

Research Article

Effect of Excess Silicon on the Formation of Ti_3SiC_2 Using Free Ti/Si/C Powders Synthesized via Arc Melting

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The aim of this study is to investigate the effect of excess silicon on the formation of Ti_3SiC_2 from free Ti/Si/C powders synthesized via arc melting. The reactant mixture was prepared according to the off-stoichiometric ratio of $3Ti : (x + 1)Si : 2C$, where x (excess Si) varied from 0 to 0.5. Samples were analyzed using X-ray diffractometry (XRD), field-emission scanning electron microscopy (FESEM), and energy-dispersive spectroscopy (EDS). The relative density and porosity of products were calculated using the Archimedes method. Through optimization of the arcing schedules (time) and excess Si amounts, 86.9 wt% of Ti_3SiC_2 with a relative density of 86% was obtained. For all products, Ti_3SiC_2 was identified as the main phase, while TiC, $TiSi_2$, and Ti_5Si_3 were identified as secondary phases. Ti_3SiC_2 grains were in the form of elongated platelets; they were nucleated and grew on the surface of equiaxed TiC grains. The microporosity present in the TiC-equiaxed grains affected the density and porosity of the products.

1. Introduction

Ti_3SiC_2 is a ternary layered carbide known as MAX phase compound due to the $M_{n+1}AX_n$ formula, where M is a rare-earth transition metal, A is an A-group element (usually IIIA and IVA) in the periodic table, X is C or N, and n is an integer of 1 or 2 or 3 [1]. This ternary compound has unique characteristics that combine merit properties of metals and ceramics [2]. Like metals, it has excellent electrical ($\sim 4.5 \times 10^6 \Omega^{-1} m^{-1}$) [3] and thermal ($\sim 37 W/m \cdot K$) [4] conductivities, relatively low hardness ($\sim 4 GPa$) [1] which makes it easy to machine like common metal or graphite [5, 6], high Young modulus ($\sim 325 GPa$) [7], and moderate flexural strength (260–600 MPa) [8, 9], it is not susceptible to thermal shock [10], and it has damage tolerance at high temperatures [4]. It also duplicates several ceramic properties such as good oxidation resistance of up to $1400^\circ C$ [11, 12], relatively low density ($\sim 4.52 g/cm^3$) [1], and high decomposition temperature ($\sim 1700^\circ C$) [1], and some researchers have also reported that its melting temperature is up to $3000^\circ C$ [13]. Most detailed descriptions

of thermal, electrical, oxidation, mechanical, and chemical properties were given by Barsoum et al. [1–5, 7, 12]. This material shows good promise for use in many structural and high-temperature applications and for wear and corrosion protection. These applications include turbine blade and stators, heavy duty electrical contacts, and bearing.

Ti_3SiC_2 was firstly synthesized as a thin film in 1967 by chemical reaction [14] and in the 1980s by chemical vapor deposition (CVD) [15, 16]. Later, Ti_3SiC_2 was synthesized as a bulk specimen by arc melting [17] or common sintering [18] of elemental Ti–Si–C powders. In the early 1990s, Ti_3SiC_2 single phase was synthesized as a dense specimen from Ti–Si–C or Ti–Si–TiC powders blended by hot pressing (HP) [19], hot-isostatic pressing (HIP) [9], and reactive hot-isostatic pressing (RHIP) [20]. Unfortunately, these synthesis routes (HP, HIP, and RHIP) require high temperatures ($>1400^\circ C$), long sintering times (several hours), expensive equipment, and skillful operators for equipment preparation. However, in the 2000s, a rapid solid-solid or solid-liquid reaction (few seconds) synthesis process was developed to produce a near single phase (bulk

form) of Ti_3SiC_2 . It is a self-ignited or self-sustained reaction where the reactant is exposed to extreme heat and produces a high exothermic reaction [17] with neighboring particles. To be exact, the self-ignition reaction is dependent on the type of heating source (i.e., electric induction, electric charge, laser, and beam) and the mode of combustion (either a combustion that occurs simultaneously or heterogeneously) [21] through a sample volume.

Two types of heating sources are frequently employed in this reaction: (1) electric induction, where the heat is thermally propagated through the sample, that is, self-propagating high-temperature synthesis (SHS) [13, 22–26], thermal explosion (TE) [21], and SHS coupled with hot isostatic pressing (SHS-HIP) [13, 27], and (2) electric-charge, where heat is generated from electrodischarge among particles [28] which is due to the current flowing between two polling sites (anode and cathode), that is, pulse discharge sintering (PDS) [11, 29–31], spark plasma sintering (SPS) [28, 32] or plasma-activated sintering [33–35], arc melting [17], and also from welding methods. Most researchers followed these methods to synthesize Ti_3SiC_2 single phase by using several starting mixtures (e.g., $\text{TiH}_2/\text{Si}/\text{C}$ [14], $\text{Ti}/\text{Si}/\text{C}$ [9, 10, 18–20, 23, 24, 27, 29, 36–47], $\text{Ti}/\text{SiC}/\text{C}$ [25], $\text{Ti}/\text{Si}/\text{TiC}$ [26, 31], and TiC/Si [48]) and varying the composition of the starting reactant powders (e.g., Ti, Si, C, SiC, TiC, Al, etc.). Unfortunately, some of these methods required the assistance of external pressure together with a high-temperature (>1500°C) postannealing step for long sintering times (several hours) to obtain a near single-phase Ti_3SiC_2 [17, 27].

