Structural Evolution during Reactive Mechanical Milling of TiC/Ti-Al Nanocomposites**

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High-energy Mechanical Alloying (MA) has been used successfully to produce numerous equilibrium or non-equilibrium alloy phases starting from blended elemental or pre-alloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys.[1-3] MA, as a non-equilibrium, low temperature, and solid-state powder treatment process, involves repeated cold-welding, fracturing, and re-welding of powder particles in a high-energy ball mill.

Titanium aluminides (TiAl) are of great importance for intermediate-temperature (600 to 850 °C) aerospace and power-generation applications because they offer significant weight savings over today’s nickel-based superalloys.[4] Furthermore, TiAl alloys possess a unique combination of high specific strength, high elastic modulus, and excellent antioxidation capabilities.[5] However, the limited room-temperature ductility and the decreased high-temperature strength are the most-significant impediments to broadening their practical applications.[6] In order to improve their ductility, recent research efforts have focused on the preparation of ultrafine grained nanocrystalline TiAl.[7] On the other hand, the synthesis of ceramic reinforced TiAl-matrix nanocomposites is an important consideration in improving their high-temperature performance. In particular, the preparation of in situ particulate-reinforced nanocomposites is regarded as the most-promising method.[8] The ultrafine particulates that are formed in situ are thermally stable and possess coherent and compatible interfaces with the matrix, thereby assuring that the composite system has enough strength to transfer stress.

MA provides us with an innovative process of the in situ preparation of ceramic-particulate-reinforced nanocomposites materials. Ultrafine, nanometer-sized grain sizes coupled with a uniform distribution of the reinforcing phases are expected to improve the obtainable mechanical properties of composites prepared by the MA route. Nevertheless, MA is a complex process and accordingly involves a large degree of uncertainty in obtaining the desired phases and microstructures. Significant experimental research is still required to study how the phases, microstructures, and compositions of MA-processed powder are evolved during ball milling. A theoretical understanding of the formation mechanisms behind the microstructural development of milled powders is also regarded as necessary.

In this work, TiC/Ti-Al nanocomposite powders were synthesized in situ by MA of a mixture consisting of elemental Ti, Al, and graphite powder, with a nominal composition of Ti50Al25C25. The phase, microstructure, and composition transformations of the milled powders were characterized and reasonable mechanisms for the powder formation during the reactive MA process are proposed.

Results and Discussion

The X-ray diffraction (XRD) spectra of the starting elemental-powder mixture and the milled powders at different MA times are shown in Figure 1. Strong diffraction peaks for C (graphite), Ti, and Al can be clearly observed before milling. After 8 h of milling, the C peaks disappear completely and, meanwhile, diffraction peaks for a new phase, TiC, are identified. Further milling for 16 h, 24 h, and 32 h does not result in any apparent changes in the intensities of the peaks corresponding to TiC. Figure 1 also reveals that the intensities of the peaks due to Al decrease gradually for milling times between 0 h and 16 h. On milling up to 24 h, the Al peaks completely vanish.

Figure 2 shows a further identification of the diffraction peaks of the milled powders in the vicinity of the standard Ti peaks (ICPDS Card No. 44-1294). It is clear that the identified peaks generally shift towards higher Bragg angles.

The XRD identification reveals two different manners for the formation of the TiC carbide phase and the Ti-Al solid-solution phase (Fig. 1 and Fig. 2). The TiC phase is formed completely after a relatively short MA time of 8 h, whereas the disappearance of the Al elemental peaks and the formation of the Ti-Al solid-solution phase are completed.

