Original Article

Constitutive behavior and microstructural evolution in Ti–Al–Si ternary alloys processed by mechanical milling and spark plasma sintering

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\textbf{A B S T R A C T}

Severe plastic deformation is closely related to the microstructural behaviors of intermetallics or grain refinement by mechanical milling and subsequent rapid sintering process, i.e. high energy ball milling and spark plasma sintering. In this study, the Ti–Al–Si ternary powders were synthesized to investigate their phase transformation by plastic deformation during the mechanical milling in each process time and composition. The sintered-bodies Ti–Al–Si ternary alloys were fabricated by spark plasma sintering among the rapidly consolidated powders, except for the distribution of single phases in accordance with the Al-melting. The microstructures of intermetallics in Ti–Al–Si ternary alloys were composed of titanium aluminides and titanium silicides, and even ternary compounds as a \( γ \)-phase. In particular, the twinning or stacking faults induced by severe plastic deformation were revealed through crystallographic patterns and microstructural evidence. These defects were caused by the slip system for TiAl\textsubscript{3} (fcc) or Ti\textsubscript{3}Si\textsubscript{5} (hcp) phases, depending on the grain refinement and generation of ambient intermetallics. To estimate the possibility of these defects, various approaches were taken to obtain experimental measurement of the twin probability and stacking fault energy derived from TEM and XRD analyses.

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1. Introduction

There are significant challenges facing the general use of Ti–Al alloys in various industries required that anti-corrosion and lightweight, such as aerospace and automotive \cite{1–3}. In particular, they face limits of brittleness and strength at high temperatures. However, these limits can be improved on several techniques: (i) Imparting of ductility, e.g. severe plastic deformation (SPD) by mechanical alloying (MA), (ii) Control of microstructures, e.g. grain refinement and the formation of intermetallics, and (iii) Additive elements to enhance the mechanical properties, e.g. Si, Cr, Mo, and Nb.

Recently, many studies have developed methods of the synthesis of nano-structured materials using high-energy ball
milling (HEBM) accompanied by MA [4,5]. The aim at the MA process is the preparation of multi-component alloy nanostructures of excellent mechanical properties in the (1–100) nm range of grain size, inevitably accompanied by the SPD phenomenon [6,7]. Under SPD, various defects are induced, such as high density of crystalline defects by internal stresses, phase transformation with microstructural evolution, solid state amorphization, dissolution of precipitates, and deformation of twin phase related to dislocation pile-up [8–11]. In particular, plane defects (twin, stacking fault) are closely associated with the brittle-ductile transition, given applied slip dislocation. Crystallographically, metallic materials in close-packed structure that allow the activation of a number of slip systems had the ability to take plastic deformation, i.e. FCC and BCC: sufficient slip system, HCP: limited to slip system with temperature-dependence [12,13].

Intermetallics for TiAl-based compounds (TiAl, TiAl2, TiAl3, Ti3Al) is enabled with excellent properties, such as high melting point, good stiffness, and resistance to oxidation at elevated temperature [14,15]. These compounds can be fabricated by the powder metallurgy process, such as the casting/melting process [16,17], reactive sintering [18,19], and spark plasma sintering (SPS) [20,21]. In comparison to the conventional melting process, modern techniques, such as the SPS method, are attracted to the control of intermetallics of high-temperature materials that can function effectively as nano-graded materials for simultaneous consolidation and alloy without pores and cracks.

On the other hand, Si has been reported to be the most promising material as an additive to improve the high-temperature strength of the Ti–Al system. In particular, Ti5Si3 intermediate phase has considerable stiffness, and even so shows oxidation and corrosion effects [22,23]. For these reasons, much theoretical evidence has been reported on the 1990s of the Ti–Al–Si system. C. R. Azevedo et al. [24,25] reported the variation in solubility with respect to the content of Al and Si in the Ti-rich corner, and the microstructural evolution (e.g. eutectoid/ peritectoid reaction) after the heat treatment or cooling was traced by thermodynamic calculation. K.P. Rao et al. [26] reported that Ti–Al–Si powders of various compositions were synthesized through MA, so that the phase behavior by annealing was investigated by their milled structures. Notably, A. Knaïslova et al. [27] reported the microstructural and mechanical properties of intermetallics based on the Ti–Al–Si ternary system fabricated by powder metallurgy.

