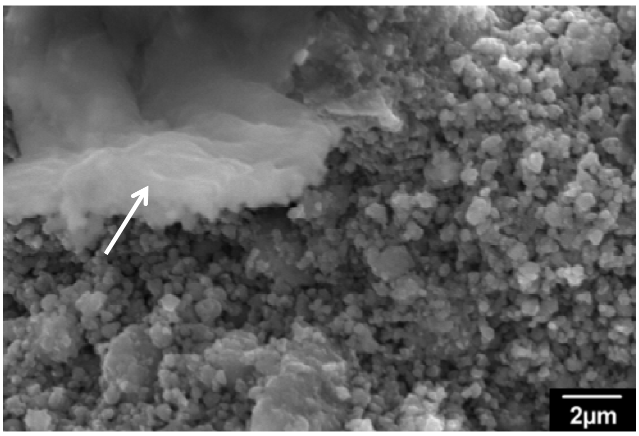

Figure 4. SEM micrograph of the fracture surface of as-sinteredTi_3SiC_2 in different location. Arrow indicates a melted-like region.

the amorphous-like XRD pattern. Thus, some of the specimens exhibit amorphous-like XRD pattern.

Milling under air atmosphere may introduce contamination into the system (Suryanarayana, 2004). Saji et al (Saji, 1994) found that the content of O,N, and C is increased as the increase of milling time if air was used as milling atmosphere. The MSR may occur in the powder during the milling; however, the number of MSR and the heat released may be lower than in the reference works (Jin, 2007, Liang, B.Y.M.Z.Wang, 2009) due to the presence of contamination.

It is also possible that when oxide particularly amorphous oxide existed during the milling, it will cover other particles. Hence, when the MSR ignites, only particles or parts that are not covered by oxide can undergo the process. Then, further milling time refines the particle size. Other evidence that supports the mechanism described above is that, there is no bulk products obtained in as-milled specimens as obtained in several works (Liang, B.Han, 2009).

The condition above suits the condition of Ti_3SiC_2 specimen that was milled based on reference works. TiC may dominate the result even though the MSR in the system is limited. The formation of TiC is not only achievable by MSR, but also by gradual reaction through elemental diffusion (Jia, 2009).

After sintering, all results show an improvement. The intensity of all corresponding peaks is enhanced significantly. The enhancement may be resulted from the mechanisms described in the following. The first possible mechanism is that the sintering enhances the nucleation process of corresponding phases i.e. Ti_3SiC_2 mechanical alloyed powder mixture in the solid state (Li, J.-F., 2002). Mechanical alloying makes the powder very active because of their large surface areas and mechanically induced strain. Therefore, the corresponding phase can be obtained by sintering at relatively lower temperature.

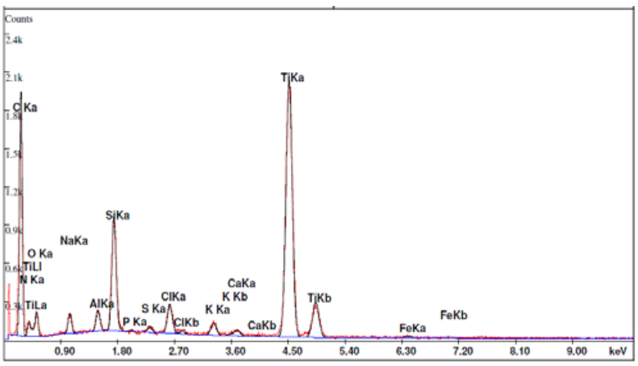

Figure 5. EDX spectrum of a sintered Ti_3SiC_2 specimens.

The second possible mechanism involves an assumption that the corresponding phases have already existed in the as- milled powder, but it is in nanocrystalline or amorphous state. During sintering the amorphous phase undergoes crystallization (Pei, 2005). The crystal growth also happens in the nanocrystalline phase. Hence, the intensity of all phases i.e. Ti_3SiC_2 and TiC is enhanced after sintering.

XRD pattern of sintered specimen exhibited improvement in the amount of Ti_3SiC_2. However, the dominant phase is still TiC. Therefore, it is most likely that the formation mechanism of Ti_3SiC_2 in this work occurred in the following manner:

- First, the MSR occurs during milling and forms Ti_3SiC_2, titanium silicides and TiC. However, since the MSR is limited due to the contamination during milling, the result is not satisfactory. Further milling time decreases the particle size, reaching the nanocrystalline or amorphous state.
- Second, the sintering enhances the intensity of the phases by inducing crystallization on amorphous phases, while the nanocrystalline phases undergo crystal growth. Nucleation of Ti_3SiC_2 may also occur during the sintering, leading to the increase of the amount of Ti_3SiC_2.

Ti_3SiC_2 is successfully prepared by mechanical alloying under air atmosphere from elemental powders, although the result is dominated by TiC. The processing route that is used in this work involves milling in air atmosphere, followed by cold compaction. The last stage is pressureless sintering at 1000 °C in vacuum furnace. Improved milling parameter should be applied in order to have better purity of Ti_3SiC_2. Milling atmosphere is probably the most important parameter that should be improved. Sintering temperature can be varied in order to improve the result after sintering. However, it should be notice that higher sintering temperature may lead to decomposition of Ti_3SiC_2 then promoting the formation of TiC (Li, S.-B.ZhaiZhou, 2005, Li, J.-F., 2003).

Conclusions

Ti_3SiC_2 has been successfully produced from elemental powders by a processing route that involves high energy ball milling in air atmosphere, and pressureless sintering at 1000°C. The purity of as-milled Ti_3SiC_2 fabricated in this work was low. The as-milled Ti_3SiC_2 was dominated by TiC phases, with low amount of titanium silicides $TiSi_2$ and Ti_5Si_3. Air atmosphere, particularly oxygen played a significant role in determining the result of the as-milled powder by increasing the decrease rate of particle size and introducing contamination to the powder during milling which may disrupt further mechanism. The amount of Ti_3SiC_2 in as-sintered product was improved after pressureless sintering at 1000 °C. However, the main phase was still TiC.

Sintering process improved the result by inducing crystallization to amorphous phases, crystal growth to nanocrystalline phases and promoting nucleation of Ti_3SiC_2.

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