Two alternative routes for reactant powder preparation commonly received by researchers are the use of excess Si addition and the use of either graphite or carbon black powders. By varying the amount of excess Si addition in the reactant mixture of $\text{Ti}/\text{Si}/\text{C}$ powders, most researchers have successfully fabricated a bulk form of Ti_3SiC_2 through self-ignition reaction. However, when the same mixture was used in pressureless self-ignition for both electric induction and electric charge methods, the purity of the Ti_3SiC_2 produced has never exceeded 60 wt% [17, 21, 44]. Therefore, an alternative route which may influence the yield of Ti_3SiC_2 formed is the addition of excess Si in the starting reactant mixture. In most cases, the purity of Ti_3SiC_2 was reported to be very sensitive to any discrepancies in the stoichiometric formulation [27], especially the Si content [9, 18–20, 23, 24, 27, 29, 36–47]. The amount of excess Si has been varied at $x = 0\text{--}0.5$ for $3\text{Ti}:(x+1)\text{Si}:2\text{C}$ mixture, in order to produce high purity of Ti_3SiC_2 [23, 38, 42]. However, a few authors have found contrasting results [29, 31, 43]. The aim of excess Si addition is to compensate the loss of evaporated Si when the mixture is sintered above 1414°C (i.e., Si melting point) [49], and the deficiency of Si usually favors the formation of TiC [27, 50]. The addition of excess Si is required in self-ignition reactions since the reactant sample has been subjected to extreme temperatures and high heating rates. In most syntheses, TiC and Ti–Si binary phases were always present in the synthesized products [26]. On the other hand, graphite (C_g) selection is basically used to facilitate the passing of currents through the sample [25], especially when

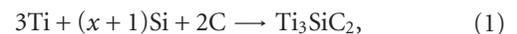
using an electric charge as a heating source. Graphite is more efficient as an electrical and thermal conductor compared to carbon black (C_b) because the thermal conductivity of graphite ($160\text{ Wm}^{-1}\text{K}^{-1}$) is higher than carbon black ($5\text{ Wm}^{-1}\text{K}^{-1}$) [51].

The only research that used arc melting was done by Arunajatesan and Carim [17] in 1995. They used free $\text{Ti}/\text{Si}/\text{C}$ powders as the starting reactant, and the output was only 58 wt% of Ti_3SiC_2 . The amount of Ti_3SiC_2 was increased to 99 wt% when the same product was postannealed in a vacuum furnace for 100 h. However, no research studying the effects of excess Si on the formation of Ti_3SiC_2 using arc melting has been published. This method will offer crucial advantages such as shorter sintering time (within seconds), low energy consumption, yield of high-purity product as the arcing concept is similar to PDS and SPS method, as well as being easy to control since it is associated with the self-sustaining merit from high exothermic reactions. Hence, a synergistic combination of the arc melting method and the variation of excess Si addition amounts is proposed. This option offers great potential for the rapid yielding of Ti_3SiC_2 to above 60 wt%.

Therefore, the objectives of this work is to study the effects of excess Si in the reactant $\text{Ti}/\text{Si}/\text{C}$ mixture powders on the formation of Ti_3SiC_2 and to establish a process route to produce over 60 wt% of Ti_3SiC_2 using the relatively inexpensive and readily available arc melting method.

2. Experimental Details

Commercially available Ti (particle size $\sim 40\ \mu\text{m}$, 99% purity), Si ($\sim 2\ \mu\text{m}$, 99% purity), and C_g ($\sim 2\ \mu\text{m}$, 99.9% purity) powders from Sigma-Aldrich Inc. were used as the starting raw materials. The reactant mixture was prepared with a stoichiometric ratio according to the following reaction:



where the amount of x varied from 0 to 0.5. These raw materials were dry-mixed using a heavy duty high-speed mixer (Fast-Mill FM 2) with ZrO_2 balls. The powder-to-ball ratio was set at 10:1, and the materials were mixed for 1 hour. The mixtures were compacted in a stainless steel die (pellet form) with a diameter of 13 mm under 4 tons of load using a cold-pressed machine (Hand Press Hydrotec). The experimental procedure was divided into two stages: Stage 1 which was dedicated to the optimization of the arcing time and Stage 2 which focused on the optimization of excess Si addition. In Stage 1, pellets ($3\text{Ti}:\text{Si}:2\text{C}$) were arced using an arc melting apparatus (UNI-ARC D.C. inverter TIG welder model 200C) at a constant arcing current ($I = 90\ \text{A}$) [52] for several arcing times ($t = 3\text{--}90\ \text{s}$), shielded by pressureless high-purity argon gas (99.99%). The distance between the end-tip (anode) of the tungsten electrode to the surface of the pellet (cathode) was fixed at approximately $\sim 5\ \text{mm}$. In Stage 2, pellets containing different amounts of excess Si (x) were arced at a constant arcing current (90 A) for the optimum

TABLE 1: Details of excess Si and arcing parameters.

