

Short Communication

## Mechanical Analysis of the Effects of Different Mechanical Alloying Periods on Ni<sub>3</sub>Al Intermetallic Compound Fabrication Quality

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Ni and Al elemental powder mixtures with composition Ni<sub>75</sub>Al<sub>25</sub> (at %) were mechanically alloyed in a planetary ball mill under different mechanical alloying (MA) durations. X-ray diffraction (XRD), scanning electron microscope (SEM) and simultaneous thermal analysis (STA) were conducted to study phase transformations, morphology changes and thermal property of Ni-Al mixture during MA. Ni<sub>3</sub>Al intermetallic compound was formed successfully after 10h of milling, which was the shortest formation period that ever reported for this intermetallic compound. The nanocrystalline Ni<sub>3</sub>Al with the lowest crystallite size of 12.6nm was synthesized. Refinement of crystallite size with increasing internal strain was significant as milling duration was increased gradually. During formation of the Ni<sub>3</sub>Al, the powder particles have undergone incidents of welding, microforging, fracturing, rewelding and agglomeration.

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### 1. INTRODUCTION

The development of intermetallic compounds has been driven primarily by the need for structural and non-structural materials with better specific strength and modulus than monolithic metals or alloys, especially at high temperatures. Among the intermetallic compounds, nickel aluminide (Ni<sub>3</sub>Al) offers a combination of attractive properties such as high melting temperatures, high hardness, low density, good oxidation, corrosion resistance, and good thermal conductivity [1]. These attractive properties make Ni<sub>3</sub>Al a potential material for the aircraft and automotive industries. However, poor toughness at room temperature and inadequate strength and creep resistance at elevated

temperature are the major limitation for the application of this material [2]. One approach for improving its ductility is by reducing the crystallite size to the nanometer scale [3,4]. On the other hand, for optimization of room temperature toughness and high temperature strength, microstructural modifications are also required.

There are several techniques for synthesizing intermetallic compounds. Mechanical alloying (MA) is typically used commercially and is capable of synthesizing materials with alloying phases in both equilibrium and non-equilibrium manners [5]. MA is a solid-state powder processing technique that enables production of homogenous materials starting from blended elemental or prealloyed powder mixtures in a high energy ball mill [5-7]. Moreover, powder mixtures can be mechanically activated to induce chemical reactions in MA. As a result, pure metals, intermetallics, nanocomposites, ceramics and other commercially materials can be produced at room temperature or at least at much lower temperatures than that are normally required [8,9]. Other advantageous attributes of MA includes refinement of grain sizes down to nanometer range, disordering of ordered intermetallics and possibility of alloying of difficult alloy elements [5,10].

In this study, nanocrystalline Ni<sub>3</sub>Al intermetallic was synthesized by mechanical alloying. Although the synthesis of Ni<sub>3</sub>Al intermetallic compound by MA has been previously reported [10-13], the mechanism of Ni<sub>3</sub>Al formation by MA is still not clear. Besides, very limited studies were done in investigating the synthesis of Ni<sub>3</sub>Al in short milling hour. According to the majority of previous studies, Ni<sub>3</sub>Al was synthesized successfully after 20 MA hours and above [6,10-13]. The microstructure transformation, morphology changes and thermal property of Ni<sub>3</sub>Al as a function of MA hours were investigated in this study in order to observe the process of this solid state synthesis reaction and to provide a clearer picture of the involved mechanisms.

## 2. MATERIALS AND METHODOLOGY

The starting powders were Ni powder (99.9 %, particle size about 44 $\mu$ m) and Al powder (99 %, particle size about 74 $\mu$ m). The mixtures with composition Ni<sub>75</sub>Al<sub>25</sub> (at %) were milled using a planetary ball mill (Retsch-PM 400 MA type, Germany) for 5-40h at 300rpm in a stainless steel jar with steel balls of 20mm in diameter under the argon atmosphere. The ball to powder ratio of 10:1 was applied in this study. In order to minimize excessive cold welding of the powder particles to the grinding medium and the container wall, about 2 wt % zinc stearate (Zn(C<sub>18</sub>H<sub>35</sub>O<sub>2</sub>)<sub>2</sub>) was added into the powder mixtures, to act as process control agent (PCA) [14].

