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# Thermal stability and phase formation of mechanically alloyed Ti-Al-Si-C powders

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Two quarternary Ti-Al-Si-C powder mixtures, 55Ti-27Al-12Si-6C and 55Ti-36Al-6Si-3C, were mechanically alloyed. The as-alloyed and heated powders have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). XRD patterns showed diffuse halos of amorphous like phase for 20–40 h milled powders, but TEM examinations demonstrated that the 40 h milled powders were mainly composed of Ti solid solutions, with some amount of amorphous phase. SEM observations displayed that the lamellar structures of Ti and Al formed at the early stage of milling process subsequently led to the formation of nano- or sub-micrometer particles of homogeneous composition after prolonged milling to 40 h. It is deduced that the solid-stated reaction by inter-diffusion of components should be responsible for phase formation during mechanical alloying. DSC curves of the 40 h milled powders exhibited two sharp exothermal peaks, and the investigation on thermal stability of the 40 h milled powders indicated that $Ti_5Si_3$ was first formed at lower temperature, followed by $Al_2Ti_4C_2$and TiC at intermediate temperature (820°C), and these phases were stable at elevated temperatures. These results raise the possibility of synthesizing TiAl-based composite with titanium silicides and titanium carbides as reinforcements by proper selection of powder compositions. *© 2004 Kluwer Academic Publishers*

## 1. Introduction

Mechanical alloying (MA) has been widely used to synthesize equilibrium phases and metastable phases such as supersaturated solid solutions, amorphous phase, and nonocrsytalline materials. Just as silicon is added to TiAl-based alloys to form $Ti_5Si_3$, carbon is also a promising element in TiAl-based alloys for both solid solution effect and dispersion strengthening by precipitation of TiC or $Ti_2AlC$ [1–3]. Some investigations indicated that TiC could be synthesized by mechanically alloying elemental powder mixtures of Ti-C [4, 5], and multiple systems of Ti-Ni-C [6], Ti-Al-Fe-C [7] and Ni-Al-Ti-C [8, 9]. Mechanical alloying of Ti-Al-Si-C systems towards synthesizing TiAl-based composite containing Si and C has not been reported in the literature. In this study, two compositional Ti-Al-Si-C powder mixtures were mechanically alloyed in order to explore a promising way of producing TiAl-based composites with titanium silicides or titanium carbides of ultra-fine grain size.

## 2. Experimental procedure

Two Ti rich powder mixtures, namely, 55Ti-27Al-12Si-6C (at.%) and 55Ti-36Al-6Si-3C (at.%) with high and low Si and C combinations were chosen based on Ti-Al-Si and Ti-Al-C ternary diagrams in order to form reinforcements consisting of intermetallics such as $Ti_5Si_3$ and titanium carbides of TiC and $Ti_2AlC$. The commercial elemental powders of Ti, Al, Si and C (graphite) with nominal purity of 99.9% and an average particle size of 45 $\mu$m (<325 mesh) were used as starting powders.

MA of the chosen powders was performed using a planetary ball mill with stainless steel vials and balls with ball-to-powder weight ratio of 30:1 under argon protection. At predetermined intervals, i.e., 5, 10, 20, and 40 h, small amounts of milled powders were taken out for analysis. In order to avoid excessive heating, every 15 min of milling was followed by the same length period of stopping to allow cooling of vial and balls.

The structural evolution of milled and/or annealed powders was characterized by X-ray diffraction (XRD) with Cu $K_\alpha$ radiation and the morphology of the milled particles was examined by scanning electron microscope (SEM). Transmission electron microscope (TEM) observation was also performed on 40 h milled powders. Specimens for TEM were prepared by depositing the powders directly onto copper grids coated with carbon film.

The stability of 40 h milled powders was investigated by differential scanning calorimetry (DSC) using

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heating rate of 10°C $\text{min}^{-1}$. Based on the DSC curves, heat-treatment of 40 h milled powder was performed at different temperatures to study the phase transformations, maintaining same heating rate and atmosphere as in DSC. After heating the milled powder to the required temperature, it was held at that temperature for 15 min.

