

Investigation of a Discus-Milling Process Using a Powder Mixture of Al and TiO₂

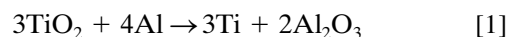
Z.G. LIU, S. RAYNOVA, and D.L. ZHANG

In this study, a powder mixture of Al and TiO₂ was employed to investigate the milling process in a discus mill. In this first report on this novel mechanical mill, several variables, including the milling time and powder charge and their effects on the microstructural evolution of powder particles, are monitored and studied. The study reveals that the dominant parameters of the milling process are the milling time and the starting powder charge, similar to the other high-energy ball-milling processes. The longer the milling time and the smaller the starting powder charge, the more homogeneous the mixing and the finer the microstructure of the powder particles. The reaction between Al and TiO₂ was not observed with a milling period as long as 6 hours, for the present materials. However, the reaction between Al and TiO₂, during the subsequent heat treatment, is influenced by the milling condition. The powders with the longer milling times and finer mixing microstructures also form a finer microstructure, after the reaction between Al and TiO₂ during heat treatment. The methods for achieving an optimal milling efficiency for the Al-TiO₂ system are discussed.

I. INTRODUCTION

SINCE the 1970s, various mechanical milling processes have been invented and the alloying process during milling has been investigated intensively, due to the successful application of ball milling in producing oxide dispersion strengthening (ODS) superalloys.^[1] The influence of the milling parameters has been determined, either theoretically or experimentally. The milling media, the milling atmosphere, the milling time, and some other factors have been found to contribute to the alloying process and to the microstructure evolution of the resultant powder particles. More recently, a novel mill, called a discus mill, has been applied to the production of nanostructured composite materials.^[2,3] Different from the ball-milling processes conventionally used in laboratories, a discus mill employs as milling media two matching alloy discuses in a cylindrical bowl. During milling, the discuses rotate and vibrate irregularly in the bowl. Material powder particles trapped between the discuses and between the discus and the bowl wall experience compression and shear, which cause plastic deformation, fracturing, and cold welding. With the accumulation of a large number of plastic deformations, and with fracturing and cold-welding events, the formation of composite powder particles is realized. Further milling refines the composite structure and eventually leads to alloying. Compared to the conventional, laboratory-scale ball mills, this discus mill possesses several advantages: (1) a large amount of powder charge (typically more than 0.5 kg per batch); (2) a low risk of contamination, since the impacts between the discuses always involve trapped powders; and (3) a high efficiency, stemming from the first advantage. However, so far, there has been no published report on a detailed investigation of the milling process involving a discus mill.

In the current study, we investigated the discus milling process by monitoring the evolution of the powder particle size and the microstructure during the milling of a mixture of Al and TiO₂ powders. This starting powder mixture was designed with a composition that followed the nominal displacement reaction during subsequent heating:



Heat treatment was performed on the as-milled powders, as well, to evaluate the quality of the milled powders and the influence of milling conditions.

II. EXPERIMENTAL DETAILS

The discus mill employed in the present study is made by Rocklabs Ltd. (Auckland, New Zealand). As illustrated in Figure 1, there are two matching discuses (195-mm ID) in a cylindrical bowl (with an i.d. size of 238 × 76 mm), which all are made of high-Cr, high-carbon steel. The bowl is set in a fixing racket and is locked by an air-pressing lock. An electric motor is used to activate the horizontal rotation and the vertical vibration of the bowl (together with the racket). The movement of the bowl drives the rotation and the vibration of the discuses inside. The bowl can be evacuated and backfilled with argon.

The starting materials were a TiO₂ powder (anatase, 99 pct purity, with an average particle size of 200 nm) and an Al powder (industrial grade, 99.5 pct purity, with an average particle size of <60 μm) (Figure 2). The two component powders were mixed at a composition following Eq. [1], TiO₂:Al = 3:4 (atomic ratio). The milling was carried out under the protection of an Ar atmosphere (with an O₂ content of <8 × 10⁻² vol pct).

The powder charge in the bowl is required to be no less than 50 vol pct of the volume of the bowl, because a lower powder load may cause severe wear and possible breakage of the discuses. To assure that this requirement was satisfied, a minimum Al/TiO₂ powder charge of 500 g was used for the discus mill employed in the present experiments.

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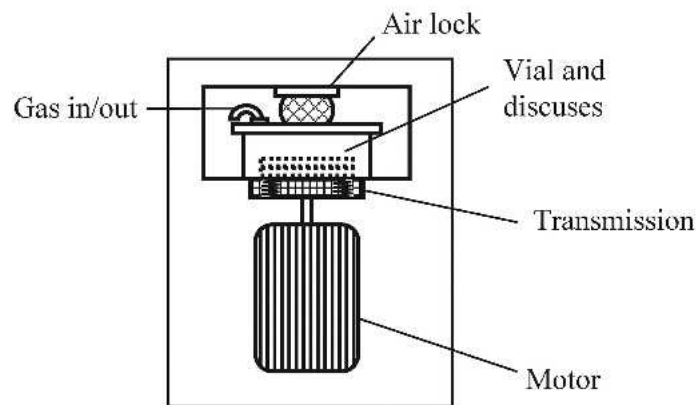


Fig. 1—Schematic illustration of the disc mill.