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within a long MA time of 24 h. Thus, it is reasonable to consider that the formation of TiC is through a rapid interdiffusion and an abrupt reaction between the Ti and C elements through reaction (1):

\[
\text{Ti} + \text{C} \rightarrow \text{TiC}
\]  

(1)

The large negative enthalpy of formation \( (H) \) of the TiC \((-184.502 \text{ kJ mol}^{-1}, \text{Table 1}) \) is believed to be the driving force for reaction (1), leading to an exothermic, self-sustaining, and rapid formation process of TiC. On the other hand, according to Table 1, the change in the Gibbs free energies \( (\Delta G) \) in reaction (1) is \(-180.843 \text{ kJ mol}^{-1}\). A negative \( \Delta G \) also favors the spontaneous occurrence of the above reaction. Differently to the abrupt formation of TiC, the Ti-Al solid solution is formed in a progressive manner via the gradual solution of Al into hcp Ti. As is revealed in the literature,\(^{[10,11]} \) in the case of MA of near-equiatomic compositions of Fe and Al elemental powder, a gradual and progressive formation of the Fe-Al solid solution has also been found. Differently, as is evident from Atzmon’s work,\(^{[12]} \) the Ni-Al phase is formed in an abrupt manner via a self-sustaining combustion reaction between the Ni and Al elemental powders during the MA process. The difference in their formation mechanisms is ascribed to the variation in their formation enthalpies. As indicated in Table 1, the Ni-Al phase has a considerably larger negative formation enthalpy \( (\Delta H) \) than that of Ti-Al and Fe-Al. Consequently, during MA of an elemental-powder mixture of Ni and Al, the larger amount of heat release caused by the exothermic reaction tends to significantly enhance the local, microscopic temperature rise of the powder, thereby resulting in an immediate formation of the Ni-Al solid solution. However, the formation of a Ti-Al solid solution cannot be realized through such a rapid, highly exothermic, and self-sustaining process, due to the limited negative enthalpy of its formation (Table 1).

The refinement effect of the crystallite size and the increase in the internal lattice strain of the milled powder may be responsible for the increase in the width of the peaks (Fig. 2). Figure 3 shows the calculated mean crystallite sizes of the Ti-Al and TiC and the lattice strain of the Ti-Al at various MA times. The crystallite size of the Ti-Al phase reached 26.5 nm.
after 8 h of milling, and was followed by a slight decrease to 23.1 nm in the powder milled for 16 h. At an even-longer MA time of 24 h, the obtainable crystallite size of the Ti-Al decreased sharply to 14.2 nm. On further milling, for 32 h, the Ti-Al crystallite size remained steady at 13.5 nm. Figure 3 also reveals that the estimated average crystallite size of the present TiC phase was 13.3 nm for the powder milled for 8 h. Prolonging the applied MA time to 32 h, the TiC crystallite size decreased gradually to 7.6 nm. The lattice distortion of the Ti-Al as a function of MA time was calculated from the XRD line width, and is provided in Figure 3. The lattice strain increased slightly from 0.19% to 0.23% on increasing the MA time from 8 h to 16 h. It was enhanced abruptly to a high value of 0.64% after 24 h of milling. On extending the processing time, the strain approached a steady-state value of 0.68%.

The microstructural evolution of the milled powders with applied MA time is shown in Figure 4, which reveals that the microstructural characteristics of the milled powders (for example, particle shape, particle size and size distribution, powder dispersion state) were significantly influenced by the applied MA time. After 8 h of milling, the starting, irregularly shaped powder particles became flattened, fractured, and refined (Fig. 4a), with the average particle size decreased to 20.6 \( \mu m \). However, the distribution of particle sizes in the milled powder exhibited a large degree of non-uniformity (Fig. 4a). Differently, on milling up to 16 h, significantly coarsened powder particles with a near-spherical structure (Fig. 4b) and a mean particle size of 44.5 \( \mu m \) were formed, showing a homogeneous particle-size distribution (Fig. 4b). After increasing the MA time to 24 h, the milled powder was fractured intensively to form fine and ellipsoidal particles (Fig. 4c) leading to a sharp decrease in the average particle size to 1.1 \( \mu m \). In this instance, however, a non-uniform, broad range of particle-size distribution was produced (Fig. 4c). At the even higher MA time of 32 h, the powder particles became considerably finer and more homogeneous in their structures (Fig. 4d). A narrow, uniform distribution of particle sizes was obtainable in this case. The mean particle size, 0.7 \( \mu m \), was further refined to a sub-micrometer scale. The obtained experimental results also reveal that further MA above 32 h did not cause any apparent changes to the powder structure and particle size. Furthermore, the Brunauer–Emmett–Teller (BET) specific surface areas of the powders after 8 h and 16 h of milling were quite low (0.38 m\(^2\) g\(^{-1}\) and 0.25 m\(^2\) g\(^{-1}\), respectively). When the applied MA time reached 24 h, the specific surface area of the milled powders increased sharply to 3.12 m\(^2\) g\(^{-1}\), and was followed by a slight increase to 3.53 m\(^2\) g\(^{-1}\) at the even higher MA time of 32 h.

