

Formation of NiAl intermetallic by gradual and explosive exothermic reaction mechanism during ball milling

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Abstract: NiAl intermetallic has been produced by mechanical alloying in a high energy vibrator mill using elemental Ni and Al powder mixture. The NiAl powders were formed in two ways. One by a gradual exothermic reaction mechanism during a long time continuous milling and the other by explosive exothermic reaction mechanism that occurred when opening the milling vessel to the air atmosphere after a short time milling. Prolonged milling for both cases resulted in change of morphology and refinement of grain size down to nano scale.

Keywords: A. Nickel aluminides, based on NiAl; C. Mechanical alloying, Combustion synthesis.

1. Introduction

Intermetallic compounds based NiAl are being recognized as potential high temperature structural materials because of their low density (5.86 g/cm³), high melting point (1911 K) and excellent oxidation resistance up to 1573 K, as well as good thermal conductivity[1,2]. These properties have made NiAl a suitable material for structural application such as gas

turbine engine rotor blades and stator vanes. However, the major barrier to the structural application for NiAl is its low ductility at ambient temperature and low strength and creep resistance at elevated temperature. Significant efforts have centered on enhancing the mechanical properties of intermetallics through grain refinement [3, 4]. One approach to enhance ductility has been to alloy the intermetallic compound with other elements and to control its microstructure through a careful preparation route [5].

One of the processing paths which has shown potential for enhancing ductility and creep resistance is mechanical alloying [6, 7]. Mechanical alloying (MA) offers a number of advantages for processing intermetallic compounds such as grain refinement and the formation of fine dispersoid particles [8, 9]. MA is also a promising technique to produce oxide dispersion strengthened intermetallic-matrix composites, such as NiAl-Al₂O₃ and Al₃Ti-Al₂O₃. Adjusting the oxygen content via close control of the milling atmosphere produces the oxides [10, 11]. It has been observed that grain growth in NiAl can be considerably hindered and limited by having suitable alumina additions [12].

The first preparation of nickel aluminides was performed by Ivanov et al [13], who studied MA of the Ni-Al system. Later, Atzmon found that the formation of NiAl by MA occurs by self-sustained reaction in individual particles and is accompanied by a large explosive energy release [14, 15]. Explosive reaction was also reported to occur when the grinding container was opened soon after milling was stopped [16].

A bulk material of intermetallics can also be produced by a very simple fabrication technique based on combustion synthesized from a powder mixture of elemental compounds [17, 18]. The reaction mechanism of combustion synthesis of intermetallics compounds have been repeatedly studied and discussed by many researchers [19, 20].

In this study, the formation of NiAl intermetallic was investigated by both long time continuous milling and short time milling operation accompanied by sudden explosive reaction by milling a mixture of Ni and Al powders.

2. Experimental procedure

In this investigation, elemental 99.9% purity Ni and 99.8% purity Al powder with average particle size of 50 and 20 μm , respectively, were used. In all experimental operations, 15 grams of mixed powders with composition of $\text{Ni}_{50}\text{Al}_{50}$ were canned together with 300 grams steel balls (10 mm in diameter) into a hardened steel vial (85 mm in diameter and 80 mm in height). To prevent sample oxidation, the powders were sealed in the vial under argon atmosphere and a fresh sample was used for each ball milling run. Ethanol in the quantity of 5 wt% was added to avoid sticking of the powders to the vial. A vibratory ball mill (RPM \approx 200) was employed for mechanical alloying operation. The rise of vial temperature was monitored with a HANA thermometer inserted on the vial side.

The mechanically alloyed powders were characterized by X-ray diffraction with $\text{CuK}\alpha$ radiation. The crystallite size was calculated from X-ray diffraction (XRD) peak broadening after separation of the contributions of internal strain and instrumental broadening by standard procedure [21]. The milled powders morphology was characterized by Cambridge S-360 scanning electron microscope. The thermal behavior of the powders was examined using a Linsice L81 differential thermal analyzer where the sample was heated from room temperature to 750°C in a purified argon atmosphere at a rate of 25°C/min. Energy dispersive analysis by X-ray and atomic absorption spectroscopy (using Shimadzu AA-680) was conducted to identify the iron contamination. The Fe

contamination due to the wear debris from the steel balls and vial was less than 0.8 at.% after 24 hr of milling.