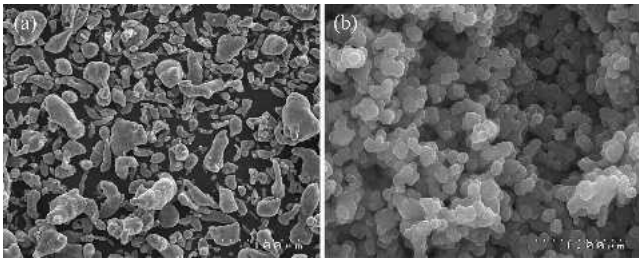


Fig. 2—Starting powders: (a) Al and (b) TiO₂.

Three different charges of powder, 500, 600, and 700 g, were applied, which roughly correspond to a fill volume fraction of 60, 65, and 70 pct in the bowl. An extra 3 to 5 pct of Al powder was added, to compensate for the loss of Al powder due to its stronger cold-welding tendency during milling. A process control agent (PCA), isopropyl alcohol, was added at the level of 1.0 wt pct. The milling duration varied from 1 to 6 hours.

Heat treatment of the as-milled powders was performed in a tube furnace under the protection of an Ar atmosphere. The milled powders were heated up to 850 °C at 10 K/min, and held for 2 hours before furnace cooling down to room temperature.

The milled powders were subjected to particle-size analysis, using a MASTERSIZER* laser particle-size analyzer to

*MASTERSIZER is a trademark of the Malvern Instruments Ltd., London, United Kingdom.

monitor the particle size change with milling time. The microstructure evolution of the powder particles during milling, and the subsequent heat treatment, was characterized using an S-4100 scanning electron microscope (Hitachi Corp., Tokyo, Japan), an X'Pert X-ray diffraction (XRD) (Phillips, Amsterdam, The Netherlands) machine, and an SDT2960 differential thermal analyzer (TA Instruments, New York, NY). The as-milled samples were mounted in resin, ground and polished, and etched with Nital solution, before scanning electron microscopy (SEM) observation.

III. RESULTS

The microstructural evolution of the powder particles with increasing milling time was monitored by the SEM examination of cross sections of the powder particles produced with different milling times. Figure 3 shows the microstructural evolution of the powder particles produced with various starting powder charges, 500, 600, and 700 g, with increasing

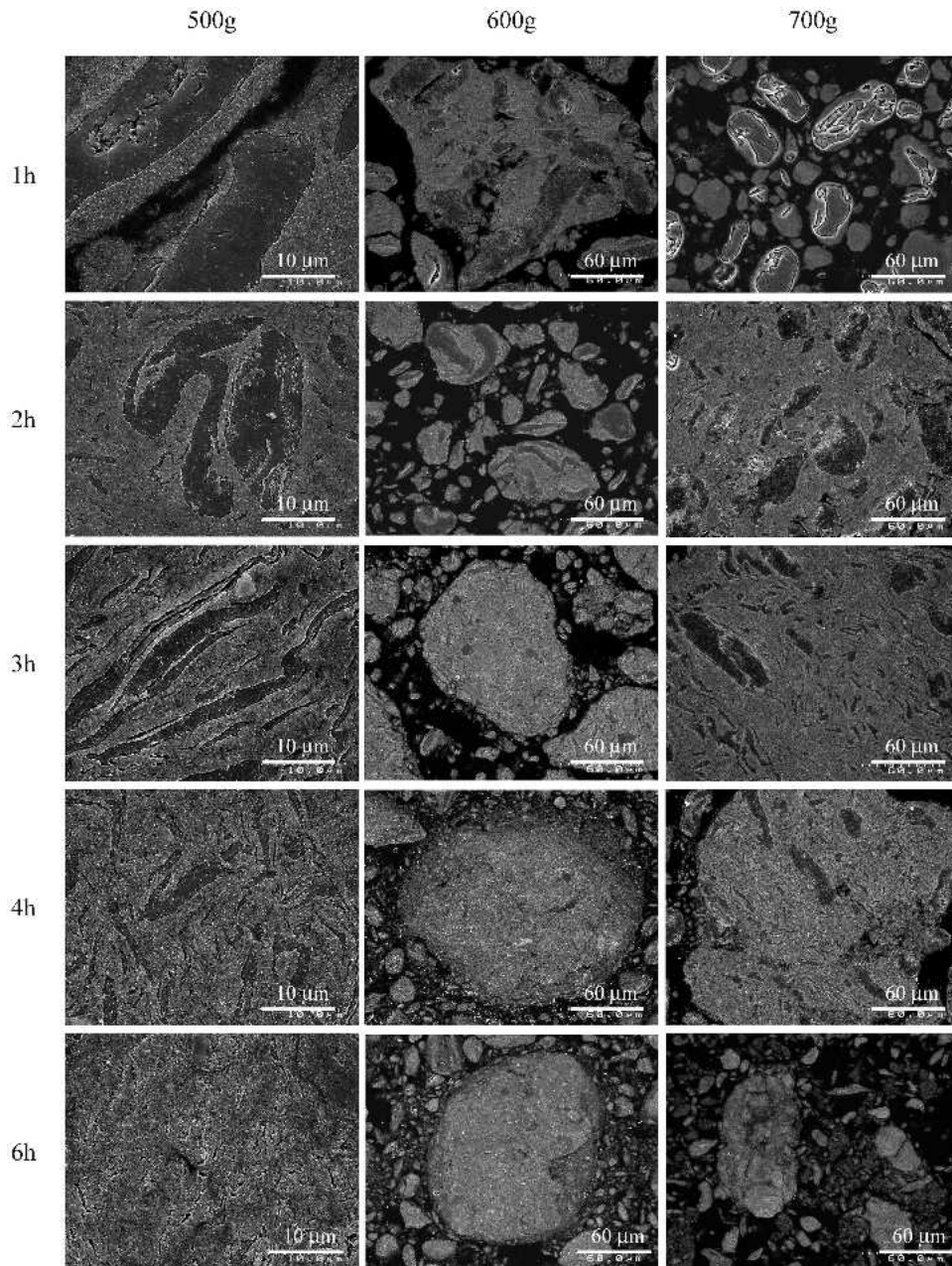


Fig. 3—The SEM micrographs of the etched cross section of the milled Al/TiO₂ composite powders, with different starting powder charges and milling times. The dark plates on the photos are of Al, while the relatively bright areas are of TiO₂.