However, there is a lack of evidence that relates to several challenges to the Ti–Al–Si ternary system. For example, it is worthwhile considering the details given in the following: (i) The positive impact on the formation behavior of intermetallics on the reduction of brittleness in the Ti–Al–Si ternary system, (ii) The relationship of structural defect (i.e. twin phase and stacking fault) and mechanical properties, (iii) Comparison of sintering behaviors in accordance with the degree of pre-alloying (i.e. single-phase, super-saturated solid solution, amorphous, and intermetallics) in the synthesis of Ti–Al–Si powders.

The aim at this study is to investigate experimental evidence for microstructural evolution and mechanical properties based on Ti–Al–Si ternary alloys processed by mechanical milling and spark plasma sintering methods.

2. Experimental

Initial powders of Ti (Ave. 28.7 μm), Al (Ave. 9.2 μm) and Si (Ave. 20.1 μm) with purity of 99.9 % were used for mechanical alloying (by pulverisette 5 planetary mill, FRITSCH Ltd.). These powders were synthesized with the desired composition of Ti50Al50Si5 and Ti40Al40Si20 by atomic ratio. Table 1 presents the details of the ball milling information.

To prepare the densely compacted Ti–Al–Si ternary alloys, controlled grain growth by means of spark plasma sintering was employed at a range of temperature of (500–1000) °C with 60 °C/min heating rate and under 60 MPa sintering pressure. Then, total process time was approximately 17 min. without sustaining at a certain temperatures.

The grain sizes and internal strain of the Ti–Al–Si ternary alloys were measured by Stokes and Wilson’s formula [28] using the XRD patterns:

\[
b = b_2 + b_\alpha - k\lambda/(d\cos\theta) + 4e\tan\theta
\]

where in Eq. (1), b is the Full-width at half-maximum (FWHM) of the mechanical correction value of the diffraction peak; b_2 and b_\alpha are the measured values of the decrease by the internal stress and the FWHM, respectively; k is the Sherrer constant of 0.9; \lambda is the X-ray radiation wavelength using CuK\alpha radiation (1.5494 Å); d and e are the measurements of the grain size and internal strain, respectively; and \theta is the Bragg angle.

To clarify the microstructural evolution, Ti–Al–Si ternary alloys were investigated depending on milling time and composition using the TEM analysis. Notably, by means of the selected area electron diffraction (SAED) patterns and fast Fourier transform (FFT), images were identified clearly with the distribution of intermetallics indicating structural defects. In this case, corresponding to the single phase/intermetallic, the phase indexing was investigated from the XRD patterns to match the Joint committee on powder diffraction standards (JCPDS) card providing by the High-Score Plus application.

Estimation of the structural defects, such as twin and stacking faults, were calculated as experimental measurements. Firstly, the twin fault probability (\beta) was determined by Eq. (2):

\[
\beta = \frac{d_{\text{incl}}}{d_{\text{twin}}} \times 100\%
\]

Where in Eq. (2), \beta is the twin fault probability of percentage; d_{\text{incl}} is the interplanar spacing of the slip system (in this study; FCC: d_{110}, HCP: d_{11-20}) observed by TEM images; and d_{\text{twin}} is the average width of the twinned regions in the grains [29,30]. Secondly, following Eq. (3), the TEM method was applied for the various approaches to measurement of the stacking fault energy (SFE), i.e. thermodynamic calculation, XRD, and ND methods [31–33].

\[
\text{SFE} = \frac{\mu \mid b_\parallel^2}{8\pi d} \left( 2 - \frac{v}{1 - v} \right) \left( 1 - \frac{2\nu \cos 2\alpha}{2 - \nu} \right)
\]
Table 1 – High energy ball milling process parameters for the Ti–Al–Si multi-component powders.

<table>
<thead>
<tr>
<th>Composition (at.%)</th>
<th>Milling time (h)</th>
<th>Rotation speed (rpm)</th>
<th>Atmosphere</th>
<th>Ball : Powder (ratio)</th>
<th>PCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti50Al15Si5</td>
<td>5, 15, 25</td>
<td>250</td>
<td>Ar gas</td>
<td>15:1 (STS ball vial)</td>
<td>Ethanol (4 wt.%)</td>
</tr>
<tr>
<td>Ti40Al15Si15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Where, \( d \) is the SF width; \( \mu \) is the shear modulus; \( b \) is the magnitude of the Burgers vector of the partial dislocations; \( \gamma \) is the Poisson’s ratio; and \( \alpha \) is the angle between the Burgers vector of the undissociated dislocation and the dislocation line.