Stage	Number of sample	Reactant	Excess Si (x)	Arcing parameters	
				I (A)	t (s)
1	1	3Ti + Si + 2C	0	90	3
	2	3Ti + Si + 2C	0	90	5
	3	3Ti + Si + 2C	0	90	10
	4	3Ti + Si + 2C	0	90	15
	5	3Ti + Si + 2C	0	90	30
	6	3Ti + Si + 2C	0	90	45
	7	3Ti + Si + 2C	0	90	60
	8	3Ti + Si + 2C	0	90	75
	9	3Ti + Si + 2C	0	90	90
2	10	3Ti + Si + 2C	0	90	
	11	3Ti + 1.1Si + 2C	1.1	90	
	12	3Ti + 1.15Si + 2C	1.15	90	Optimum time as
	13	3Ti + 1.2Si + 2C	1.2	90	obtained in stage 1
	14	3Ti + 1.25Si + 2C	1.25	90	(denoted as t_1)
	15	3Ti + 1.3Si + 2C	1.3	90	
	16	3Ti + 1.4Si + 2C	1.4	90	
	17	3Ti + 1.5Si + 2C	1.5	90	

arcing time (t_1 that obtained from Stage 1). The amount of excess Si and arcing parameters are listed in Table 1.

Phase composition of the samples was analyzed using an X-ray diffractometry (Bruker AXS D8 Advance) with $\text{CuK}\alpha$ radiation operating at 40 kV and 30 mA at a scanning speed of $0.02^\circ/\text{s}$ and a 2θ range of $20\text{--}90^\circ$. The qualitative and quantitative analyses of these XRD profiles were performed using the calibrated standard method (automatic mode: default) using Rietveld refinement of PANalytical X'Pert Highscore Plus software. The expected residual (R_{exp}) and good of fit (S) of XRD profiles were recorded as an indicator for refinement quality level. It is noted that the value of R_{exp} should be below 20 while S value should be below 4 for good-quality refinement process. The profile errors can be reduced by switching the calibrated standard mode from default to semiautomatic process. The profile error could be reduced to around 5–10%. Morphology of products was observed using field-emission scanning electron microscope (FESEM model SUPRA 35VP ZEISS) equipped with energy-dispersive spectroscopy (EDS). Lastly, the relative density and porosity of arced samples were calculated based on the Archimedes' method.

3. Results and Discussion

3.1. Stage 1: Optimizing Arcing Time. Figure 1 shows the XRD patterns of compacted 3Ti:Si:2C powder mixtures after arcing at a constant 90 A for various arcing times (5–90 s). The Ti_3SiC_2 phase peaks (ICSD: 98-005-3834) were clearly seen in all samples, with the main peak located at $2\theta = 39.5^\circ$. Similarly, the presence of TiC (ICSD: 98-011-1108) as the main ancillary secondary phase can be seen from their medium peaks intensities, where the main peak

is located at $2\theta = 41.8^\circ$. The intensity of Ti_3SiC_2 peaks increased with increasing arcing times of up to 5 s. Further prolonging the arcing time only reduces the Ti_3SiC_2 content. However, the intensity of TiC peaks is not consistent below 30 s. Peaks of Ti silicides that is, Ti_5Si_3 (ICSD: 98-007-1873) and TiSi_2 (ICSD: 98-001-3102), and free elements (i.e., Ti and C) can also be detected at certain arcing times. No $\text{TiC}_{<x}$ and $\text{Ti}_5\text{Si}_3\text{C}_{<x}$ peaks were observed, as was claimed by El-Raghy and Barsoum [53] and Wu et al. [54]. They proposed that $\text{Ti}_5\text{Si}_3\text{C}_{<x}$ forms firstly at $800\text{--}1400^\circ\text{C}$. In this work, the corresponding peaks of TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_{<x}$ were proven as TiC and Ti_5Si_3 ; due to the presence of fine C in the Ti/Si/C system, the rapid reaction between Ti-melt and C produced TiC. The high stability of TiC present clarifies that its decomposition is not likely to occur at low temperatures. Therefore, it is reasonable to propose that the first compounds to appear were TiC and Ti_5Si_3 , instead of $\text{TiC}_{<x}$ and $\text{Ti}_5\text{Si}_3\text{C}_{<x}$. As compared to Ti_3SiC_2 , the intensity of the Ti_3SiC_2 peaks is higher than TiC and Ti_5Si_3 ; hence, the formation rate of Ti_3SiC_2 is higher than that of TiC and Ti_5Si_3 . The pulse-discharge arcing in the sample is believed to have occurred at temperatures higher than 1400°C . However, TiSi_2 , Ti, and C were observed at 75 and 90 s, corresponding to the decomposition of Ti_5Si_3 . Therefore, it is believed that arcing at longer times (>75 s) only leads to the production of TiSi_2 , Ti, and C which are the decomposition products of Ti_3SiC_2 and/or Ti_5Si_3 .

Table 2 summarizes the results of compacted Ti/Si/C mixture produced using the arc melting method. The different arcing time (3–90 s) was identified as the arcing parameter. All results are listed with values of R_{exp} (<12.6) and S (<3.4), which indicate good refinement processes. In all cases, the products were formed in two main phases, that is, Ti_3SiC_2 and TiC, consisting of small composition of