## 3. Results and discussion

### 3.1. Formation of metastable phases during mechanical alloying

The XRD patterns of the powder mixture of 55Ti-27Al-12Si-6C after different milling times are shown in Fig. 1. The crystalline diffraction peaks from Ti, Al Si and C are evident for the starting powder mixture. After 5 h milling, the pattern showed a remarkable change, with Ti peaks becoming broader and intensity decreasing dramatically. While Al peaks disappeared completely, only some traces for Si peaks existed (Fig. 1b). This indicated that inter-diffusion between different atoms had occurred and Ti solid solution was formed at that early stage of milling process. Further milling to 10 h showed (Fig. 1c) a broad diffuse peak around $2\theta = 35$–$45°$, with Ti(110) peak still overlapped the diffuse peak, and Si trace could also be observed. In the case of 55Ti-36Al-6Si-3C powder mixture (XRD patterns not provided here), it was found that only diffuse halo appeared after 10 h milling. No significant changes occurred for milling to 20 h (Fig. 1d). After 40 h milling, the diffraction patterns were characterized by a smooth and diffuse halo, as displayed in Fig. 1e. It can be deduced from XRD phase evaluation that the time required to achieve the final state decreased with increasing Al content in the powder mixtures.

At present, little work has been found on mechanical alloying of Ti-Al-Si-C systems. However, studies performed on Ti-Al, Ti-Si and Ti-Al-Si systems indicate that the nature of final phases obtained in as-milled powder mixtures depends mainly on the experienced milling conditions such as the type of milling equipment, milling intensity and atmosphere [10–13]. Guo *et al.* [10] reported that, for Ti-Al powder mixtures in the concentration range of 20 to 50 at.% Al, mechanical alloying first led to the formation of an hcp Ti(Al) solid solution, followed by transformation into amorphous state. On the contrary, Oehring *et al.* [11] observed that high intensity mechanical alloying led to the formation of metastable hcp solid solutions for Al concentration up to 60 at.% whereas fcc solid solution was found for 75 at.%. The co-existence of hcp solid solution and amorphous phase were observed in 50Ti-50Al powder by lowering the milling intensity. For Ti-Si powder mixtures, earlier studies state that a two-phase mixture of a supersaturated hcp solid solution and an amorphous phase coexist in the final stage of milling of 92Ti-8Si. When Si concentration was raised to 37.5 at.%, the amorphous phase was prominent with only a small fraction of intermetallic compound $Ti_5Si_3$ [14]. In a series of Ti-Al-Si systems, a homogeneous amorphous phase or a two-phase mixture of amorphous and hcp phases were obtained upon milling for less than 50 h, and a combination of $\alpha_2$ or $\gamma$ and $Ti_5Si_3$ was formed after subsequent annealing [15].

The diffuse halo of XRD patterns after 10–20 h milling in the present cases displayed the typical characteristics of amorphous phase. TEM observation demonstrated that the 40 h milled powders were mixtures of Ti solid solution, amorphous phase, and a small fraction of single crystalline phase. The bright field