milling time. It has been identified that, for the powder produced with a short milling time, *e.g.*, 1 hour, a coarse composite structure was formed. In the particles, slightly deformed Al particles (dark) and fine TiO₂ particles (bright) were cold welded to form composite particles with various particle sizes. Generally, Al plates or particles act as cores. With increasing milling time, the composite structure was significantly refined, as was indicated by a reduction of the size of the Al cores and the refinement of the sandwich structure in the composite powder particles (Figure 3). Higher-magnification SEM images still revealed the Al and TiO₂ phases, although the boundaries between them were not so clear. A homogeneous mixing of these two components was achieved in the 6-hour milled powders, although some very thin and small Al pieces

were distinguishable. It has been found that the microstructure refinement was slower in the powders that had a larger starting powder charge. With the same milling time, the microstructure of the powder particles produced with a larger powder charge is clearly coarser, compared to their counterparts with a smaller powder charge (*i.e.*, 500 g). The Al particles were less deformed in the samples with the larger powder charge. This is attributed to the fact that, with a larger starting powder charge, the same energy input is used to deform and mix a larger amount of powder, which in turn leads to a lower efficiency in the deformation of the powder particles and a lower level of mixing within a given length of time.

An XRD analysis of the powders milled for different times did not reveal the formation of any new phases. (The XRD

patterns of the as-milled powders, together with those of the heat-treated powders, will be shown in Section IV). Only a peak broadening and weakening of the XRD patterns, due to the grain refinement of the Al phase, were observed. The peaks that corresponded to the TiO_2 did not change much, which indicated that the TiO_2 phase experienced hardly any grain refinement and plastic deformation; this is consistent with the microstructure observed.

The change in the gas pressure and temperature of the milling vial was monitored, as well. Figure 4 shows the gas pressure inside the vial and the temperature of the milling vial as a function of milling time (up to 2 hours), with a 500-g powder charge. It was found that the pressure in the

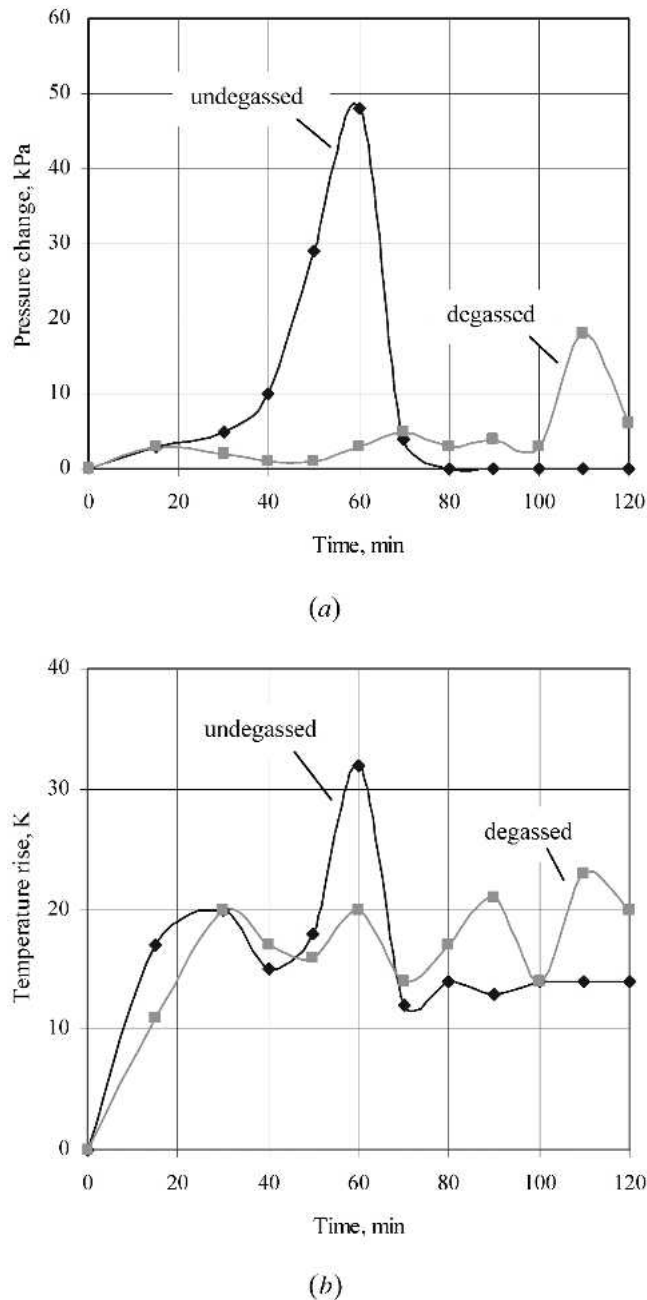
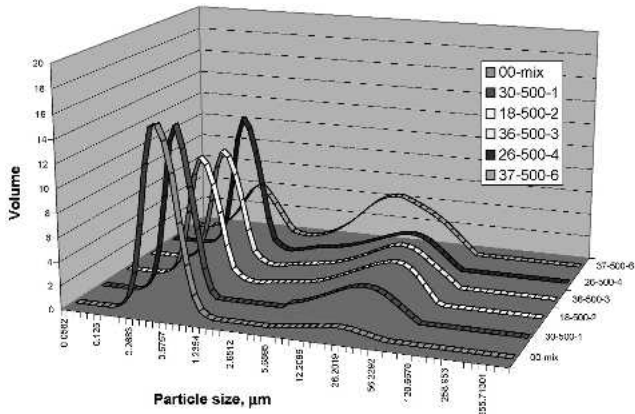


Fig. 4—(a) The pressure inside the vial and (b) the temperature of the vial, as a function of milling time for both undegassed and degassed starting powders.