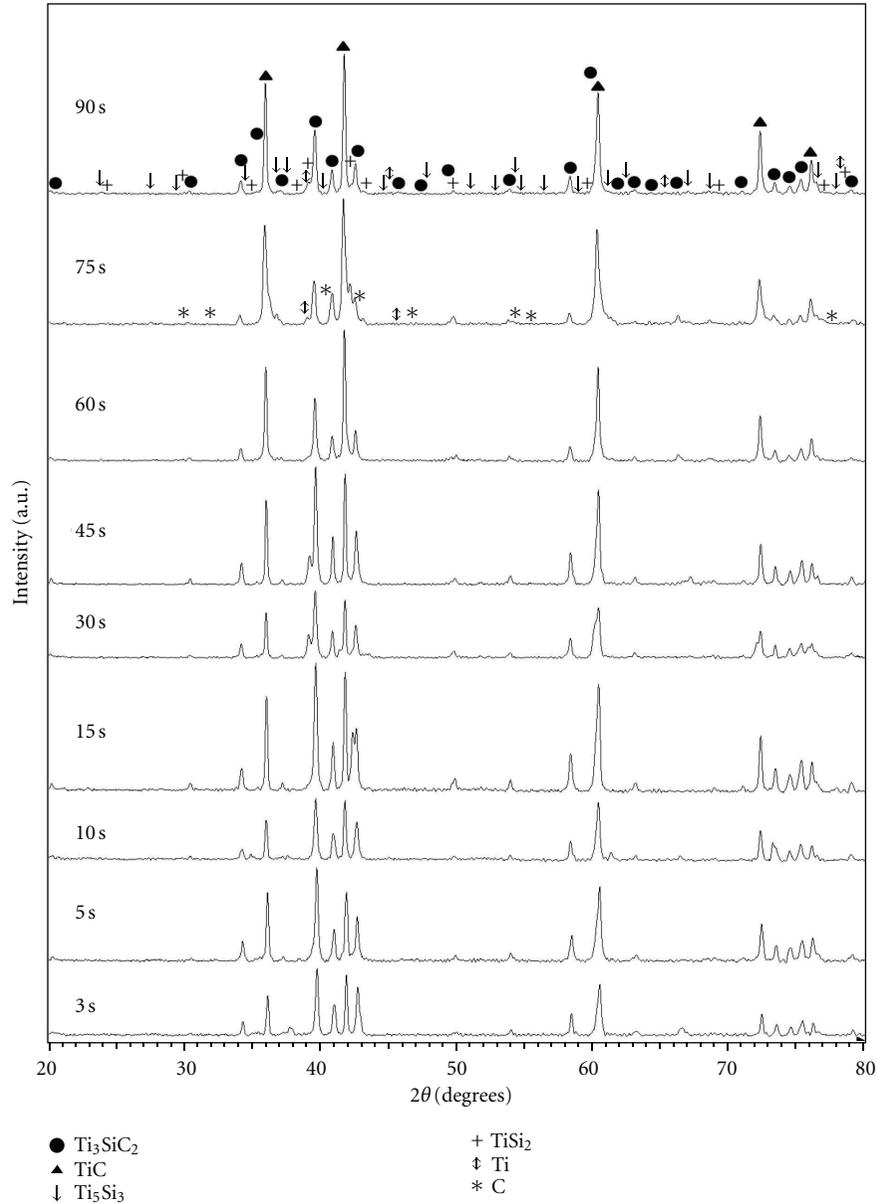


FIGURE 1: XRD patterns of compacted 3Ti/Si/2C powders arced at a constant 90 A for various arcing times (3–90 s).

other phases such as Ti_5Si_3 , TiSi_2 , Ti, and C. The Ti_3SiC_2 composition percentage of the as-synthesized samples arced at 5 s was higher than other arcing schedules. The highest Ti_3SiC_2 percentage in sample number 2 was 62.2 wt%. This demonstrates the significant effect of arcing time on the Ti_3SiC_2 formation. However, the lattice parameters of these synthesized samples were not consistent to each other. This was due to the difficulty of arcing control because of the exothermic reaction.

Figure 2 shows the weight percentage, relative density, and porosity of samples of Ti_3SiC_2 and TiC phases, arced at a constant 90 A for various arcing times (3–90 s) in accordance to Table 2. The Ti_3SiC_2 phase was obviously formed at a short arcing time (~5 s). Initially, from 3 s to 5 s, the Ti_3SiC_2 content changed slightly and reached a maximum

at 5 s. As arcing time was increased to above 5 s, Ti_3SiC_2 decreased; this implies that the optimal arcing time (t_1) for Ti_3SiC_2 formation from compacted 3Ti/Si/2C powders is 5 s. The Ti_3SiC_2 yield in this study is superior compared to that produced in previous work reported by Khoptiar and Gotman [21] which yielded only 45 wt% Ti_3SiC_2 using free postannealed thermal explosion. However, the TiC content was similar to Ti_3SiC_2 content at the lower arcing time of 30 s. The results showed a reverse trend when arcing time was prolonged to above 30 s. The trend in porosity is very much proportional to the amount of TiC phases present. The relative density of all samples was within the range of 82.9–87.5% and showed the reverse of the trend in porosity.

Figure 3 shows FESEM micrographs (as observed at dense polished sample surface and porous site) of a sample

TABLE 2: Results obtained by different arcing parameters.