Thirdly, a comprehensive model was presented to predict the SFE using the relationship of minimum grain size. This model can be expressed by the formula for Eq. (4):

\[
\frac{d_{\text{min}}}{b} = A \cdot \frac{\gamma}{G \beta}^{0.5}
\]

where in Eq. (4), \( d_{\text{min}} \) is the minimum grain size derived from XRD patterns; \( b \) is the magnitude of the Burgers vector of the partial dislocations; \( \gamma \) is the SFE; \( G \) is the shear modulus; and \( A \) is a constant related to the hardness (H), melting temperature (°C), self-diffusion activation energy (Q), and shear modulus, i.e. in this case, the ‘A’ value is approximately 0.5 [34].

The mechanical properties of the Ti–Al–Si ternary alloys were measured for hardness (kg/mm²) and fracture toughness (MPa·m¹/₂) with a load of 5 kgf (HV 5) for the 15 s. In order to obtain the numerical value (\( K_{\text{IC}} \)) of the fracture toughness, the crack propagation lengths of the four directions of the indentations were determined to apply the cracking resistance, which was calculated by the Antis [35] formula for Eq. (5):

\[
K_{\text{IC}} = 0.016E^{1/2}P/C^{3/2}
\]

Where, \( E \) is the elastic modulus (Ti: 110.3 GPa, Al: 68.0 GPa, Si: 179 GPa); \( H \) is the hardness; \( P \) is the applied load; and \( C \) is the length of crack propagation.

3. Results and discussion

Fig. 1 shows the structural evolution of Ti–Al–Si multi-component powders for different milling times for XRD patterns. Figs. 1 (a) and (b) show that in the 5 h milling time, it was found to maintain a single phase almost identical to the initial raw material powders. From the milling time of 15 h, the phase behavior was transformed into supersaturated solid solution (see Fig. 1 (a)) or intermetallics (see Fig. 1 (b)) formed by substitution into the matrix by mechanically alloying, in accordance with the repeated flattening, cold welding, fracturing, and re-welding [36]. At 25 h of milling time, structural evolution was associated with the further noticeable broadening of peak intensity [23]. For example, typical evidence was presented, with one being amorphization by the collapse of the supersaturated solid solution, the other being the formation of substitutional solid solution by the rapid crystallinity decrease of intermetallics. These phenomena are considered to be caused by the actively occurring inter-diffusion and decomposition between the Ti, Al, and Si atoms, which accelerates the lattice distortion due to grain refinement and internal energy increase [37,38]. In particular, the formation of the amorphous phase largely depends on the content of Al in the Ti/Al (°x), e.g. Ti50Al5Si5, x = 0.47, Ti40Al15Si15, x = 0.53, J.B. Al-Dabbagh et al. [39] reported that the max solubility of Al in Ti is 50 at.%; under \( x > 0.50 \), the formation of intermetallics may be dominant, even in a ball milling process of 100 h. In addition, J.H. Zhang et al. [40] reported that to \( x < 0.50 \), as the Al content increased, the formation of
Table 2 – Variation of lattice parameters and crystalline structures in the Si rich corner of the Ti_{40}Al_{45}Si_{15} ternary system (ref. Fig. 1 (b)).

<table>
<thead>
<tr>
<th>Mechanical milling time</th>
<th>Phase state</th>
<th>Lattice parameters (Å)</th>
<th>Crystalline structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 h</td>
<td>Ti</td>
<td>a = 2.9551, b = 2.9511, c = 4.6843, V = 35.33 g/pm³</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>a = 5.4304, b = 5.4304, c = 5.4304, V = 160.14 g/pm³</td>
<td>Cubic</td>
</tr>
<tr>
<td>15 h</td>
<td>Ti</td>
<td>a = 2.9504, b = 2.9504, c = 4.6833, V = 35.31 g/pm³</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>a = 3.9030, b = 3.9030, c = 3.9030, V = 59.46 g/pm³</td>
<td>Cubic</td>
</tr>
<tr>
<td>25 h</td>
<td>Ti(Al) or Ti(Al,Si)</td>
<td>a = 2.9440, b = 2.9440, c = 4.6780, V = 35.11 g/pm³</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>a = 3.9020, b = 3.9020, c = 3.9020, V = 59.41 g/pm³</td>
<td>Cubic</td>
</tr>
</tbody>
</table>

Ti(Al) supersaturated solid solution to an amorphous phase was promoted, which is attributed to the fine particle size.