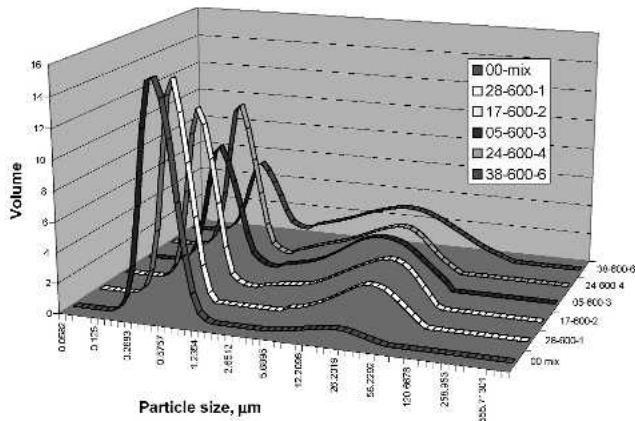
vial did not change much during the first 40 minutes of milling, but increased to about 1.5 atm with increasing milling time, to about 60 minutes; it then dropped to normal pressure, after milling for 70 minutes. This was a typical phenomenon for the other milling conditions. The temperature also showed a rise-and-drop profile similar to that of the pressure, with a maximum temperature rise of 30 °C. Both pressure and temperature changes were within the safety range. The pressure increase was attributed to the release of the gas absorbed by the fine TiO_2 powders and the temperature rise. To verify this assumption, the starting powders were degassed in an oven at 300 °C overnight, before being subjected to milling. The gas pressure inside the vial and the temperature of the vial as a function of milling time, during the milling of the degassed powders under the same condition, are also shown in Figure 4. It was clearly shown that the large pressure increase after milling for 40 minutes was eliminated. Instead, a small pressure increase, of about 0.2 atm when the milling time was more than 100 minutes, was observed. At the same time, the temperature rise was also lowered to less than 25 °C, throughout the milling process.

Particle-size analysis was also performed on the powders, to monitor the particle-size change with milling time and the amount of the powder charge. The particle size of all the milled powders exhibited a bimodal distribution, with one peak in the range of 30 to 400 nm and the other in the range of 20 to 50 μm (Figure 5). The two peak values of the particle size distribution corresponded roughly to the particle size of the two starting materials, TiO_2 and Al. It was observed that, with increasing milling time, the mean size of the finer particles increased slightly, while the mean size of the coarser particles significantly decreased, as shown in Figure 6. The trend was independent of the starting powder charges. The slight increase in the mean size of the finer particles can be attributed to the cold welding of the TiO_2 particles to the fractured Al fragments, while the significant decrease in the mean size of the coarser particles can be attributed to the fracture of the formed composite powder particles. The increasing milling time also led to a gradual decrease in the volume fraction of the finer particles and the corresponding significant increase of the volume fraction of the coarser particles, as suggested by the changes of the areas of the two peaks with milling time (Figure 5).

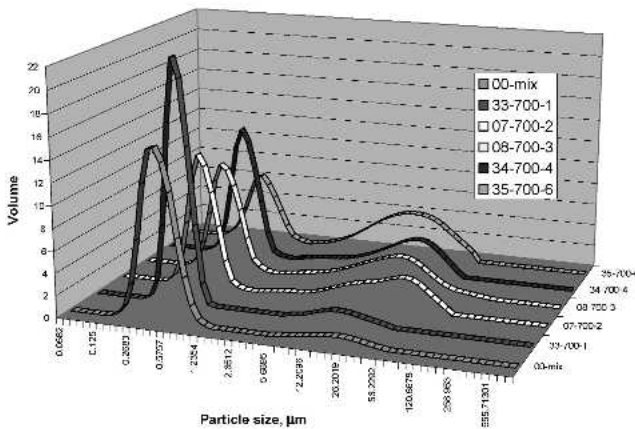
Thermal analysis was performed to study the influence of milling conditions on the reaction behavior between the Al and TiO_2 of the milled powders. Typically, the differential thermal analysis (DTA) curves of the Al/ TiO_2 composite powders showed two peaks. One was an endothermic peak at about 660 °C, which corresponded to the melting of the Al upon heating, and the other was an exothermic peak, which corresponded to the reaction between the Al and the TiO_2 . As an example, Figure 7 shows the DTA curves of the powder produced with the 500-g charge and with different milling times. On all the DTA curves, the endothermic peak at about 660 °C, which corresponded to the melting of Al, did not change with milling times. However, the exothermic reaction peak was strongly influenced by the milling time. The peak temperature of the exothermic reaction was lowered significantly, from about 1000 to about 890 °C, as the milling time increased from 1 to 2 hours. The peak temperature was lowered slightly, to about 880 °C,



(a)