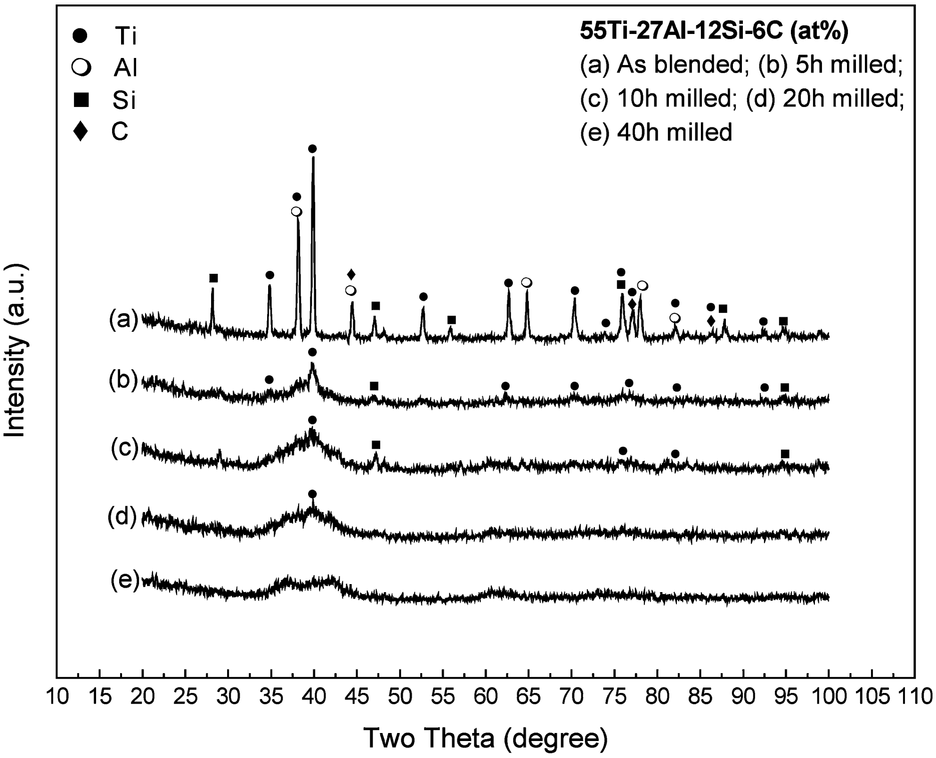

*Figure 1* X-ray diffraction patterns of 55Ti-27Al-12Si-6C powder mixture at various stages of mechanical alloying.

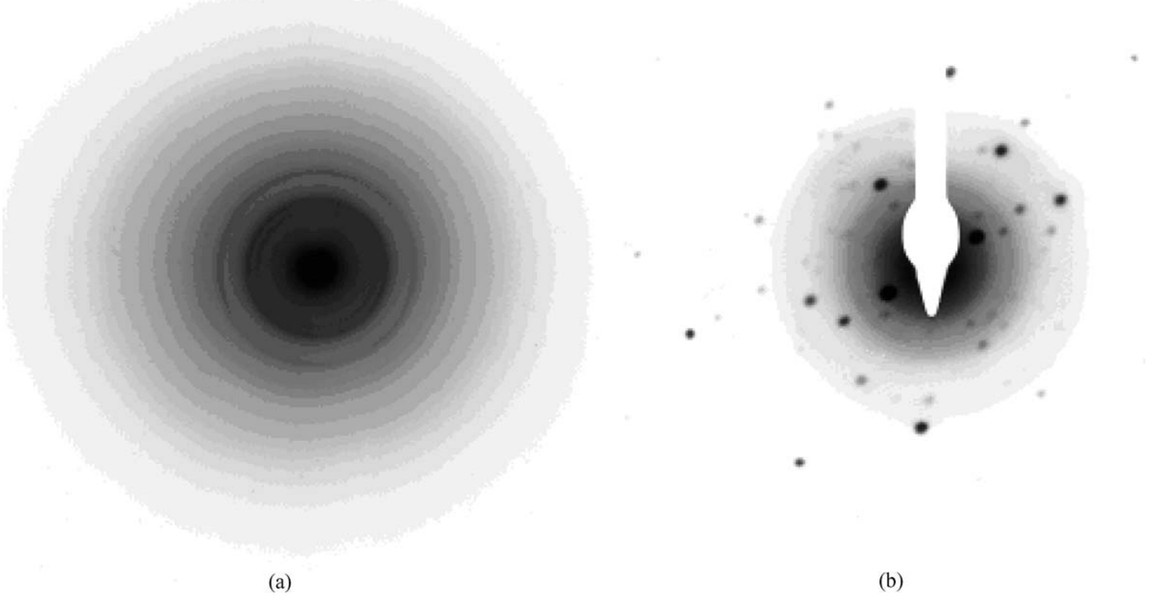
(a) (b)

*Figure 2* Selected area diffraction patterns of 40 h milled 55Ti-27Al-12Si-6C powder at two different locations.

image (BFI) of 40 h milled powder of 55Ti-27Al-12Si-6C indicated particles with wide size distribution, ranging from 30–200 nm, with some large particles that are agglomerations of many small ones. Typical selected area diffraction (SAD) patterns of the milled powder obtained at different locations are shown in Fig. 2. The diffraction rings in Fig. 2a indicate that the milled powders possess polycrystalline phase, which is consistent with our previous investigation on Ti-Al-Si milled powders [16]. However, the SAD patterns of some other locations showed diffusion halo and sharp spot patterns (Fig. 2b), which indicate partial amorphization of Ti solid solution and some crystalline particles.