3. Results and discussion

3.1. Continuous Milling

To study the formation of the NiAl compound in more detail, a thermometer was attached to the vial during the milling process and its voltage monitored as a function of time. Fig. 1 shows the vessel temperature as a function of milling time for two cases of absence and presence of the powders in the vessel. In both cases during the first 100 minutes of milling operation, rate of temperature rise was fast and then slowed down gradually to an almost identical equilibrium value after 6 hr. For the case 2 the vessel temperature starts to increase with a slow rate after 7 hr milling operation. This means that from this time a reaction is happening inside the vessel.

During the early stage of ball milling, powder particles trapped between colliding balls undergo extensive deformation followed by cold-welding at the freshly formed reactive surfaces. The resulting particles show an irregularly convoluted multilayer structure which is further refined by successive collisions. After 7 hr ball milling the particles became too small and too numerous and the energy of impact was dissipated over a large area, so that no single spot reached the required temperature for ignition. By the prolonged milling, the kinetic energy input in the system led to a reduction of the lamellar layer thickness and achieved closer contact between particles. After reaching a critical lamellar thickness, true alloying occurred at room temperature in the individual grains due to mutual interdiffusion. The gradual formation of NiAl in the individual grains accompanied by temperature rise in the vessel, Fig. 1, confirmed this mechanism.

Fig. 2 illustrates the evolution of XRD patterns during the course of milling $\text{Ni}_{50}\text{Al}_{50}$ elemental blend. Here the formation of NiAl can be noticed within 12 hr of mechanical alloying. This milling time led to the disappearance of the XRD peak for Al, while the Ni peaks persisted up to 18 hr. A reason for the disappearance of the Al XRD peaks can be crystallite refinement of Al to a level of about few nm. Crystal refinement causes broadening of the XRD peaks of Al and a consequent decrease in the peak heights. On the other hand the disappearance of Al peaks in comparison with Ni peaks can be related to the atomic scattering factors of the elements. The element with the lower atomic number, and hence lower atomic scattering factor, has a lower intensity and hence with continued milling it tends to disappear sooner than the higher one. Accordingly, in the Al-Ni system, Ni ($Z=28$) peaks persist while Al ($Z=13$) peaks disappear.

Fig. 3. illustrates the average grain size and lattice strain of NiAl with milling time. As can be seen the grain size is reduced to 22 ± 10 nm after 24 hr ball milling. These values are comparable to those reported by other investigators [21, 22].

3.2. Discontinuous Milling

Opening the vessel to air atmosphere after 4 to 8 hr milling operation caused the formation of NiAl intermetallic by a self-sustaining reaction mechanism. Fig. 4 shows a video output of this reaction. Self-sustaining reaction is a process in which the original elements, when ignited, explosively transform into NiAl intermetallic, due to the exothermic heat of the reaction. Soon after opening the vessel to air atmosphere the whole powder mixture turned red hot, subsequently the temperature increased rapidly to ignition temperature and the whole sample became white hot leading to completion of the explosive

exothermic reaction. The driving force for the reaction is the negative heat of formation of compound (heat of formation for NiAl is -118 KJ/mol). This results in a release of energy (as heat), which sustains and propagates the reaction through the body of the elements. In fact, opening the vessel to air atmosphere provides the initial ignition by releasing heat due to oxidation of elemental aluminum.

No self-sustaining reaction was observed for Ni₅₀Al₅₀ elemental powder mixture at any milling time above 8 hr. In fact, the 8 hr milling time seems to be a critical milling time in which exceeding that time no further ignition reaction takes place when the vessel is exposed to air atmosphere and the milling process leads to a continuous diffusive reaction, as pointed out earlier. In order to study the effect of vial temperature on the ignition reaction, a few samples were milled from 1 to 7 hr and then cooled in the sealed vessel before opening it to air atmosphere. No self-sustaining reaction was observed. The results of these experiments indicate that the self-sustaining reaction induced by oxidation of elemental aluminum powder depends on the temperature of the samples.

Fig. 5 shows X-ray diffraction patterns of Ni₅₀Al₅₀ elemental powder mixture before and after the explosive exothermic reaction. The non-reactive pattern indicates only the presence of Al and Ni elements, whereas after the self-sustaining explosive reaction, NiAl intermetallic and Al₂O₃ compound are clearly detected in the XRD pattern.