Stage	No.	Reactant	Arcing parameters		Phases detected (weight fraction, wt%)							Lattice parameters Ti_3SiC_2		
			I (A)	t (s)	Ti_3SiC_2	TiC	Ti_5Si_3	TiSi_2	Ti	C	R_{exp}	S	$a = b$ (Å)	c (Å)
1	1	3Ti + Si + 2C	90	3	50.1	27.6	22.3	—	—	—	10.378	2.412	3.0660	17.6300
	2	3Ti + Si + 2C	90	5	62.2	37.8	—	—	—	—	11.418	2.068	3.0715	17.6900
	3	3Ti + Si + 2C	90	10	55.7	34.0	10.7	—	—	—	10.236	2.476	3.0786	17.6849
	4	3Ti + Si + 2C	90	15	53.3	30.0	10.3	—	—	—	12.638	2.327	3.0669	17.6640
	5	3Ti + Si + 2C	90	30	54.0	23.1	—	12.3	—	—	10.171	3.380	3.0666	17.6406
	6	3Ti + Si + 2C	90	45	42.7	33.1	24.3	—	—	—	11.077	2.285	3.0679	17.6440
	7	3Ti + Si + 2C	90	60	35.7	56.9	7.4	—	—	—	11.558	2.676	3.0680	17.6690
	8	3Ti + Si + 2C	90	75	29.4	57.8	—	4.2	1.8	0.2	12.423	2.188	3.0694	17.6775
	9	3Ti + Si + 2C	90	90	23.1	60.4	13.7	—	2.7	—	12.004	1.976	3.0644	17.6505

TABLE 3: Results obtained by different excess Si contents in starting reactant.

Stage	No.	Reactants	Arcing parameters		Phases detected (weight fraction, wt%)							Lattice parameters Ti_3SiC_2		
			I (A)	t (s)	Ti_3SiC_2	TiC	Ti_5Si_3	TiSi_2	α -Ti	C	R_{exp}	S	$a = b$ (Å)	c (Å)
2	10	3Ti + Si + 2C	90	5	62.2	37.8	—	—	—	—	11.418	2.068	3.0715	17.6900
	11	3Ti + 1.1Si + 2C	90	5	74.2	24.9	—	0.9	—	—	10.418	2.068	3.0681	17.6657
	12	3Ti + 1.15Si + 2C	90	5	76.7	21.2	—	2.1	—	—	12.432	1.443	3.0699	17.6860
	13	3Ti + 1.2Si + 2C	90	5	86.9	9.4	—	3.8	—	—	12.619	2.326	3.0686	17.6746
	14	3Ti + 1.25Si + 2C	90	5	64.6	30.4	—	5.0	—	—	11.767	1.384	3.0718	17.6887
	15	3Ti + 1.3Si + 2C	90	5	56.1	32.0	—	11.9	—	—	11.569	2.447	3.0689	17.6680
	16	3Ti + 1.4Si + 2C	90	5	54.6	41.3	—	2.7	0.4	1.0	10.292	1.258	3.0694	17.6920
	17	3Ti + 1.5Si + 2C	90	5	30.0	47.8	4.0	6.2	1.7	1.3	12.848	2.806	3.0666	17.6407

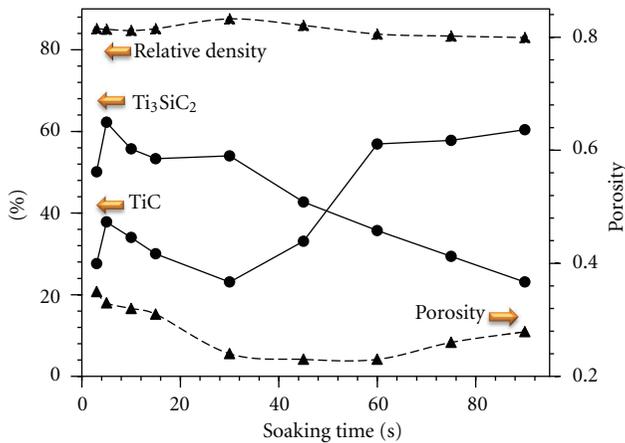


FIGURE 2: Effects of soaking times on the relative density, porosity, and phases detected (wt%).

arced at 90 A for 5 s. At least two types of grains can be seen: elongated platelets and equiaxed grains. The grain size of the elongated platelets (i.e., thickness) is 1–8 μm , while the equiaxed grain size is about 2–16 μm . They are surrounded by the irregular appearance of the melt region. Identification of grains was confirmed using EDX analysis. As shown in Figure 3(a), the elongated platelets and equiaxed grains can be identified as Ti_3SiC_2 and TiC, respectively, while TiSi_2 and/or Ti_5Si_3 is the melt region. These micrographs confirm

the nucleation and growth of Ti_3SiC_2 within the TiC grains (Figure 3(b)), which is similar to the observation made by previous researchers [49]. However, it can be obviously seen that Ti_3SiC_2 formed on the surface of TiC grains. This directly proves that Ti_3SiC_2 formation on TiC surface is possible. It is marked as an interface of Ti-Si and TiC grains. Therefore, the interface between them is governed by Ti_3SiC_2 formation, as similarly reported by Riley et al. [24]. However, the nucleation and growth of Ti_3SiC_2 within the Ti_5Si_3 grains are unclear. Microporosity appeared within the TiC grains. This is in agreement with Li et al. [36] who reported that the flame front (combustion) of the heat propagation was not completed and C was diffused into the Ti site to form TiC_x , leaving a large amount of microporosity inside the grains. The arrow in Figure 3(a) also refers to the microporosity obtained in TiC grains. Meanwhile, Figure 3(b) confirms that no micro-porosity was seen on the surface of this TiC grain.