The solid-state reaction by inter-diffusion of components must be responsible for phase formations observed in the present investigation. During the first 5 h milling, ductile Ti and Al particles must have deformed and welded to form large particles with layered or lamellar structures, while the brittle Si and C particles were crushed and the small fragments were embedded in large Ti particles, as displayed in the SEM micrograph given in Fig. 3, which is cross-sectional view of 5 h milled powder of 55Ti-36Al-6Si-3C. EDS (electron dispersive spectrum) analysis proved that the light areas are Ti particles or rich in Ti (marked as A and B in the figure), the gray areas are Ti solid solutions (locations

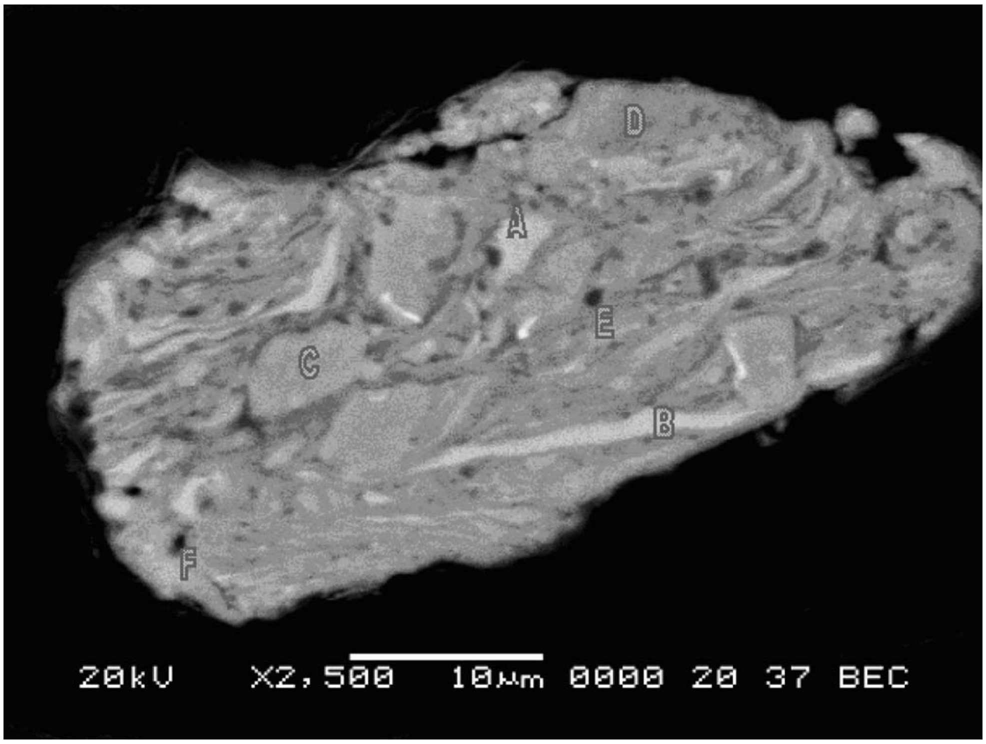

*Figure 3* SEM image of cross-sectional view of 55Ti-36Al-6Si-3C powder after 5 h of mechanically alloying.

C and D), and the black spotted areas are embedded Si or C pieces (locations E and F). At this stage of milling, SEM and EDS results indicated that the milled particles were heterogeneous in composition and structure. The formed multi-layered structure could increase the contact area of different particles thereby enhancing the inter-diffusion process. Owing to the larger diffusivity of Al in Ti ($1.06 \times 10^{-21}$ cm$^2$ s$^{-1}$) compared to that of Ti in Al ($2.9 \times 10^{-23}$ cm$^2$ s$^{-1}$), the migration of Al into Ti lattice is dominant, while the small atoms of C could move into the interstitials of Ti or Al lattice. On the other hand, the solubility of Al and Si in Ti could be substantially increased by mechanical alloying, for example, it was reported [17] that as much as 60% Al and 37.5% Si can be dissolved into Ti during such processing. It was found from EDS analysis that after 5 h milling, only the gray areas (C and D in Fig. 3) attained approximately the nominal composition of the starting elemental powder mix. With prolonged milling to 40 h, the powder contained much finer particles that tend to agglomerate into clusters, with the composition being homogeneous.