On the other hand, the relatively silicon rich corner of the Ti–Al–Si ternary system (i.e. in this study, Ti_{40}Al_{45}Si_{15}) is important to understanding of the relation between the decrease of lattice parameter and the milling time in detail that is presented in Table 2. In terms of the structural behavior of Si, as milling time continues, the lattice parameter rapidly decreased (from 5.4304 to 3.9030) Å with distortion in the initial cubic structure simultaneously caused by the transformation of orthohombic structure. Consequently, due to this phase transformation, it can be considered that the finer Si is substituted as Ti(Al) at a milling time of 25 h.

Spark plasma sintering was performed at the temperature of 1000 °C (60 °C/min) with applied pressure on 60 MPa, which presented the shrinkage displacement profiles during the process of the Ti–Al–Si ternary system compacts (see Fig. 2). In particular, different sintering-shrinkage behaviors were shown depending on the composition and milling time of the Ti-Al-Si ternary alloy powder. It is believed that the phase behaviors of the alloyed powders shown in Fig. 1 dominate the alloying and densification behaviors due to their inter-diffusion. For example, 5 h-milled powder which hardly achieved alloying were forced to fabricate vulnerable sintered bodies of rapid shrinkage behavior due to the melting phenomenon occurring at the solid/liquid interface of the Al-component. On the other hand, almost identical shrinkage behavior was observed in supersaturated characteristic and even amorphous in alloy powders with Ti-rich corner of composition (i.e. Ti_{50}Al_{45}Si_{5}). Notably, the 15 h-milled powder of mechanically alloyed in the Al-rich corner of composition (i.e. Ti_{40}Al_{45}Si_{15}) showed that relatively gradual shrinkage behavior. In the 25 h-milled powder were considered to stepwise shrinkage behavior that the secondary shrinkage to form Ti_{5}Si_{3} by the Si being dissociated from the solid solution after the Ti_{5}Al alloy corresponding to the primary shrinkage in the Ti(Al, Si) supersaturated solid solution was completed.

The sintering of powder synthesized in single phase under 5 h milling was terminated at around (520–550) °C due to the melting of Al phase during sintering, so that densely sintered-body could not be obtained. As shown in the invariant reaction [41] (vii) of the Ti–Al–Si ternary system according to the temperature in Table 3, the Al single phase was melted to the liquid (L) state at the given temperature range, and the process was terminated without reaching the alloy temperature (579 °C). For reference, these phases correspond to the ternary system intermetallics known as tau (τ₁, τ₂) phases [48,49]. Likewise, in the XRD patterns of Figs. 3 (a) and 3 (b), it can be seen that the sintered body produced with the 5 h milled powder presents only a single phase behavior of Ti, Al, and Si.

Figures 4 and 7 show the microstructural evolution of Ti–Al–Si sintered-bodies prepared by 5 h milled powders. In particular, the BF (see Figs. 4 (a) and 7 (a)) and optical (see Figs. 4 (b) and 7 (b)) images, showed that Ti, Al, and Si single phases were randomly distributed, without forming intermetallics with each other.

On the other hand, the mechanically alloyed, such as supersaturated (see Fig. 1 (a)) and intermetallics (see Fig. 1 (b)) powders in the synthesis process were presented with having different sintering behaviors, depending on their structural characteristics.

The Ti-rich corner of composition (i.e. Ti_{50}Al_{45}Si_{5}), in 15 h milled powder synthesized with the supersaturated solid solution is examined as forming a thermodynamically stable phase Ti–Al–Si ternary intermetallic (i.e. τ₁: Ti_{5}Al_{5}Si_{3}, τ₂: Ti_{5}Al_{5}Si_{3}) after consolidation and inter-diffusion by a rapid shrinkage displacement variation starting at around 600 °C (see Table 3), which is shown in Fig. 2, and which structural evolution is presented in Fig. 3 (a). In addition, the rapid densification behavior at 600 °C is related to the formation of
Fig. 2 – Schematic of the Ti–Al–Si compacts during the rapid sintering process at different milling times and compositions: (a) temperature-shrinkage displacement profile and (b) variation of relative density.