3.2. Stage 2: Optimizing Excess Si Addition. Figure 4 shows XRD patterns of excess Si samples after arcing at a constant 90 A for 5 s. It is found that the varying amount of excess Si in the reactant mixture directly influenced the Ti_3SiC_2 yield. This can be seen from the intensity of the main Ti_3SiC_2 peak ($2\theta = 39.5^\circ$). The strongest peak can be observed for the sample with excess Si of $x = 0.2$. It is proposed that the presence of sufficient Si produces a large wetting area in the compacted mixture which reacts with Ti to form the Ti-Si melt region. This Ti-Si reacts with TiC to form Ti_3SiC_2 ,

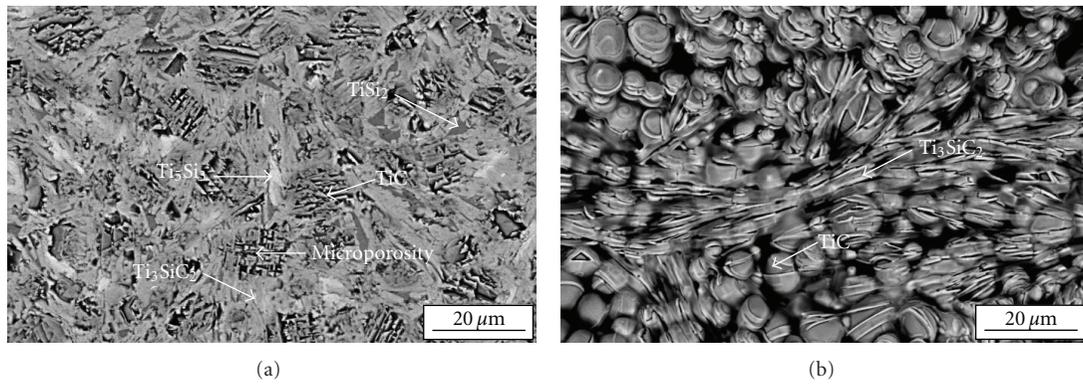


FIGURE 3: FESEM morphology of sample ($x = 0$) scanned at (a) the dense surface and (b) pore site after arcing at a constant 90 A for 5 s.

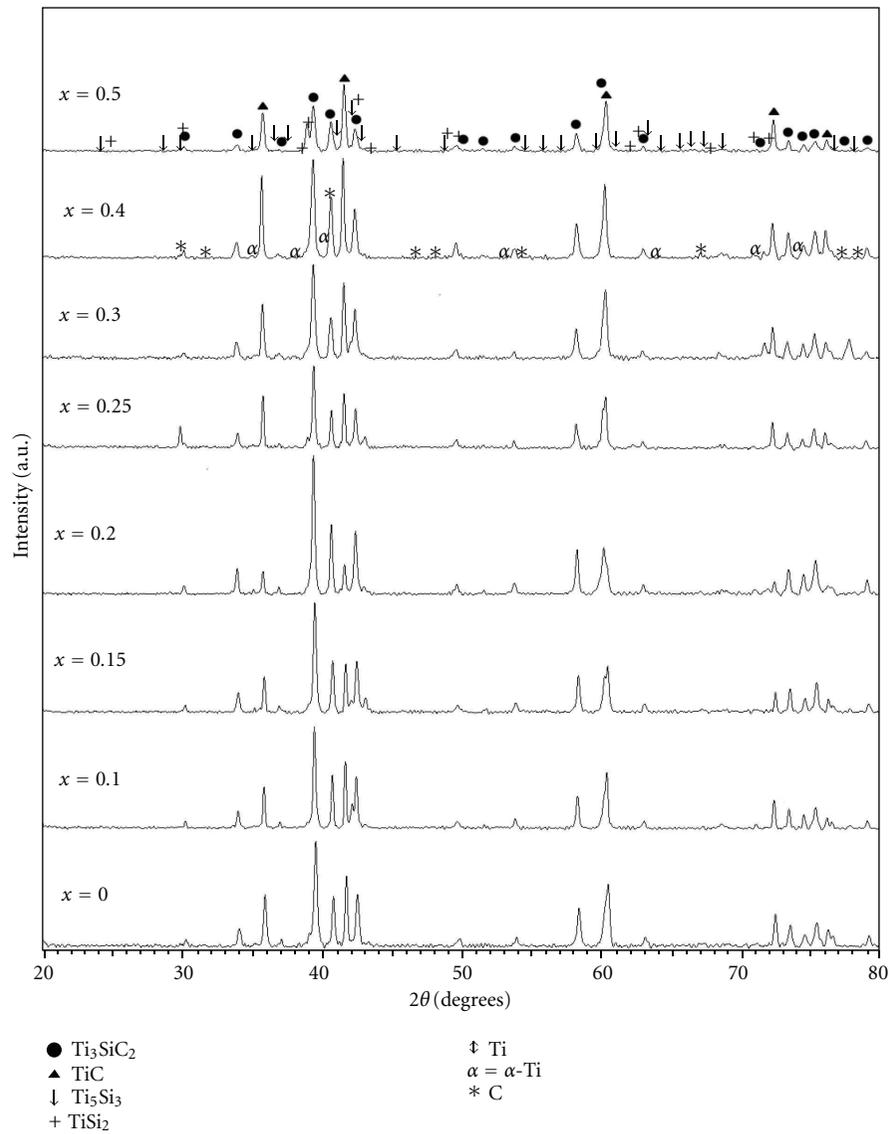


FIGURE 4: XRD patterns of compacted $3\text{Ti}/(1 + x)\text{Si}/2\text{C}$ powders after arcing at a constant 90 A for 5 s.