A reasonable mechanism for the formation of in situ TiC-particulate-reinforced Ti-Al solid-solution matrix nano-composite powder by MA of a Ti, Al, and graphite elemental-powder mixture (Fig. 5a) is elucidated as follows:

- **Stage I (Fig. 5b):** At the initial stage of MA, the powder particles get trapped between the grinding balls and undergo severe plastic deformation repeatedly due to the impact forces imposed on them by the grinding medium, resulting in flattening, fracture, and refinement of the particles (Fig. 4a). The Al atoms start to dissolve in the hcp Ti lattice in a gradual manner, creating primary Ti-Al solid-solution zones within the matrix (Fig. 2). The rapid
formation of the TiC reinforcing phase is completed through the exothermic and self-sustaining reaction between Ti and graphite (Fig. 1), due to the considerably large negative enthalpy of its formation.

- Stage II (Fig. 5c): With MA continued, more Al atoms penetrate deep into the interior regions of the Ti matrix and become dissolved in the whole Ti volume until the complete formation of Ti-Al solid solution (Fig. 1). Because of the heavy plastic deformation experienced by the powders, the flattened particles get cold-welded together and form significantly coarsened TiC/Ti-Al composite powder due to the continued impact of the grinding balls (Fig. 4b).

- Stage III (Fig. 5d): With increasing MA time, the composite powder particles get work-hardened and have a limited ability to accept further plastic deformation, resulting in the absence of agglomerating forces. Consequently, the tendency to fracture starts to predominate over cold-welding. The powder particles get fractured again, producing particles with a fine, equiaxed morphology (Fig. 4c).

- Stage IV: A steady-state equilibrium is obtained in the MA system as a balance is reached between the rate of fracturing, which tends to decrease the mean composite-particle size, and the rate of cold-welding, which tends to increase the average particle size. The particle-size distribution at this stage is uniform and narrow (Fig. 4d), since particles larger than the average are reduced in size at the same rate that the fragments smaller than the average grow via agglomeration of smaller particles.

In order to further determine the chemical compositions of the milled powders, energy dispersive X-ray (EDX) spectroscopy characterization at selected areas on the particle surfaces, as indicated by the white squares in Fig. 4, were performed, with the results provided in Figure 6. At the relatively short MA time of 8 h (Fig. 4a), the detected Al elemental content on the particle surface was very low (Fig. 6). The Al elemental concentration on the particle surface increased significantly when the MA time reached 16 h (Fig. 4b and Fig. 6). Thus, one can conclude that a large number of regions in which the Al atoms started to dissolve into the Ti lattice appeared on the surfaces of the milled powders, thereby creating a primary hcp Ti-Al solid-solution matrix with the 29 location slightly changed with respect to that of pure Ti (Fig. 2). On further milling up to 24 h, however, the weight fraction of the Al element measured on the surfaces of the milled particles shows a decrease (Fig. 4c and Fig. 6). In this situation, it is reasonable to consider that more Al atoms penetrated from the surface deep into the interior regions of the Ti particles and, accordingly, became dissolved in the whole Ti volume, leading to the complete formation of the Ti-Al solid solution,\(^{10}\) as also revealed in the XRD spectrums (Fig. 1). With the applied MA time prolonged to 32 h, the detected Al elemental content showed no apparent change (Fig. 4d and Fig. 6). In this situation, a steady-state formation of the Ti-Al solid-solution phase occurs since a balance is maintained between cold-welding and fracturing of particles, leading to the equilibrium chemical compositions of as-milled powders. On the other hand, as revealed in Figure 6, no apparent variation in the C element weight fractions on the milled-particles surfaces is observed on increasing the MA time from 8 h to 16 h. A further increase in the MA time to 24 h enhanced the C elemental content markedly on the surfaces of these significantly refined particles (Fig. 4c and Fig. 6). Under this condition, due to fracture of the TiC/Ti-Al composite-powder particles, fresh surfaces are continuously created. More TiC reinforcing phase, which is developed in situ in the interior of Ti-Al matrix, tends to be exposed to the newly formed particle surfaces. As the MA time was further increased to 32 h, the detected C elemental concentration decreased slightly (Fig. 6).