An aim of this study was the characterization of the early stages of the Al-Ni self sustaining reaction and its comparison to continuous thermal diffusion reaction. For continuous milling operation of Al₅₀Ni₅₀, reaction of a substantial fraction of the powder to form NiAl was observed after 8 hr and longer. The NiAl compound was formed gradually with milling time, although, sometimes, the formation process appeared to be abrupt. This

was evidenced by an increase in vial temperature. Increasing milling time to 14-18 hr a steady state condition was reached, and the resulting powder was a mixture of the reacted NiAl and elemental Ni powder, as verified by x-ray diffraction, Fig. 2. When the milling process was stopped after 4 to 8 hr, and the vial opened to air atmosphere, the fast oxidation of the elemental aluminum powder led to an explosive exothermic reaction. In contrast to the case of continuous thermal diffusion, x-ray diffraction results show the presence of NiAl + Al₂O₃, with no visible amount of the elemental phases, Fig. 5. Explosive reaction can result in the formation of NiAl in the solid state, or as a liquid, which then solidifies upon heat loss to the vial. Energy saving and short time processing are the main advantages of combustion synthesized fabrication technique, whereas coarse particles and inhomogeneous microstructures are the disadvantages of the method. In comparison, mechanical alloying technique is capable of producing homogeneous, fine grained alloys in the solid state, thus providing a processing technique that can avoid the large grained inhomogeneous structure.

Fig. 6 shows the morphology of the particles before and after the explosive exothermic reaction. As evidenced by the SEM micrographs, the particles are flat and flake shape before the reaction but change to a spherical shape after the exothermic reaction. Visual inspection showed that the resulting material consisted of large aggregates of powder particles. The size of the reacted particles is 10 to 50 times larger than that of the non-reacted particles. It is emphasized that the Al₂O₃ particles remain in the synthesized NiAl as inclusions. At high temperature the grain size of the NiAl is very large when no particles were added, while very small when a low volume fraction of the Al₂O₃ particles are added. As the volume fraction of the particle of Al₂O₃ increases, the grain size decreases

remarkably [12]. Consequently, a controllable addition of these particles is very effective for the grain refinement of the synthesized NiAl.

The crystallite size of the elemental Ni-Al powder mixture was found to be much influenced by the milling time, Fig. 7 shows this effect. Comparing the crystallite sizes of the milled and non-milled powders, it is clear that some refinement occurred during milling operation. It is seen that the crystallite size of the powder decreases fairly linearly during the first 2-6 hr of milling operation. The crystallite size and consequently the crystallite refinement of the elemental Al powder changes more rapidly than elemental Ni powder. This is one of the reasons that, as have been shown earlier, the Al XRD peaks in Fig. 2 disappears sooner than the Ni peaks. The ignition temperature, the rate or velocity of sustaining reaction and the microstructure evolution of the reacted product are affected by the milling time, a fact which to a large extent can be ascribed to the decreasing crystallite size.

The differential thermal analysis (DTA) traces of the powders and its variation with milling time are shown in Figs. 8 and 9. It is seen that the ignition temperature is decreased from 577°C to 374°C after 4 hr ball milling of Ni₅₀Al₅₀ elemental blend. The measured ignition temperature for the non-milled Ni-Al elemental powder mixture (i.e. 577°C) is in a good agreement with other investigators [23]. The ignition temperature is a function of the microstructural parameters such as particle size, crystallite size and interfacial area between the reactants. Since the milling process refines the particle size and develops the interfaces, T_{ig} decreases with milling time.

The XRD patterns for prolonged milling after the explosive reaction of powders are shown in Fig. 10. The patterns do not show any particular changes in NiAl peak intensity

up to 13 hr ball milling and the presence of residual Ni element even after 13 hr milling operation is still observed. Fig. 11 illustrates the microstructures of NiAl powders after prolonged milling of the explosively reacted powders for different milling times. Comparison of Figs. 11 and 6(b) shows that, after 9 hr milling, the morphology of particles is changed and flake-like particles are produced.

4. Conclusion

- (1) Continuous milling of Ni₅₀Al₅₀ causes the gradual formation of NiAl intermetallic after 8 hr milling operation.
- (2) Opening of the milling vessel to air atmosphere after 4 to 8 hr ball milling leads to a self-sustained reaction and explosive formation of NiAl intermetallic.
- (3) Initiation of self-sustaining reaction is provided by the heat of oxidation reaction between mechano-chemically activated fine Al powders and oxygen. That is, the heat becomes a trigger for combustion synthesis between reactant elements of Ni and Al powders.
- (4) Crystallite size of elemental Ni-Al powder and ignition temperature decreases with milling time.

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Fig. 1. Vessel temperature as a function of milling time (15 g equimolar Ni-Al, 300 g steel balls).

Fig. 2. XRD patterns for Ni₅₀Al₅₀ blend at different milling times showing NiAl formation for continuous milling.

Fig. 3. Variation of crystallite size and lattice strain of NiAl with milling time.

Fig. 4. Video output showing the steps of explosive reaction after opening the container to the air atmosphere after 4 hr milling operation.