Fig. 3 – XRD patterns of the Ti–Al–Si multi-component sintered-bodies for different milling times: (a) Ti<sub>50</sub>Al<sub>45</sub>Si<sub>5</sub> alloy sintered-body and (b) Ti<sub>40</sub>Al<sub>45</sub>Si<sub>15</sub> alloy sintered-body.

TiAl<sub>3</sub> [50]. This intermetallic is formed by a kind of solid–liquid sintering mechanism under the excess of unconsumed aluminum when forming the ternary intermetallics, in which quasi-liquid Al phase near the melting temperature rapidly reacts with the Ti powder to simultaneously terminate the reaction against elements [51].

The microstructural evolution of sintered-body fabricated by 15 h milled powder can be investigated clearly through
the TEM images shown in Fig. 5. The Ti₃Al phase is oriented preferentially on the (130) and (200) planes in the A region inside the BF image of Fig. 5 (a); in addition, the distribution of Ti₃Al₅Si₁₂ phase of nanocrystalline can be confirmed by the ring pattern (see the B region in Fig. 5 (a)). In addition, in the C region, it is considered that a typical plane defect of SAED pattern appears around the TiAl₃ phase (004) and (200) planes. This is obvious from the HR-TEM and FFT images of the formation of twin phase, due to the accumulation of the dislocation shown in Figs. 5 (b) and (c). In particular, Fig. 5 (c) shows the FFT images in accordance with defects at the TiAl₃/TiAl phase. The D region shows typical diffraction spots of tetragonal structure regularly arranged, whereas the E region is a comprehensive pattern estimated to be the cubic structure of reciprocal overlapping with that irregularly arranged by twin phase. In particular, deformation of twining on the TiAl₃ phase was reported to be due to structural transformation from D₀₂₂ (tetragonal) to L₁₂ (cubic) by a severe plastic deformation under the annealing of higher temperature (> 620 °C). That it to say, the L₁₂ structure has a higher symmetrical structure, which improves the ductility, caused by its independent slip systems occurring in the (111) [112]-type twinning systems, and their allowing accommodation of plastic deformation [52].

On the other hand, 25 h milled powder synthesized with the amorphous phase is inter-diffused as forming non-stoichiometric ternary intermetallics (Ti₅₅Al₀.₇₅Si₂₂₂), without phase-transforming the crystalline structure of the matrix
phase (α-Ti). The reasons indicated that the inter-diffusion reaction against Ti, Al, and Si elements occurred, and activated the Kirkendall effect [53] in the crystallization of the amorphous phase with sufficient Kirkendall porosity.

Associated with the crystallization of the amorphous powder after the rapid sintering process, their microstructural evolutions are presented in Fig. 6. In the BF image of Fig. 6(a), the amorphous powders milled for 25 h were confirmed to maintain finer grain sizes, even after rapid sintering compared with Fig. 5(a). It can clearly be seen that nano-sized intermetallics were randomly distributed among the corresponding regions (A: TiAl₂, B: Ti₅Al₃S₇S₂₂, C: Ti₅Al₄). In addition, in the D region in Fig. 6(b), twin phase with relatively dense distribution can be observed exhibiting mirror diffraction spots to those that were formed inside the TiAl₂ phase of the tetragonal structure, compared with Fig. 5(c). On the other hand, as shown in Fig. 6(e), it can be seen that the twin phase was formed only in the Ti₅Al₂/TiAl₂ interface, which consists of FCC structure. It is considered that the Ti₅Al₃S₇S₂₂ containing temperature-dependent HCP structure did not induce activation of the slip systems [54] satisfying the occurrence of severe plastic deformation.

The aluminum rich corner of the composition (i.e. Ti₄Al₄Si₃S₅) in 15 h milled powder, with the pre-allowed mechanically into lamellar structures [55] in the form Ti₅Al₂ or Ti₅Al₃Si₂ with non-stoichiometric, exhibits a relatively gentle shrinkage variation behavior (see Fig. 2), because it has densification and inter-diffusion, while retaining its bonding stability stably during the sintering. Fig. 3(b) demonstrates the formation of TiAl₂ and Ti₁₅Al₂S₅S₂₂ as intermetallics. In particular, it was reported [56] that the reaction to TiAl₂ occurs to the aluminum side of solid-liquid and solid state reactions after the Ti(Al) supersaturated solid solution formation, sequentially according to temperature. In addition, it was confirmed that Ti₅S₂Si₃, which is thermodynamically stable intermetallic, was formed in the 2nd shrinkage region occurring at a temperature of above 750 °C, and it is considered to correspond to the invariant reaction (vi) [42] in Table 3.