The phase of the samples before and after milling was examined using x-ray diffractometer (XRD) (Phillips X'pert MRD PW3040) with Cu K $\alpha$  radiation. The diffraction pattern was obtained by scanning the samples from 10 to 100 $^\circ$  2 $\theta$  angle at a step size of 0.02 $^\circ$ . The MA was believed to be able to cause the broadening pattern on the resulted x-ray diffraction lines due to changes in crystallite size and internal strains within the structures of powder [15]. In order to investigate and relate these factors, the William-Hall and Scherrer methods were applied. The crystallite size of powder was calculated using the Scherrer equation [14-16]:

$$S = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where  $S$  is the crystallite size,  $K$  is a constant whose value is 0.9,  $\lambda$  is the x-ray wavelength, and the width peak  $\beta$  (in rad) was determined as full width at half-maximum (FWHM). The resulted internal strain  $\epsilon$ , was calculated using the Williamson-Hall equation [15]:

$$\beta \cos \theta = \frac{K\lambda}{S} + 2\epsilon \sin \theta \quad (2)$$

A graph of  $\beta$  against  $\sin \theta$  may be plotted from Equation 2 and the internal strain is then obtained from the slope of the graph.

Simultaneous thermal analysis (STA), consisting of Simultaneous Differential Thermal Analysis (SDTA) and Thermogravimetric Analysis (TGA), was conducted on milled powder using TGA/SDTA 851 Mettler Toledo under inert argon gas atmosphere. Surface morphologies were observed under a scanning electron microscope (SEM) (Hitachi, Japan).