Fig. 5. X-ray diffraction pattern of Ni₅₀Al₅₀ elemental powder mixture before and after explosive reaction (4 hr milling operation).

Fig. 6. SEM micrographs of Ni₅₀Al₅₀ powder (a) before (b) after the explosive exothermic reaction (4 hr milling operation).

Fig. 7. Variation of crystallite size of elemental Al and Ni powders with milling time.

Fig. 8. Effect of milling time on DTA curves of the powders.

Fig. 9. Variation of ignition temperature (T_{ig}) with milling time.

Fig. 10. The XRD patterns after prolonged milling of the explosive reacted powders.

Fig. 11. Micrographs after prolonged milling of explosively reacted NiAl powders after (a) 9 hr and (b) 13 hr milling operation.

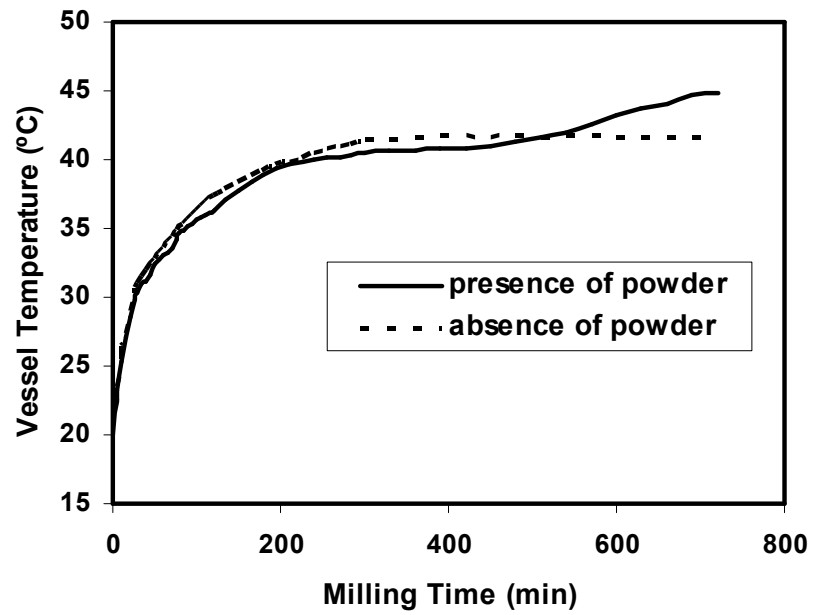


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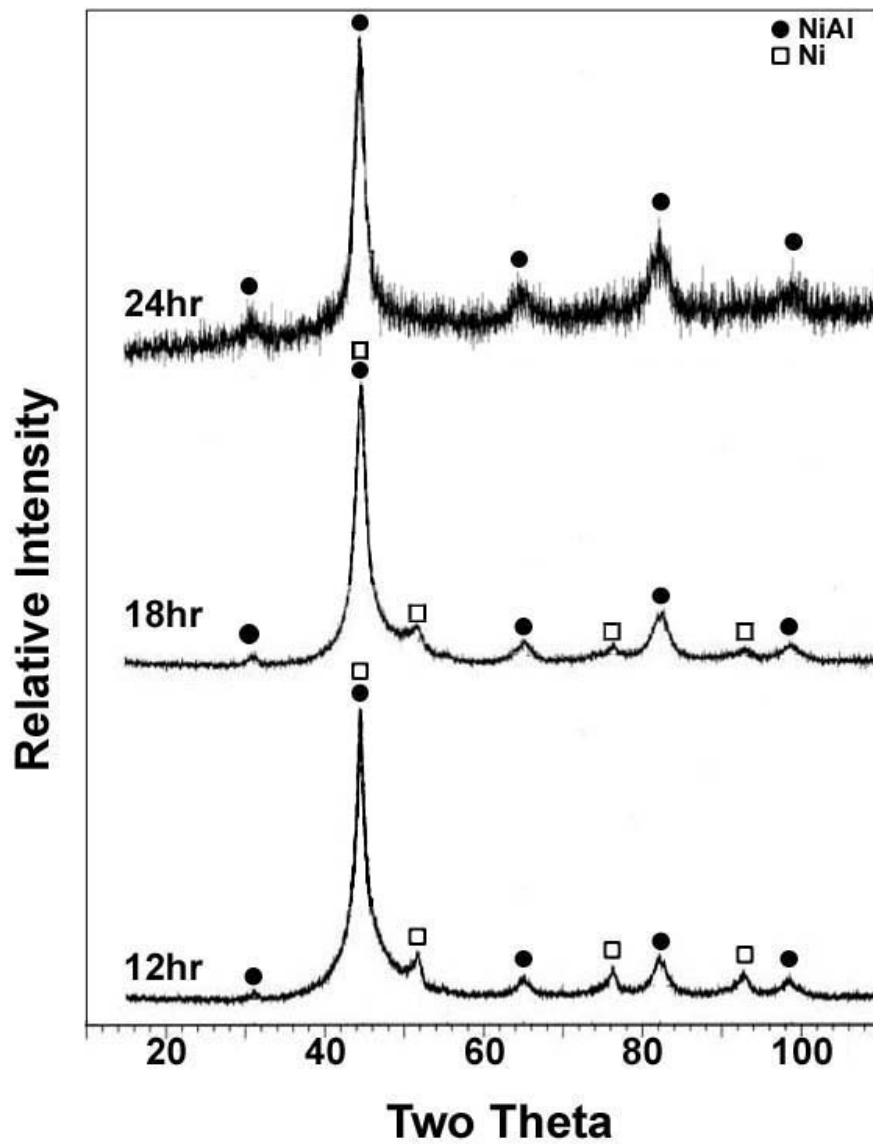