Figure 7 shows further transmission electron microscopy (TEM) and EDX spectroscopy characterizations of the interior structures and compositions of the obtained powder after 32 h of MA. The considerably fine spherical-shaped reinforcing particulates with a mean particulate size of \(\sim 8\) nm, as selectively indicated in Figure 7a, were dispersed within the matrix. EDX spectroscopy results reveal that the matrix (Zone A) involved elemental Ti and Al with a near-equal atomic proportion (Fig. 7b). Combined with the XRD results, it was confirmed that the matrix was a Ti-Al solid solution. The C, Ti, and Al elements were detected within a composite structure (Zone B) consisting of the reinforcing particulates and the matrix. The quantitative EDX-spectroscopy analysis indicates that, besides the Al and Ti elements belonging to the matrix with an equal atomic proportion (Fig. 7b), the atomic ratio of the C element and the residual Ti element was also near 1:1, revealing the formation of the stoichiometric TiC reinforcing nanoparticles (Fig. 7c). Combined with the XRD, TEM, and EDX-spectroscopy results (Fig. 1 and Fig. 7), it is reasonable to conclude that the final MA product was a typical nanocomposite powder featured by a nanocrystalline Ti-Al solid-solution matrix reinforced with the TiC nanoparticles that were formed in situ.
Figure 8 shows the average values of the microhardness of the powder particles after different MA times. The obtainable microhardness of the milled powder for an MA time above 24 h was considerably enhanced (Fig. 8) due to the significant increase in the lattice strain in the milled powder and the resultant work-hardening (Fig. 3). The final MA product, after 32 h of milling, possessed a high microhardness value of 1150 HV, showing a significant enhancement from the atomized TiAl powder (850 HV) and the ball-milled Ti-Al solid-solution powder without reinforcements (900 HV). This improvement is attributed to further strengthening of the dispersed TiC nanoparticles within the Ti-Al solid-solution matrix having fine crystallite grains and remaining lattice strain (Fig. 3).

**Conclusions**

High-energy reactive mechanical alloying of a Ti, Al, and graphite elemental-powder mixture was performed to prepare a nano-composite powder with a Ti-Al solid-solution matrix reinforced by TiC nanoparticles formed in situ. The formation of TiC was through a rapid, exothermic, and self-sustaining reaction between the Ti and C elements. The Ti-Al solid solution was developed by the gradual and progressive solution of Al into the Ti lattice. A successive evolution of the particle morphology from a flattened and fractured structure to a highly coarsened spherical one and, eventually, to a fine and equiaxed one occurred on increasing the milling time. The microstructural development was determined by the competition between cold-welding and fracturing of the particles. The final TiC/Ti-Al nanocomposite powder that was obtained after 32 h of milling possessed a mean particle size of 0.7 μm and a BET specific surface area of 3.53 m² g⁻¹. The average crystallite size of Ti-Al and TiC reached 13.5 nm and 7.6 nm, respectively. Due to the high lattice strain (0.68%) of the milled powder and the reinforcement by the TiC nanoparticles, the microhardness of the TiC/Ti-Al nanocomposites reached a high value of 1150 HV.