Fig. 8 shows the microstructural evolution of the sintered-body prepared by the 15 h milled powder and the resulting construction of stacking faults. The BF image and the SAED patterns of Fig. 8(a) show the Ti₅S₂Si₃ phases (see the A region) with a grain size of (30–50) nm preferentially oriented on the (0002) and (10–10) planes, which also includes trace of locally observed stacking fault defects. Stacking fault defects (see the FFT image with D region in Fig. 8(c)) in the HCP structure could be predicted to be defective by traces of ‘Moire fringes’ [57] observed in the Ti₅S₂Si₃ phases, as shown in Fig. 8(b) with the DF images. In other words, a kind of interference phenomenon in which a partial dislocation [58] combined by the accumulation of dislocations and a perfect lattice was superimposed can be converted into an HR-TEM image. In addition, the distributions of other intermetallics were found to be a mixed phase as Ti₅Al₃S₅S₇ in the B region, whereas typical trace of mechanical alloying in the C region was observed showing the agglomeration of Ti₅Al₃/Ti₅S₂Si₃ with lamellar structure.

The 25 h milled powder with the formation of supersaturated solid solution dominant synthesized powder shows major shrinkage variation steps in two temperature ranges. Namely, (i) (400–580) °C: formation of Ti (Al, Si) supersaturated solid solution is dominant in the initial densification step, and (750–1000) °C: intermetallics by reaction with Al and Si remaining in the supersaturated solid solution reaction formed of TiAl₂ and Ti₅S₂Si₃ (see Fig. 3(b)).

Fig. 9 shows the microstructural characterization of the alloying of the synthetic powders, which were dominated by the supersaturated solid solution to the intermetallics. As shown in the BF image and the SAED patterns presented in Fig. 9(a), the regions described by the dotted lines represent Ti(Al, Si) as the matrix phase (see the A region), and where the stacking faults were concentrated (see the B region). Notably, Fig. 9(b), which is an enlargement of the B region, shows that the defects were concentrated (see the C region) in the coarsened Ti₅S₂Si₃ grain. It was investigated that TiAl₂ and Ti₅S₂Si₃ were formed at their interface as relatively fine grains. In summary, the coarsening of Ti₅S₂Si₃ grain and the occurrence of stacking faults (see the D region of Fig. 9(c)) were considered to conform to the following mechanisms: (i) Precipitation of Si due to the decrease of the Ti(Al, Si) binding energy of the repeated milling → (ii) Formation of Ti₅S₂Si₃ intermetallics → (iii) Induce stacking faults due to heterogeneous nucleation of Si [59] in Ti₅S₂Si₃/TiAl₂ interface → (iv) Coarsening of Ti₅S₂Si₃ grains corresponding to abnormal growth.

Table 4 shows the relationship between the lattice parameters (Å) – twin probability (β) derived from the XRD patterns of intermetallics associated with the formation of twin phase for Ti–Al–Si ternary alloys.

In the case of aluminide, the probability (β) of twinning presented the highest value (0.058) in the sintered-body fabricated by 15 h milled powder. This was a notable result that did not allow the proportional relationship between β and the milling time mentioned in the previous study [29], i.e., at a temperature that satisfies the plastic deformation of TiAl₃ phase [52]. However, the Ti₅Al₃S₅S₂₂ forms an already stable phase, so that inter-diffusion or dissolution no longer occurs at their interfaces, because of the suppression of growths of TiAl₃ grains (refer the average width of δᵥₘᵥ, was 46.75 nm (15 h milled sintered-body) → 60.46 nm (25 h milled sintered-body)) having a heterogeneous nucleation near the interface [60]. Then, their structures had undergone the twin defects that can be induced by the compressive stress states (see the lattice parameters of Table 4).

On the other hand, the silicide investigated with the high β value can be explained by the concentrated stacking faults of the coarsened Ti₅S₂Si₃, as shown in Fig. 9(b). In particular, the coarsening of Ti₅S₂Si₃ precipitates could reduce the lamellar spacing of the other mechanically alloyed intermetallics, thereby suppressing their dislocation movement, and expecting an increase in hardness at high temperatures [61].