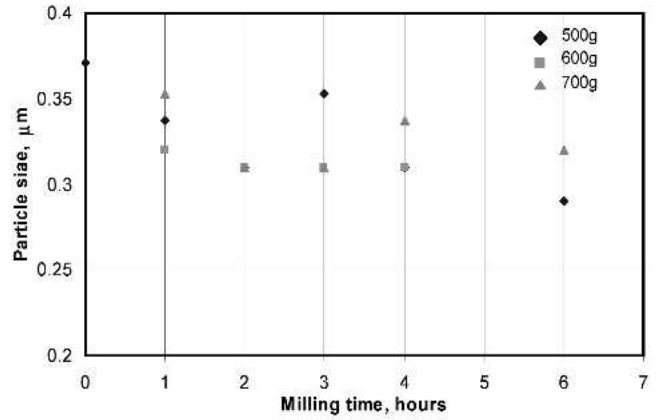
(b)



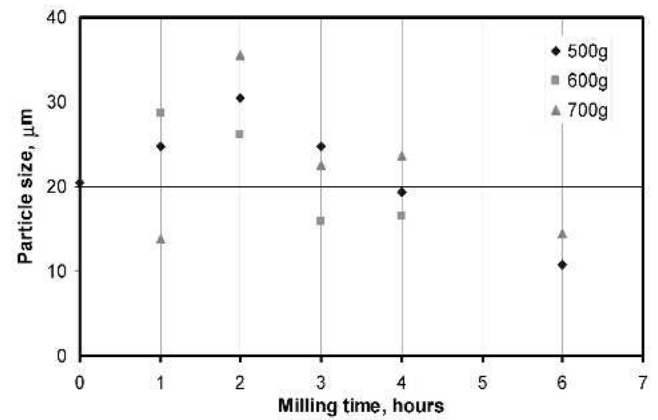
(c)

Fig. 5—Particle-size distribution of the powders milled with different times and with powder charges (in grams) of (a) 500, (b) 600, and (c) 700 g.

with increasing milling time to 4 hours. However, with increasing milling time from 4 to 6 hours, this exothermic reaction took place at a much lower temperature, around the melting point of Al, which overlapped the endothermic peak of the Al melting. This exothermic peak was identified to be from the reaction between the Al and TiO₂, to form Ti and Al₂O₃, as shown by the XRD patterns (Figure 8, for



(a)



(b)

Fig. 6—Illustration of peak particle-size change of the (a) fine and (b) coarse particles in the as-milled powder.

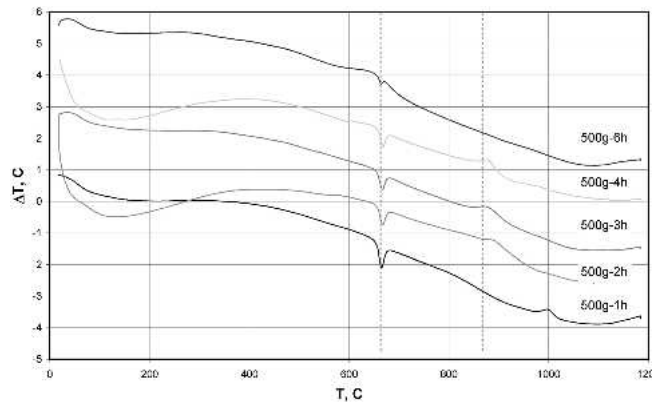


Fig. 7—The DTA pattern of the Al/TiO₂ composite powder, produced by milling of 500 g of charge for different milling times.

the powder produced with the 500-g charge). The XRD analysis of the powders after DTA, up to 1200 °C, reveals the formation of β-Ti and the transformation of the residual TiO₂ from anatase to rutile, in addition to the formation of the Al₂O₃ phase and the Ti₃Al phase. This is attributed to the fact that the continuous heating during the DTA did not allow enough time for diffusion to take place, in order

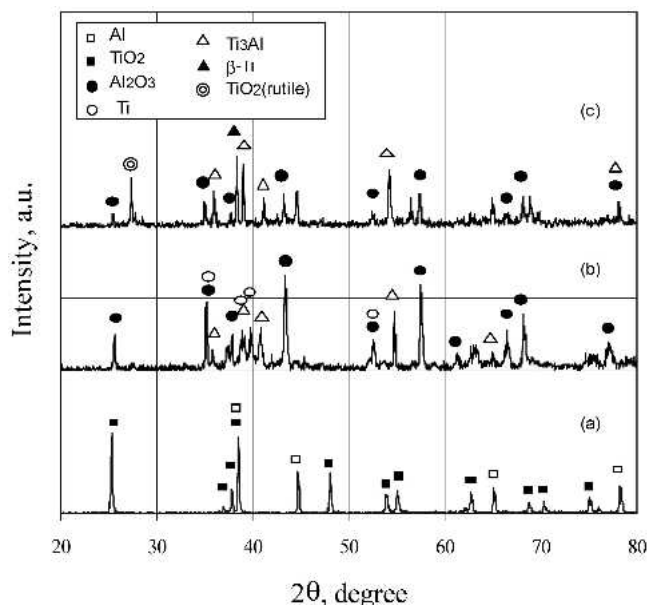


Fig. 8—The XRD patterns of the Al-TiO₂ powder, produced by milling for 1 h and with a charge of 500 g, under different conditions: (a) as-milled, (b) after heat treatment at 850 °C for 2 h, and (c) after heating in the differential thermal analyzer to 1100 °C.

to form the equilibrium phases. The same phenomenon was observed in the other powders with different charges. This is in good agreement with the observations made in the previous research on ball-milled Al/TiO₂ powders.^[4]

To study the influence of the milling conditions on the resultant powders, the milled powders were heat treated at 850 °C for 2 hours. It was found that, for all the milled powders, a reaction took place between the TiO₂ and the Al, during heat treatment. It is surprising to note that the reaction takes place even in the powders milled for only 1 hour; for these, the DTA showed a reaction taking place at around 1000 °C. This may be attributed to the possibility that long-time holding helps diffusion take place and initiates the reaction between the two components. For the other samples milled for 2, 3, 4, and 6 hours, heat treating the powders at 850 °C for 2 hours led to the formation of Al₂O₃, Ti(Al,O), and possibly Ti₃Al phases. The Ti(Al,O) was denoted to the Ti phase, with dissolved Al and O. It was also found that the relative fraction of the phases remained almost the same for the powders with different milling times.