**Experimental**

The starting powder materials were: 99.9% purity Ti powder with a polygonal structure and a mean particle size of 30 μm (Beijing Mountain Technical Development Center for Non-Ferrous Metals, PR China), 99.5% purity Al powder possessing an irregular shape and an average particle size of 16 μm (Shanghai Jinghua Scientific & Technological Research Institute, PR China), and pure graphite powder with a mean particle size of 30 μm (Shanghai Shiyi Chemical Reagents Co. Ltd., PR China). The elemental-powder mixtures containing 16 g of Ti, 4.5 g of Al, and 2 g of graphite were weighed and mixed. The atomic fractions of the Ti, Al, and C constituents were 50 at %, 25 at %, and 25 at %, respectively; that is to say, the equivalent molar ratio of TiC and TiAl was 1:1.

Mechanical milling was performed in a high-energy Pulverisette 6 planetary monomill (Fritsch GmbH, Germany). A hardened chromium-steel grinding bowl was used, whose useful capacity was 125 ml. Stainless-steel grinding balls (Five φ20 balls + fifteen φ10 balls + fifteen φ6 balls) and the powder mixture to be ground were charged into the grinding bowl, with the ball-to-powder weight ratio of 10:1. In order to avoid oxidation of the powders, the MA treatment was under the protection of an argon atmosphere. Four different milling times, 8 h, 16 h, 24 h, and 32 h, were settled periodically, while the rotation speed of the main disc was fixed at 250 rpm. In order to avoid the temperature rise within the
grinding bowl, a ball-milling duration of 20 min was followed by an interval time of 10 min.

The particle sizes of the milled powders were evaluated using a Mastersizer 2000 Laser Particle Size Analyzer (Malvern Instruments Ltd, UK). The BET specific surface areas of the milled powders were determined using nitrogen gas and an ASAP 2010 Accelerated Surface Area and Porosimetry Analyzer (Micromeritics Instrument Corporation, USA). The phases of the milled powders were identified using a Bruker D8 Advance X-ray diffraction (XRD) analyzer with Cu $K_{\alpha}$ radiation ($\lambda = 0.15418\,\text{nm}$) at 40 kV and 40 mA, using a continuous-scan mode. A quick scan of 4 degrees per minute was primarily performed over a wide range of $2\theta = 15–110^\circ$. A slower scan rate of 1 degree per minute was further used over $2\theta = 34–37^\circ$ and $39–42^\circ$ to give a more accurate determination of the diffraction peaks. The Williamson–Hall formula was used to estimate the grain size and internal lattice strain based on the XRD peak broadening (Equation (2)).

$$\beta \cos \theta = \frac{0.9\lambda}{D} + \varepsilon \sin \theta$$  \hspace{1cm} (2)

In Equation (2), $\beta$ is the full width at half maximum of the XRD peaks, $\theta$ the diffraction angles, $\varepsilon$ the internal strain, $\lambda$ the X-ray wavelength, and $D$ is the average grain size. The microstructural features of powders were characterized using a FEI Quanta 200 scanning electron microscopy (SEM) at an accelerating voltage of 20 kV. The grain morphologies of the nanocomposite powders were investigated using an FEI Tecnai G2 20 S-TWIN transmission electron microscopy (TEM). An EDAX Genesis energy dispersive X-ray (EDX) spectrometer was used to determine the chemical compositions, using an SUTW-Sapphire detector. A HXS-1000 microhardness tester was employed to determine the Vickers hardness of the powders, using a load of 0.1 kg and an indentation time of 10 s. Prior to indentation, the cross-sections of the particles were prepared by mounting a small amount of powder in a resin, followed by standard grinding and polishing procedures.

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