Fig. 10 and Table 5 show the calculation results of the stacking fault energies of the Ti–Al–Si ternary alloys that add to the results of previous studies [62–64] for Ti–Al binary alloys. It can be concluded that the variations in SFE confirmed by microstructural properties (e.g. TEM methods) was highly dependent on the milling time, and the possibility of the formation of intermetallics. For example, Fig. 10 shows the highest SFE (140 mJ/m²) in the Ti₄Al₆S₄ composition of the previous works. In other words, it is expected that the possibil-
Fig. 6 – TEM images of the Ti$_{50}$Al$_{45}$Si$_{5}$ sintered-body with sparks plasma sintering method after 25 h mechanical alloying. (a) BF image and SAED patterns indicating the intermetallics and nano-particles, (b) HR-TEM and FFT images with twinning region of dense distribution, and (c) HR-TEM and FFT images indicating a TiAl$_3$/Ti$_2$Al$_{0.75}$Si$_{2.22}$ interface.

Fig. 7 – TEM images of the Ti$_{40}$Al$_{45}$Si$_{15}$ sintered-body with sparks plasma sintering method after 5 h mechanical alloying: (a) BF image and SAED patterns, and (b) HR-TEM and mapping accompanying each element.

ity of stacking faults was high in a composition dominated by the formation of intermetallics, as exhibited by $\chi \approx 0.54$ [39]. Consequently, it was considered that the SFE can be closely influenced by the microstructural evolutions of TiAl$_3$ and Ti$_3$Si$_2$, which are intermetallics that induced plane-defects due to the plastic deformation occurring in the mechanical milling-rapid consolidation process applied to this study.

Fig. 11 shows the mechanical properties of Ti–Al–Si ternary alloys after densification by spark plasma sintering. The Ti-rich corner (Ti$_{50}$Al$_{45}$Si$_{5}$) alloys fabricated by 15 h milled powder achieved the highest hardness (see Fig. 11 (a)) at approximately 1,119.0 kg/mm$^2$. This was considered due to the grain-refinement effect of the brittle-phases due to the suppression of TiAl$_3$ heterogeneous growth of the Ti$_7$Al$_3$Si$_{12}$ phase interface. It is noteworthy that while the inherent Young’s modulus as properties closely related to the stiffness of the silicide (e.g. Ti$_5$Si$_3$, (222–253) GPa) was higher than that of the aluminate (e.g. TiAl$_3$, (202–215) GPa and TiAl$_5$, (192–196) GPa), the results of their hardness were not as expected. This is because the Al-rich corner (Ti$_{40}$Al$_{45}$Si$_{15}$) alloys underwent widely localized stacking fault defects, which supports the brittle-ductile transition applied to slip dislocation corresponding to the decrease of brittleness in Ti$_3$Si$_2$. Therefore, as shown in Fig. 11 (b), the fracture toughness has a comparative advantage to that in the alloy composition dominated by silicide, with the highest $K_{IC}$ value of Ti–Al–Si ternary alloys being approximately 4.04 MPa m$^{1/2}$. This is comparable to silicon carbide at around 4.6 MPa m$^{1/2}$. 
4. **Conclusion**

This study discussed the experimental evidence for microstructural evolution and mechanical properties based on the Ti-Al-Si ternary alloys processed by mechanical milling and spark plasma sintering methods.

1. The initial Ti-Al-Si multi-component powders were mechanically synthesized by their structural properties as the intermetallics and supersaturated solid solution, even including the amorphous phase with severe plastic deformation process.

2. The Ti-Al-Si ternary alloys were consolidated rapidly by spark plasma sintering. Their microstructural evolution was based on the invariant reaction forming thermodynamically stable phases (e.g. Ti7Al5Si12), or reacting to rich corner intermetallics (e.g. TiAl3 and Ti5Si3). The plane-defects occurring in the rich corner of intermetallics were...
Table 4 – Crystallographic parameters derived from XRD patterns of the Ti–Al–Si sintered-bodies. (i.e. related to the twin probability in d_{110}).