The SEM observation revealed that the microstructure of the Al/TiO₂ composite powder particles had a significant effect on the microstructure of the composite powder particles produced after heat treatment. Figure 9 shows the SEM micrographs of the cross-sections of the powder particles produced by heat treating the milled Al/TiO₂ composite powder with different starting powder charges and different milling times. For the 1-hour milled powder, the SEM micrographs showed three types of contrasts. By performing energy dispersive x-ray (EDX) analysis, it was confirmed that the dark, curved, threadlike area between the two gray regions corresponded to the Al₂O₃ phase. The brighter gray contrast corresponded to the resultant Ti-rich phase; the darker gray contrast corresponded to the Al-rich phase surrounded by the Al₂O₃ phase, respectively.

The more refined microstructure of the Al/TiO₂ composite powder particles produced with a longer milling time apparently led to both a more complete reaction (Figure 9) and a finer microstructure of the composite after heat treatment. With 2 hours or longer in milling time, the heat-treated powders exhibited a well-defined composite microstructure consisting of Al₂O₃ particles and a Ti(Al,O) matrix. Increasing the milling time from 2 to 6 hours led to a decrease in the average particle size of the Al₂O₃ phase, almost linearly, from about 5 down to about 0.5 μm, as shown in Figure 9. It was also found that with the same milling time, a larger starting powder charge led to less mixing, as reflected by the more incomplete reaction and the relatively coarser microstructure of the powder particles after heat treatment.

With the 600- and 700-g charges, the change in the average Al₂O₃ particle size with milling time showed the same trend as that corresponding to the 500-g powder charge. A rough comparison of the microstructure of the heat-treated powders suggests that the microstructure, after the heat treatment of the powders produced with a 700-g powder charge and a milling time of 6 hours, is almost equivalent to that produced with a 500-g powder charge and a milling time of 4 hours. Considering the limits of the powder charge (both minimum and maximum), the 500-g powder charge is favorable for a more rapid microstructure refinement, while the 700-g charge is favorable for a higher powder production rate.

The XRD analysis of the heat-treated powders also revealed that longer milling led to a more complete reaction between the two starting component materials. The XRD patterns of the heat-treated powders with a 500-g starting powder charge are shown in Figure 10. In the 6-hour milled powders, the reaction between the Al and TiO₂ leads to the formation of Ti(Al,O) and Al₂O₃ phases. In contrast, the powders produced with a shorter milling time (up to 3 hours) showed the formation of a Ti(Al,O) phase, and the existence of a Ti₃Al(O) phase as well, under the same heat-treatment condition. This implies that 6-hour milling results in the formation of a very uniform and intimate mixing of the starting materials.

IV. DISCUSSION

A. About the Milling Process

First, from the present experiments, it can be preliminarily concluded that the disc mill is a powerful tool for processing powders at a scale of several hundreds of grams per batch. This is much more than the other ball mills used in the laboratory, such as the Spex mixer/mill, Retsch (Haan, Germany) mills, *etc.*, which treat several grams or tens of grams of powders per batch, even though the microstructure evolution/alloying effect for the present disc mill may not be as fast as in the mills typically used in the laboratory.

The starting materials employed in present study, the Al and TiO₂ powders, are a ductile/brittle system. Similar to the microstructure evolution for a ductile/brittle system in other ball-milling processes,^[5] the microstructure evolution during disc milling involves the deformation, fracture, and refinement of ductile Al particles under compression and shearing, the embedding of harder and finer TiO₂ powder particles into the soft Al matrix, and the formation of Al/TiO₂ composite particles. With the prolonged milling, the composite microstructure is further deformed, hardened, fractured, and