The forming of an amorphous phase and a solid solution are competing processes in mechanical alloying. From the thermodynamic point of view, the estimated free energy by Oehring *et al.* [11] indicated that the amorphous phase has a higher free energy than hcp and fcc solid solutions in the whole concentration range of Al in Ti-Al systems. However, in multi-component cases, the situation may be different owing to the rapid diffusion of Al, Si and C into Ti lattice. The Ti solid solution is highly supersaturated after substantial mechanical alloying, and the composition-induced destabilization of solid solutions by inter-diffusion will play a major role in the amorphization [11]. If the Ti solid solution in local area is supersaturated beyond a critical value, partial amorphization will happen, and this phenomenon was also observed in milled powder of 40Ti-60Al [10].

### 3.2. Thermal stability of milled powder mixtures

DSC curves obtained with 40 h mechanically alloyed powders of 55Ti-27Al-12Si-6C and 55Ti-36Al-6Si-3C are presented in Fig. 4. The features of both the curves are similar, with two sharp exothermal peaks as well as two broad ranges of exothermal heat release apparent upon heating. The first broad heat release peak is observed around 350–525°C, and the second broad peak extends from approximately 850 to 1100°C for both the milled powders. As for the two sharp exothermal peaks, the peak positions for the smaller one are almost same at about 665°C for both powders. However, the larger sharp peaks are somewhat different for the two milled powders, with the peak from 55Ti-36Al-6Si-3C being larger than that of 55Ti-27Al-12Si-6C while the position of the peak is a bit lower for the former case. In order to investigate the phase evolution and stability of milled powders, a series of heat-treatments were performed for the 40 h milled powders based on the exothermal reactions observed in the corresponding DSC curves. The selected temperatures of 520, 700, 820 and 1150°C are just beyond the corresponding peaks in DSC curve.

XRD patterns of the 40 h milled 55Ti-27Al-12Si-6C powder mixture heat-treated at different temperatures are shown in Fig. 5. XRD pattern for powders heated to 520°C showed no significant change compared to that of as-milled powder (Fig. 5a–b), indicating that