<table>
<thead>
<tr>
<th>Name</th>
<th>Phase(behavior)</th>
<th>d (Å)</th>
<th>2 theta (°)</th>
<th>Strain energy (G)</th>
<th>Twin probability (b) d_{110}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti_{50}Al_{45}Si_{5} 5 h milled sintered-body</td>
<td>Al (matrix)</td>
<td>2.338</td>
<td>38.51</td>
<td>0.24</td>
<td>–</td>
</tr>
<tr>
<td>Ti_{50}Al_{45}Si_{5} 15 h milled sintered-body</td>
<td>TiAl (intermetallics)</td>
<td>2.289</td>
<td>39.32</td>
<td>0.68</td>
<td>0.058</td>
</tr>
<tr>
<td>Ti_{50}Al_{45}Si_{5} 25 h milled sintered-body</td>
<td>TiAl (intermetallics)</td>
<td>2.298</td>
<td>39.21</td>
<td>0.56</td>
<td>0.045</td>
</tr>
<tr>
<td>Ti_{40}Al_{45}Si_{15} 5 h milled sintered-body</td>
<td>Ti (matrix)</td>
<td>2.222</td>
<td>40.61</td>
<td>0.52</td>
<td>–</td>
</tr>
<tr>
<td>Ti_{40}Al_{45}Si_{15} 15 h milled sintered-body</td>
<td>Ti_{3}Si_{3} (intermetallics)</td>
<td>2.189</td>
<td>41.24</td>
<td>1.07</td>
<td>0.0175</td>
</tr>
<tr>
<td>Ti_{40}Al_{45}Si_{15} 25 h milled sintered-body</td>
<td>Ti_{3}Si_{3} (intermetallics)</td>
<td>2.186</td>
<td>41.30</td>
<td>2.34</td>
<td>0.0401</td>
</tr>
</tbody>
</table>

Fig. 10 – Relation of stacking fault energy and mechanical milling times measured using the TEM and d_{min} methods.

Table 5 – Properties parameters of the Ti–Al–Si sintered-bodies for calculating stacking fault energy.

<table>
<thead>
<tr>
<th>Name</th>
<th>d (nm)</th>
<th>d_{min} (nm)</th>
<th>G (GPa)</th>
<th>H(= 3r) (GPa)</th>
<th>b_p (nm)</th>
<th>v</th>
<th>α</th>
<th>2Theta (°)</th>
<th>SFE (mJ m^{-2}) by TEM</th>
<th>SFE (mJ m^{-2}) by d_{min}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti_{50}Al_{45}Si_{5} 15 h milled sintered-body</td>
<td>0.20</td>
<td>83.50</td>
<td>32.25</td>
<td>90.24</td>
<td>0.27</td>
<td>0.35</td>
<td>73.0</td>
<td>49.45</td>
<td>34.93</td>
<td></td>
</tr>
<tr>
<td>Ti_{50}Al_{45}Si_{5} 25 h milled sintered-body</td>
<td>0.08</td>
<td>45.60</td>
<td>32.25</td>
<td>102.99</td>
<td>0.27</td>
<td>0.35</td>
<td>73.0</td>
<td>49.45</td>
<td>34.93</td>
<td></td>
</tr>
<tr>
<td>Ti_{40}Al_{45}Si_{15} 15 h milled sintered-body</td>
<td>0.20</td>
<td>93.30</td>
<td>34.65</td>
<td>95.55</td>
<td>0.34</td>
<td>0.33</td>
<td>56.0</td>
<td>139.40</td>
<td>161.89</td>
<td></td>
</tr>
<tr>
<td>Ti_{40}Al_{45}Si_{15} 25 h milled sintered-body</td>
<td>0.23</td>
<td>54.80</td>
<td>34.65</td>
<td>105.50</td>
<td>0.35</td>
<td>0.35</td>
<td>66.0</td>
<td>141.89</td>
<td>193.70</td>
<td></td>
</tr>
</tbody>
</table>

investigated via microstructural evidence (e.g. heterogeneous nucleation and precipitates), and calculated for the probability and energy of the defects using XRD and TEM techniques.

3 The mechanical properties were not dominated by their inherent Young’s moduli. In particular, the fracture toughness of the titanium-silicide alloy was relatively increased, due to the brittle-ductile transition induced by the structural properties of initial powder, and the plane-defects in the consolidated products.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: https://doi.org/10.1016/j.jmrt.2019.12.056.

REFERENCES