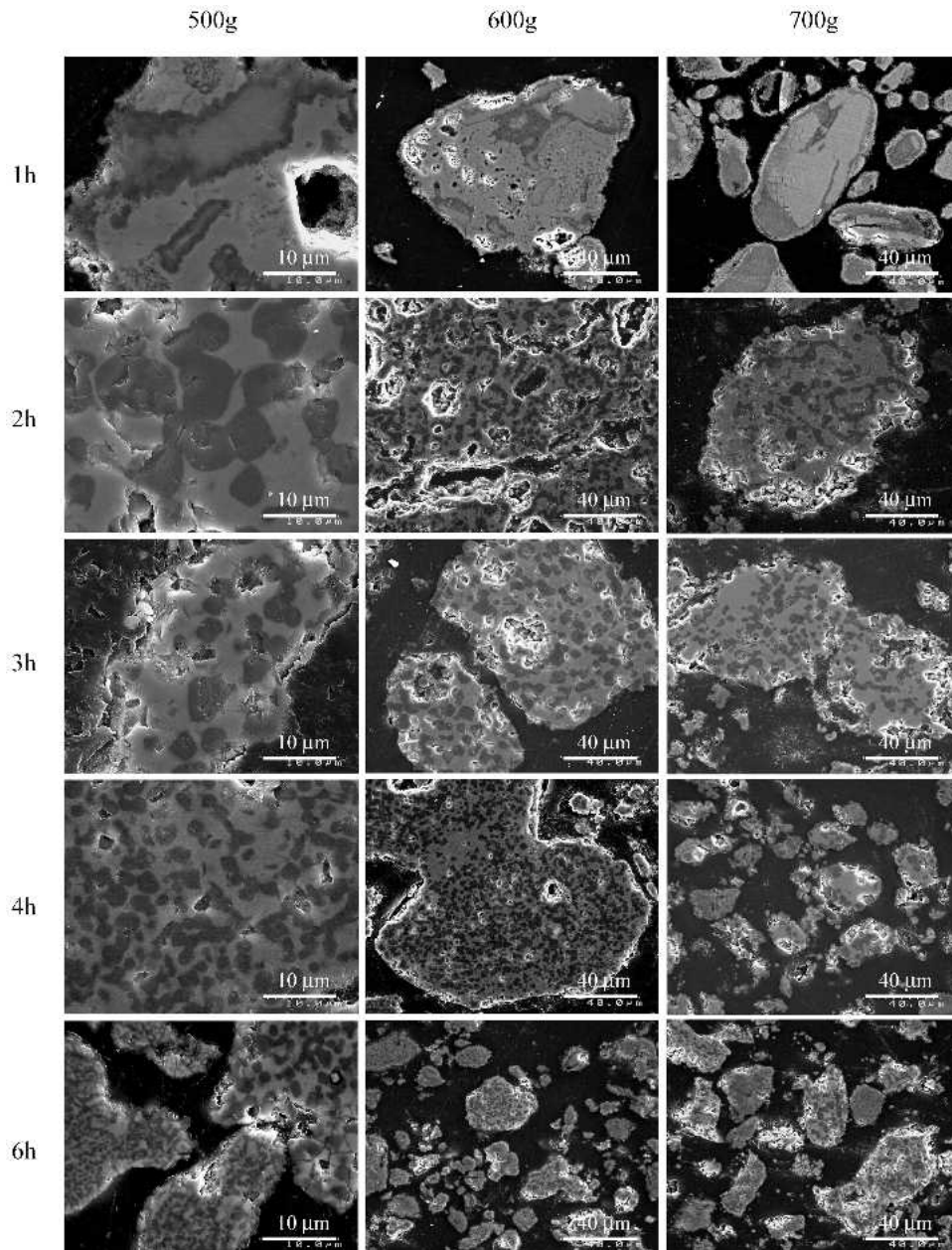


Fig. 9—The SEM micrographs of the etched cross-section of the heat-treated Al/TiO₂ composite powders, with different starting powder charges and milling times. The dark areas on the photos are Al₂O₃ phase, while the relatively bright areas are Ti(Al,O) or Ti₃Al(O) phase.

refined, finally leading to a fine composite microstructure in the powder particles.

The starting powder charge is another dominant parameter the disc-milling process, in addition to the milling time. The starting powder charge influences the disc-milling process in the same way as the weight ratio of the ball influences the powder in other ball-milling processes. The starting powder charge influences the speed of the microstructure evolution, the mixing and refinement, and the alloying effect: the lower the charge, the faster the rate of microstructure evolution speed. It has been found that a 6-hour milling of the powders with a 700-g charge produced a microstructure similar to that produced by a 4-hour milling with 500-g charge.

The monitoring of the gas pressure in the vial and the temperature of the vial during milling has revealed that the pre-

sent milling program is appropriate for controlling the pressure and temperature within the safety limit. The degassing treatment of the starting powders, at 300 °C overnight, is effective in preventing the pressure increase during milling. This is a helpful reference for the further modification of the automatic control system. The temperature rise, however, did not show evident dependence on the degassing treatment; it can be controlled by adjusting the milling/resting intervals.

B. Influence of Milling Conditions on the Resultant Powders

1. Microstructure

It is concluded from the microstructure characterization that the microstructure refinement of the as-milled powders

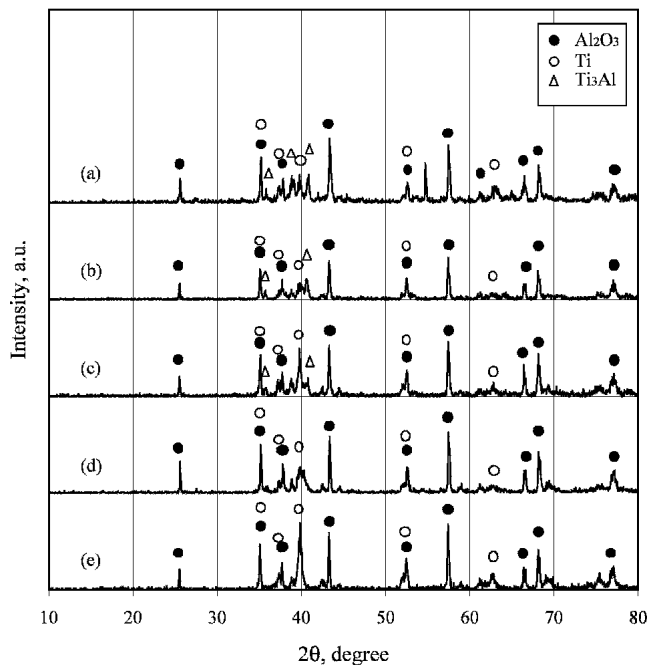


Fig. 10—The XRD patterns of heat-treated samples, produced with a starting powder charge of 500 g and milling times (in hours) of (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, and (e) 6 h.

takes place with prolonged milling time. The larger starting powder charge needs a longer milling time than does the smaller powder charge, to reach the same microstructure refinement. The degassing treatment of the starting powders is beneficial to the control of the pressure in the vial during milling, but does not show evident influence on the microstructure of the final products.