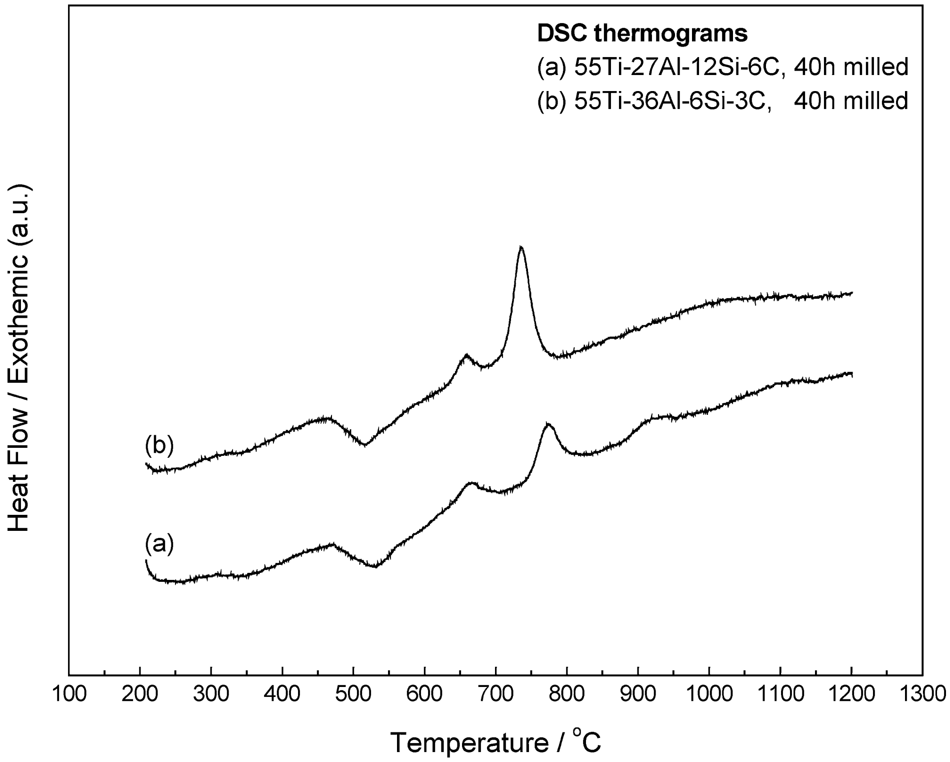

*Figure 4* DSC curves of Ti-Al-Si-C powders mechanically alloyed for 40 h: (a) 55Ti-27Al-12Si-6C and (b) 55Ti-36Al-6Si-3C.

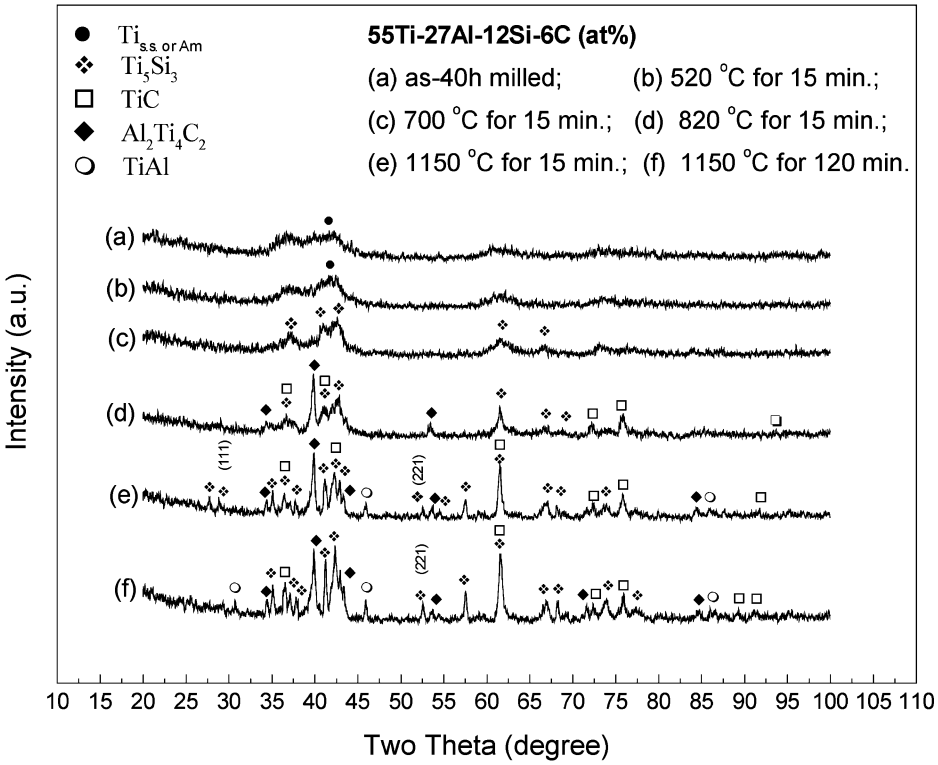

*Figure 5* X-ray diffraction patterns of 40 h milled 55Ti-27Al-12Si-6C powder after heat-treating at different temperatures.