Fig. 2. XRD patterns for $\text{Ni}_{50}\text{Al}_{50}$ blend at different milling times showing NiAl formation for continuous milling.

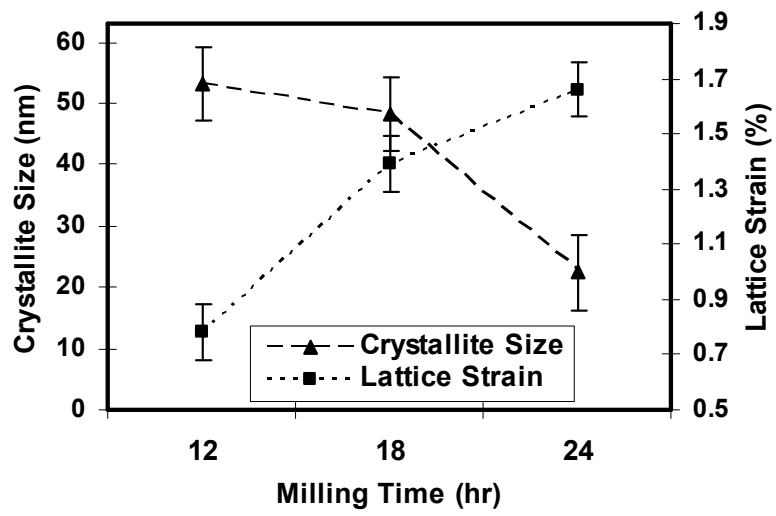


Fig. 3. Variation of crystallite size and lattice strain of NiAl with milling time.

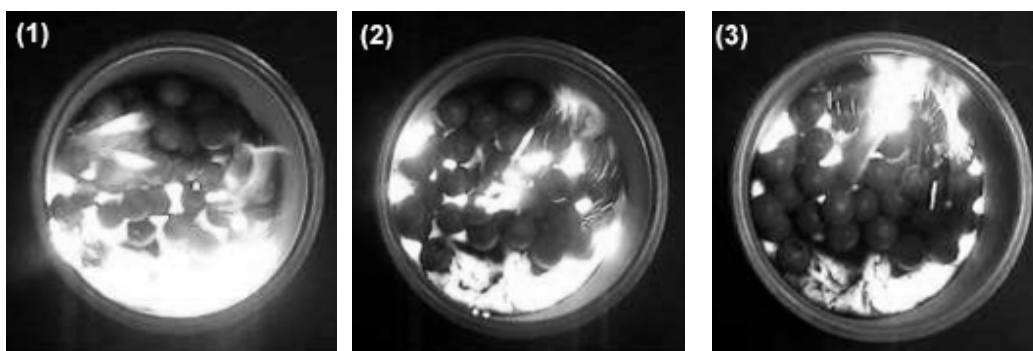


Fig. 4. Video output showing the steps of explosive reaction after opening the container to the air atmosphere after 4 hr milling operation.