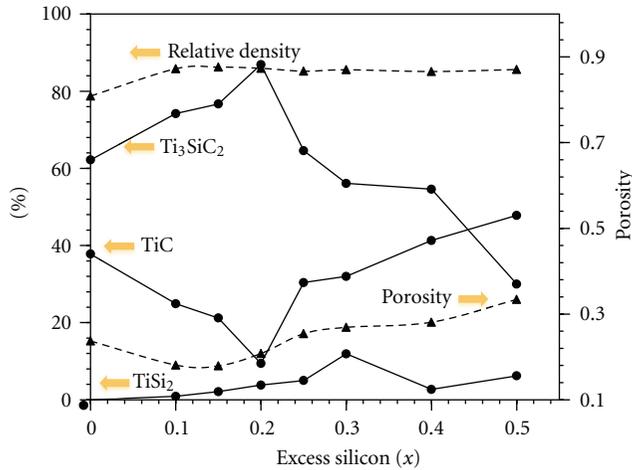


FIGURE 5: Effects of excess Si on the relative density, porosity, and phases detected (wt%).

which is in agreement with a previous study conducted by Riley et al. [24]. However, as x increased, the peak intensity of Ti_3SiC_2 decreased. This phenomenon was due to too much Si melt region surrounding the coarse Ti and C dispersed from the Ti surface. This is proven by the weak intensity of TiC peaks observed.

TiC is the main secondary phase present in all samples, along with the TiSi_2 melt region. However, small peaks of Ti_5Si_3 are only present in certain samples. The weak intensity of both TiSi_2 and TiC peaks indicate that TiSi_2 and TiC may react with each other to form Ti_3SiC_2 . Therefore, the addition of excess Si was favorable in producing TiSi_2 instead of Ti_5Si_3 . Further additions ($x \geq 0.4$) have clearly lowered the peak intensities of Ti_5Si_3 , $\alpha\text{-Ti}$, and C. It seems that it does not influence the Ti_3SiC_2 formation; instead, it was responsible for lowering intensities of Ti_3SiC_2 peaks. Hence, it is proposed that the low peak intensity of $\alpha\text{-Ti}$ present in this sample is affected by thermal activities which can be explained using two assumptions.

Firstly, the physical and electrical properties of Si powder are, respectively, smaller and weaker compared to those of Ti. Therefore, Si will stick onto the surfaces of Ti particles after the mixing and milling process; this produces resistance/barrier against current flow. Secondly, Si is classified as a good thermal conductor; hence it produces large melt regions on the surfaces of Ti particles since it has the lowest melting temperature ($\sim 1414^\circ\text{C}$) [49] in the Ti–Si–C system. Therefore, small C particles will partly diffuse into the Si melt region, while others will be trapped in the same region and are not able to react with the Ti phase to form TiC. This assumption may be relevant as well as for $\alpha\text{-Ti}$ and C phases which were observed in samples containing $x \geq 0.4$. It is proposed that the medium intensity of the Ti_3SiC_2 peaks is affected by the direct reaction between the TiC and Si melt. This is a reasonable assumption as Ti–Si presented low peak intensity.

Table 3 shows the results (phases percentage and lattice parameters) of compact excess Si samples arced at a constant

90 A for 5 s. The highest composition of Ti_3SiC_2 (86.9 wt%) was obtained from the reaction system of $3\text{Ti}/1.2\text{Si}/2\text{C}$. The value of Ti_3SiC_2 composition is parallel to the XRD pattern of sample number 13, as shown in Figure 4. Figure 5 shows the quantitative XRD analysis of phase percentage (Ti_3SiC_2 , TiC, and TiSi_2), relative density, and porosity of the synthesized samples, performed according to Rietveld refinement and calculated based on the Archimedes method, respectively. 86.9 wt% of Ti_3SiC_2 was successfully synthesized from excess Si ($x = 0.2$) sample. Therefore, the optimum degree of Ti_3SiC_2 phase formation is from the product with excess Si ($x = 0.2$). Figure 5 also shows the reverse effect for both TiC and Ti_3SiC_2 at a relatively different x . An addition of excess Si in Ti/Si/C only improves the content of TiSi_2 in the silicides melt region. Therefore, the formation of new silicides in the products should not be favored, which is in accordance with the work done by Zhang et al. [31]. The relative density of all samples with excess Si ranges between 85.19 and 86.25%, and the porosity is shown to be directly proportional to the amount of TiC present. Therefore, it is suggested that the addition of excess Si does not effectively increase the relative density of the product. On the other hand, it increased the amount of porosity in TiC grains.

Figure 6 shows the FESEM micrographs of as-polished samples arced at 90 A for 5 s with varying excess Si content in the mixture. The different amounts of Si added into the mixture affected the Ti_3SiC_2 grain size and distribution. Typically, the thickness of Ti_3SiC_2 grain size is 1–15 μm . The largest Ti_3SiC_2 grain size was obtained in the sample with excess Si ($x = 0.2$). Further additions of excess Si ($x > 0.2$) into the reactant mixture were responsible for reducing Ti_3SiC_2 grain size and its depletion into small pieces. Its effect on the equiaxed (TiC) grain size is inversely proportional to Ti_3SiC_2 . The melt region that surrounds the elongated platelet and equiaxed grains most likely belongs to TiSi_2 melt, which was formed as a necessary intermediate phase in the formation and decomposition of Ti_3SiC_2 . It is observed that the area of TiSi_2 melt is magnified on the equiaxed grains. Therefore, it is possible that a reaction would occur between the melt region and TiC in Ti_3SiC_2 formation. It is proposed that large areas of TiSi_2 melt region on TiC surfaces produce a large amount of elongated grains. This is possible because the ignition temperature is $>1400^\circ\text{C}$, which is close to the melting temperature of Si. The goal of adding excess Si is to compensate the loss of Si in the system, which agrees with a finding from a study done by Yang et al. [49]. From the discussion above, it is suggested that excess Si can be regarded as a favorable additional element to synthesize 86.9 wt% of Ti_3SiC_2 at a relatively short time, using the arc melting method. The micrograph in Figure 6(f) is an example of microporosity that exists in the equiaxed TiC grain.