2. Reaction behavior

The influence of ball milling on the microstructure and the reaction/phase transformation in the milled powder has been studied intensively.^[6-11] A general conclusion has been drawn that ball milling lowers the temperature in preparation for the reaction/phase transformation to take place during the subsequent heating process after milling. The same investigation has also been carried out in the ball-milled Al/TiO₂ system, using a Spex mixer/mill.^[4] The lowering of the reaction temperature between the Al and the TiO₂ is attributed to the reduction of the activation energy barrier and structural refinement to the reaction, due to the introduction of the high density of defects in the Al matrix and the intimate mixing of the reactants. It has been found that ball milling significantly lowers the reaction temperature between the two components, from about 1050 °C of the unmilled powder to 660 °C after milling for 5 hours, and to 560 °C after milling for 100 hours, using a SPEX mill.^[4] Our present study has shown a similar result. For example, for 500 g of charged powder, milling for 6 hours lowers the reaction temperature to about 660 °C. This implies that 6-hour disc-milling is comparable in energy introduction and microstructure refinement to a 5-hour milling in a Spex mixer/mill. Considering the fact that the Spex mixer/mill is popular in laboratory research, a powder charge of hundreds of grams in a disc mill is much more than a powder charge of no more than 10 grams in a Spex mixer/mill. The disc-milling process is more powerful and effective.

Table I. Characterization of the As-Milled and Heat-Treated Powders (500 g/800 °C/2 hours)

	Milling Time (Hours)				
	1	2	3	4	6
As-milled (μm)*	>10	5	2	1	<0.5
As-heated (μm)**	N/A	5	2	1	<0.5

*The average thickness of the Al layers in the as-milled powder particles.

**The average grain size of formed Al₂O₃ phase.

Milling influences not only the reaction temperature of the milled powders, but also the reaction path and the reaction products. The microstructures of the samples heat treated at 850 °C revealed that the influence is substantial. The influence is analyzed, using powders produced with a 500-g starting charge as an example. With 1 hour of milling, XRD analysis shows that Al₂O₃, Ti(Al,O), and Ti₃Al phases formed after heat treatment; SEM observation of the powder particles clearly shows the commencement and propagation of the reaction between the Al and TiO₂ phases. The Al₂O₃ phase and the Ti-rich phase were found to be separated by certain phases with intermediate compositions (Figure 9). This microstructure strongly implies that the reaction between the Al and TiO₂ that forms the Ti and Al₂O₃ phases has not been completed after heat treatment for 2 hours at 850 °C. This is attributed to two possible causes: the coarse-microstructure, milled-powder particles consisting of coarse Al cores surrounded by TiO₂ particles, and the low heat-treatment temperature compared to the reaction temperature. The diffusion necessary to the reaction between Al and TiO₂ has to take place across a distance as long as several tens of micrometers, which apparently significantly delays the completion of the reaction.

The microstructures of the heat-treated powders with the longer milling times (2 and 3 hours) are finer and quite similar. With the lowering of the reaction temperature from about 1000 to about 880 and 860 °C, respectively, it seems that 2 hours of heat treatment has led to the completion of the reaction. Well-defined Al₂O₃ and Ti(Al,O) phase regions were observed. The Al₂O₃ phase appears as isolated round particles, and the Ti(Al,O) phase appears as the matrix. For the 4-hour-milled powder, with its further refined microstructure before heat treatment, an even finer microstructure is produced after heat treatment, with an average particle size in the Al₂O₃ phase of about 1 μm . For the 6-hour milled powder, with a much more intimate mixing and a finer microstructure before heat treatment, an even finer microstructure is produced after heat treatment, with an average particle size of the Al₂O₃ phase of less than 0.5 μm , although a few particles as large as 1 μm are observed. This clearly shows that a longer milling time produces a finer microstructure in the as-milled Al/TiO₂ composite powder before heat treatment, which subsequently leads to a finer microstructure in the Ti(Al,O)/Al₂O₃ composite powder after heat treatment.

By comparing the microstructure of as-milled powders with their corresponding heat-treated samples, it has been found that the maximum dimension of the Al₂O₃ phase formed in the heat-treated samples is roughly equal to the maximum Al layer thickness in the as-milled powders (Table I). However, no obvious particle growth was observed at this heat-treatment temperature. This might be attributed

to the fact that, once the Al_2O_3 and Ti phases are formed, it is difficult for further diffusion to take place across the phases formed for the particle growth. A detailed study of the relationship between the reaction and the milling conditions will be published elsewhere.^[12]

The present investigation has clearly demonstrated the microstructure evolution of a ductile/hard-alloy system subjected to disc milling. It is important to control the dominant milling parameters, such as the starting powder charge, the milling time, *etc.*, to obtain the desirable microstructure and yield rate.

IV. CONCLUSIONS

The present investigation demonstrates that the disc mill is a powerful tool with which to treat powders of several hundreds of grams per batch. The mixing of the starting powder and the refinement of the composite powder particles of the Al and TiO_2 system can be reached within a few hours. The starting powder charge has a significant effect on both the composite structure formation process and the microstructure of the milled powders. Similar to other milling processes, a longer disc milling time leads to a more homogeneous mixing and refinement of the composite structure in the as-milled powders, and, subsequently, in the microstructure after heat treatment.

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