the heat release is not ascribed to any phase transformation and that the heat release may be due to the strain relaxation and/or recovery and recrystallization of the highly deformed particles. When heated to 700°C, the phase formation is slightly different for the two milled powders. In the case of 55Ti-27Al-12Si-6C powder (Fig. 5c), only traces of $Ti_5Si_3$ (in the form of $Ti_5(Al,Si)_3$) appeared and are imposed on Ti solution diffuse peaks. However, for the milled and heated powder of 55Ti-36Al-6Si-3C, the main peak from $Al_2Ti_4C_2$ was observed in addition to the traces of $Ti_5Si_3$ and TiC. With temperature increased to 820°C, i.e., after the larger exothermal peak, phases of $Al_2Ti_4C_2$ and TiC began to form in 55Ti-27Al-12Si-6C also, and the pattern was same for 55Ti-36Al-6Si-3C as well except for an increase in the intensity of $Al_2Ti_4C_2$peaks. These results indicate that (i) the smaller sharp exothermal peak around 620–700°C in DSC curves (Fig. 4) was attributed to the formation of $Ti_5Si_3$, and (ii) the larger sharp exothermal peak around 700–800°C in DSC curve (Fig. 4) was related to highly exothermic reactions for the formation of $Al_2Ti_4C_2$and TiC. The position of larger peak (at about 740°C) for 55Ti-36Al-6Si-3C is much closer to the preceding smaller peak. Thus, it can be assumed that when the milled powder was heated to 700°C and held for 15 min, the reactions for formation of $Al_2Ti_4C_2$and TiC have already begun, resulting in identical pattern with that for 820°C heated powder though formation of these phases got completed in the later case.

When heated to 1150°C, the phases that finally resulted are $Ti_5Si_3$, $Al_2Ti_4C_2$, and TiC for both powder mixtures, besides a trace of TiAl (Fig. 5e). In addition, some superlattice reflections of $Ti_5Si_3$ are present, as marked by index number on peaks, which demonstrated that $Ti_5Si_3$ was transformed to ordered state at higher temperatures. The XRD patterns indicated that, the intensity of peaks from $Ti_5Si_3$ was higher for 55Ti-27Al-12Si-6C powder, while the peak of $Al_2Ti_4C_2$ dominated in the case of 55Ti-36Al-6Si-3C. This phenomenon may be closely related to their compositions, the former composition has more Si and the latter one has more Al. In order to investigate the thermal stability of phases formed in the heating process and to observe the grain growth during prolonged thermal exposure, 40 h milled powders were kept at 1150°C for 120 min. The XRD patterns showed no distinctive features to those obtained by holding at that temperature for only 15 min, as shown in Fig. 5f in the case of 55Ti-27Al-12Si-6C. This means that the phase formation was quick during the heating process, and all the phases were in equilibrium states. The estimated lattice parameters for the three main phases formed after heating to 1150°C matched very well with corresponding JCPDS files. For instance, the parameters of the phases formed in 55Ti-36Al-6Si-3C powder are: $a = 0.74684$ nm and $c = 0.51362$ nm for $Ti_5Si_3$; $a = 0.30566$ nm and $c = 1.35116$ nm for $Al_2Ti_4C_2$; and $a = 0.43345$ nm for TiC. The minor differences found reflect the dissolving of other elements, such as Al in $Ti_5Si_3$ ($Ti_5(Al,Si)_3$). In summary, upon heating the 40 h milled powders, $Ti_5Si_3$ was the first phase formed at lower temperature, followed by $Al_2Ti_4C_2$ and TiC at intermediate temperature (820°C), and their formation was completed at higher temperature (1150°C) and led to equilibrium state.

## 4. Conclusions

The behavior of two Ti-Al-Si-C powder mixtures during mechanical alloying and the subsequent thermal stability have been investigated. The following conclusions can be drawn from these studies:

(i) Mechanical alloying of 55Ti-27Al-12Si-6C and 55Ti-36Al-6Si-3C powder mixtures mainly resulted in Ti solid solution, with small amounts of an amorphous phase and/or some crystalline particles. At the early stage of milling process, lamellar structures of Ti and Al with embedded Si and C particles were formed. With further milling to 40 h, the grain size achieved was in nano- or sub-micrometer range, and the small particles were homogeneous in composition and tend to be agglomerated.

(ii) DSC curves of 40 h milled powders displayed two sharp exothermal peaks, and the first peak was ascribed to the formation of $Ti_5Si_3$ while the second peak was caused by reactions for the formation of $Al_2Ti_4C_2$and TiC.

(iii) After heating the 40 h milled powders to higher temperature of 1150°C, three equilibrium compounds, namely, $Ti_5Si_3$, $Al_2Ti_4C_2$, and TiC, were formed.

(iv) When the milled powders of selected compositions are mixed with appropriate matrix and processed, $Ti_5Si_3$, $Al_2Ti_4C_2$, and TiC could be *in situ* formed as stable and harder reinforcements in the resultant TiAl-based composites.

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