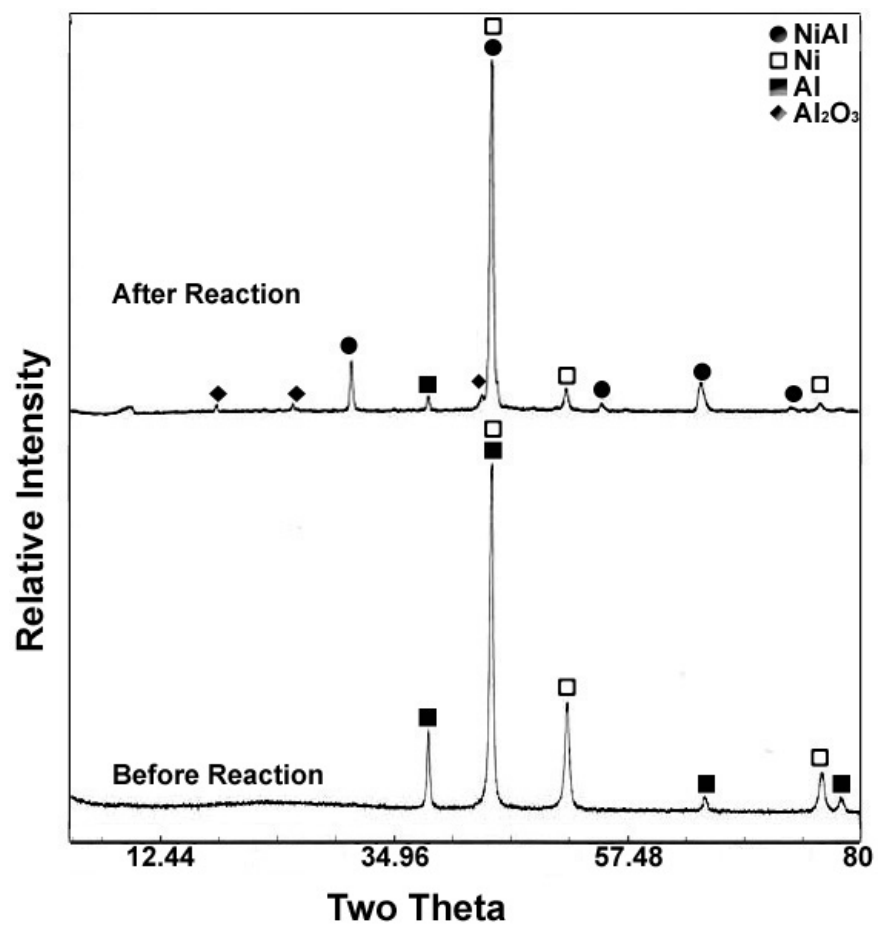


Fig. 5. X-ray diffraction pattern of Ni₅₀Al₅₀ elemental powder mixture before and after explosive reaction (4 hr milling operation).

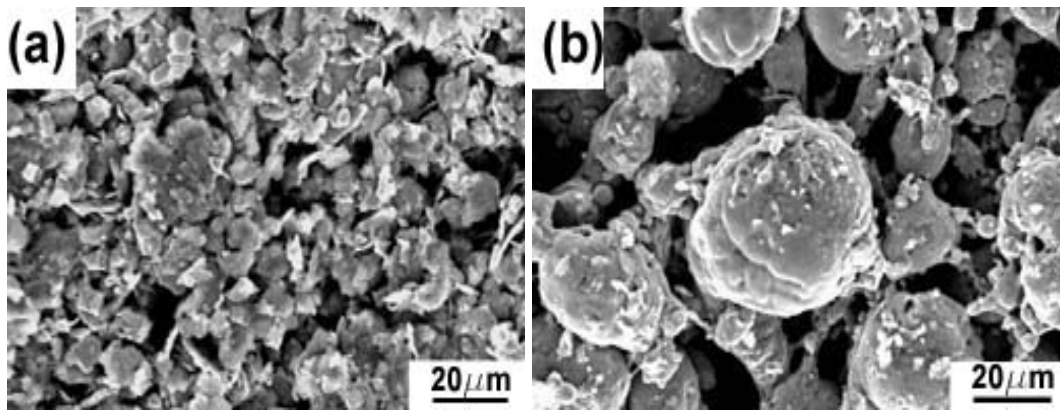


Fig. 6. SEM micrographs of $\text{Ni}_{50}\text{Al}_{50}$ powder (a) before (b) after the explosive exothermic reaction (4 hr milling operation).