4. Conclusion

86.9 wt% of Ti_3SiC_2 was successfully synthesized from compacted $3\text{Ti}/1.2\text{Si}/2\text{C}$ powders arced at 90 A for 5 s. It is an improvement of approximately 44% from the yield produced in the study conducted in 1995 using pressureless

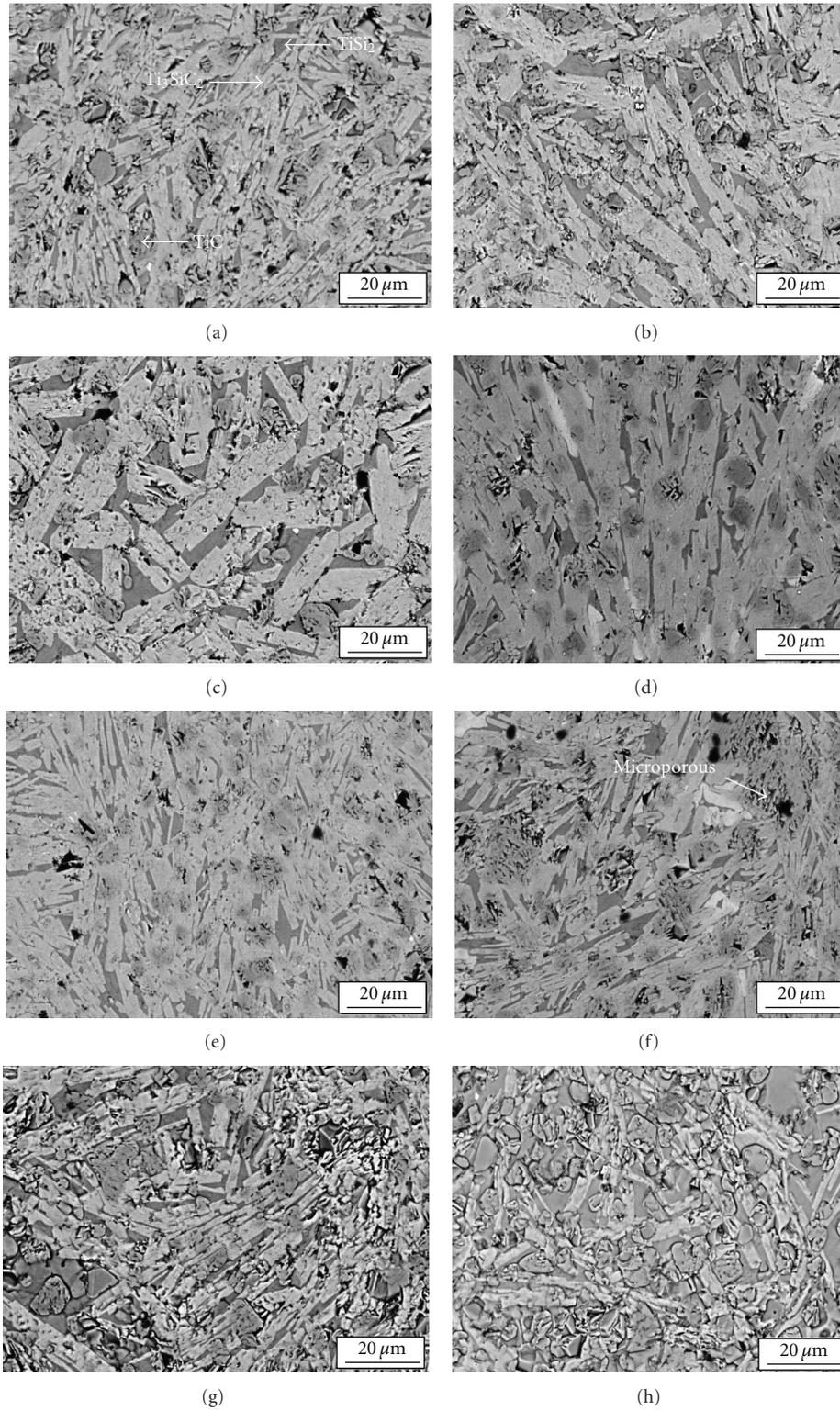


FIGURE 6: FESEM micrograph of as-polished samples containing different content of excess Si; (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.15$, (d) $x = 0.2$, (e) $x = 0.25$, (f) $x = 0.3$, (g) $x = 0.4$, and (h) $x = 0.5$ arced at a constant 90 A for 5 s.

self-ignition reaction. Ti_3SiC_2 was formed as the main phase and TiC as the main secondary phase, whereas TiSi_2 and Ti_5Si_3 were formed as secondary melt region phase. Based on product morphology, elongated platelets of Ti_3SiC_2 were found nucleated and grown on the surfaces of equiaxed TiC grains. However, these TiC grains contain a lot of microporosity which relatively affects the density and porosity of products.

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