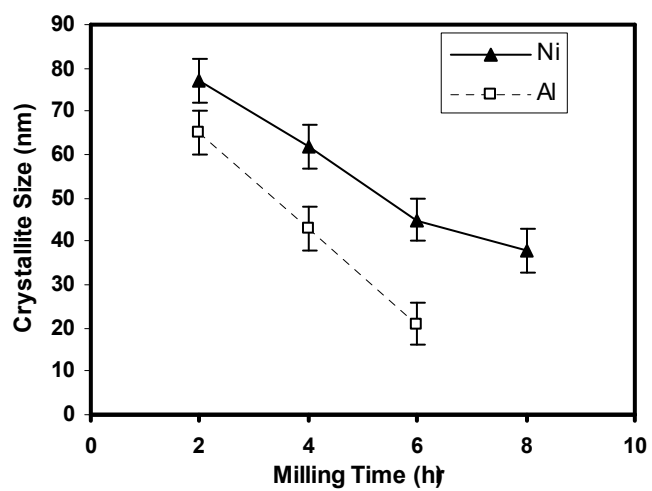


Fig. 7. Variation of crystallite size of elemental Al and Ni powders with milling time.

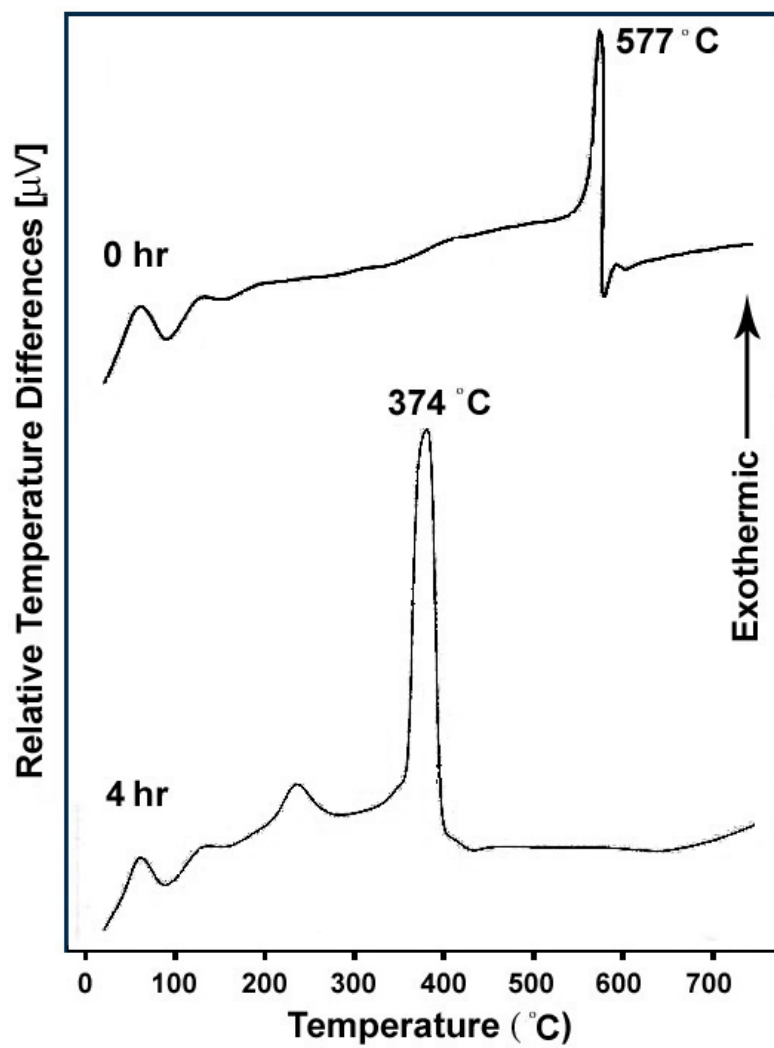


Fig. 8. Effect of milling time on DTA curves of the powders.

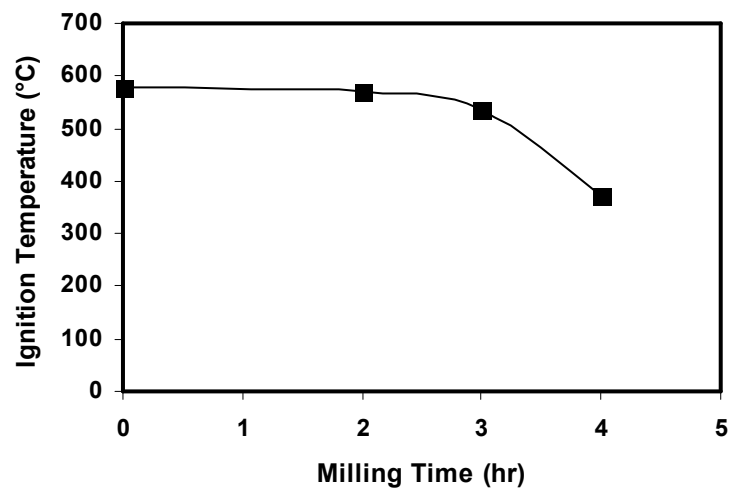


Fig. 9. Variation of ignition temperature (T_{ig}) with milling time.

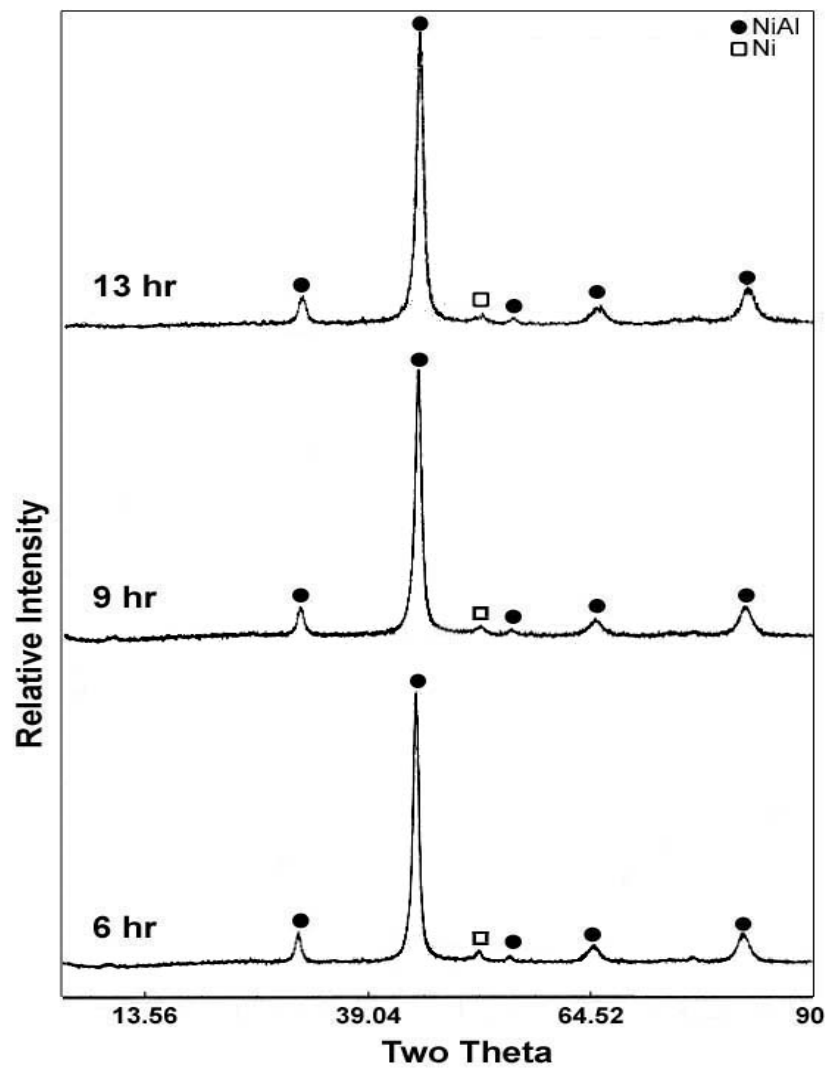


Fig. 10. The XRD patterns after prolonged milling of the explosive reacted powders.

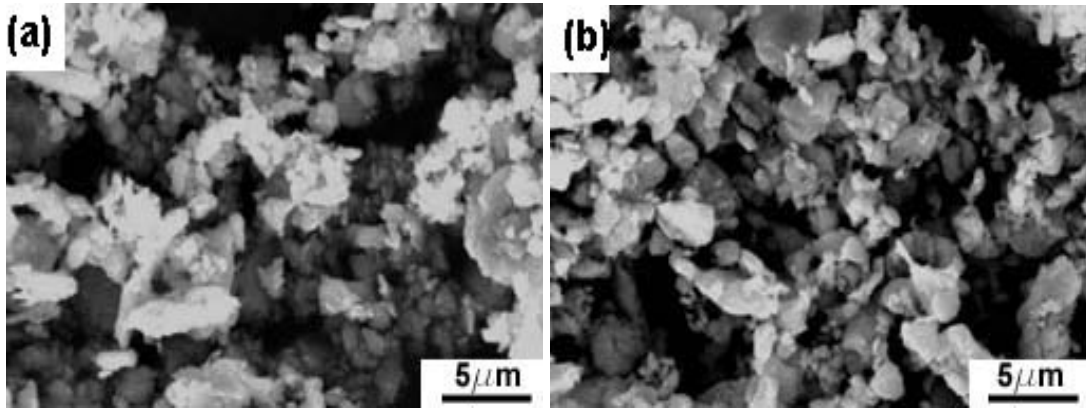


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