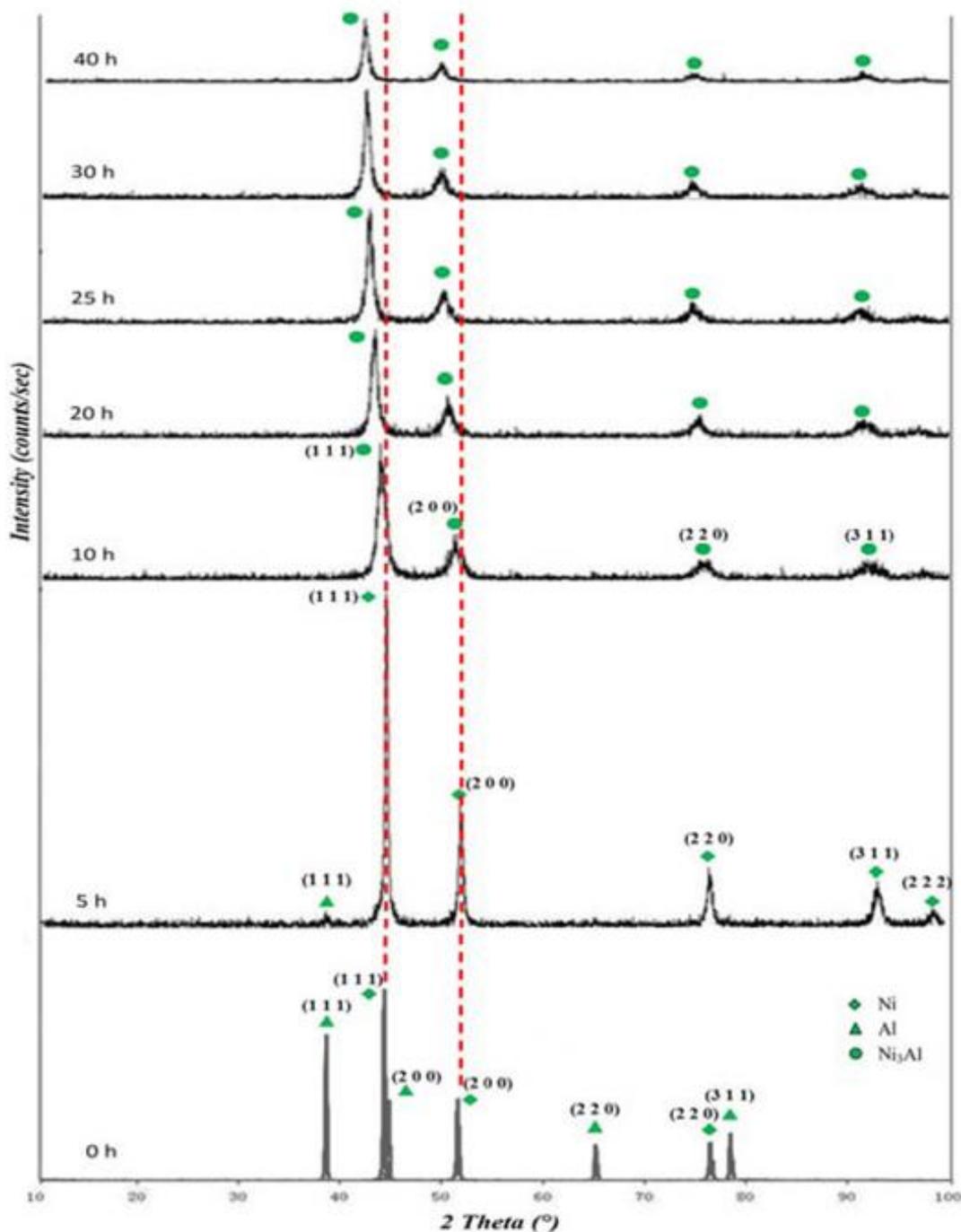
### 3. RESULTS AND DISCUSSION

#### 3.1. XRD analysis

Figure 1 shows the XRD patterns of  $\text{Ni}_{75}\text{Al}_{25}$  powder before and after different milling times. The XRD patterns of the non-milled powder showed diffraction peaks of the pure crystalline Ni and Al. In the early stage of milling, most of the XRD peaks of Al disappeared due to the milling effect. The predominant XRD peaks were due to the crystallite Ni. Increasing milling time to 10h resulted in the complete vanishing of crystallite Al peaks. At the same time, the crystallite Ni peaks displaced slightly towards the lower angles caused by the deformation of lattice due to the accumulated strains [10,15,17]. This can be correlated with Figure 2 that shows the gradual increase of internal strain with increasing milling hours. It was suggested that the Ni lattice was expanded as larger atoms Al diffused into the Ni lattice resulting in a Ni(Al) solid solution during milling process [10,13]. This structure was then identified as crystalline  $\text{Ni}_3\text{Al}$  intermetallic compound and their corresponding XRD peaks were present after milling of 10h and above. This compound had been successfully formed since the MA was believed to be mechanically-driven, spontaneous reaction [18]. A further displacement of  $\text{Ni}_3\text{Al}$  peaks to the lower angles was also observed as milling time increases. Increasing milling time to 40h led to no further structural changes of synthesized powder. It is suggested that Ni(Al) solid solution forms initially as an intermediate compound and then transforms to the  $\text{Ni}_3\text{Al}$  intermetallic compound on further milling. The resulting  $\text{Ni}_3\text{Al}$  phase at 40h of milling had a crystallite size of 12.6nm in comparison to its crystallite size of 26.7nm at 5h of milling.

The overall XRD peaks show a decrease in their intensities and an increase in broadening with the increasing milling hour as a result of the refinement of crystallite size and the increase in lattice strain. These phenomena are in good agreement with the results presented in Figure 2. The crystallite size of  $\text{Ni}_3\text{Al}$  was obtained from XRD analysis using the Scherrer equation [16], as calculated from the

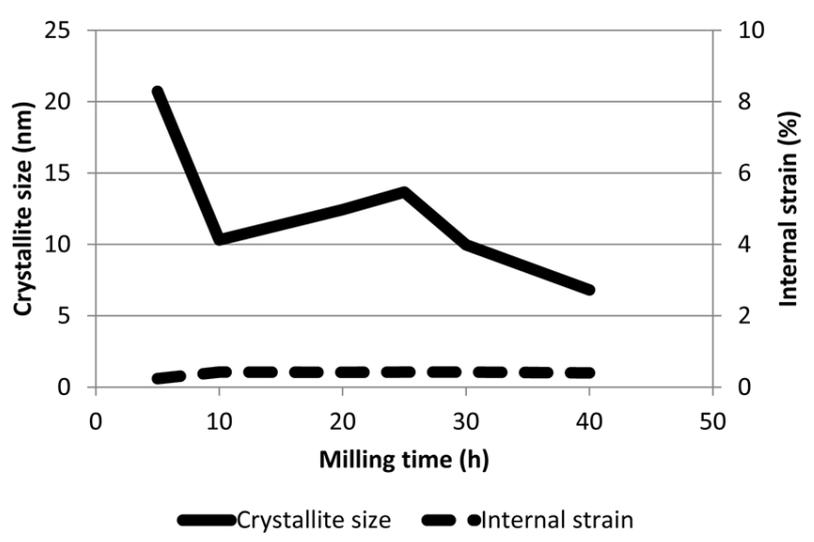
broadening of Ni<sub>3</sub>Al (111) peaks. The resulting internal strain of powder was obtained by plotting  $\beta \cos \theta$  against  $\sin \theta$  based on the Williamson-Hall equation.



**Figure 1.** XRD patterns of Ni<sub>75</sub>Al<sub>25</sub> powder milled for different milling times

Figure 2 shows that for increasing milling time, the crystallite size decreases, while the internal strain increases only slightly. This trend could be explained by the formation of defects during the milling process. The collision energy was introduced and thus promoted a distortion of lattice

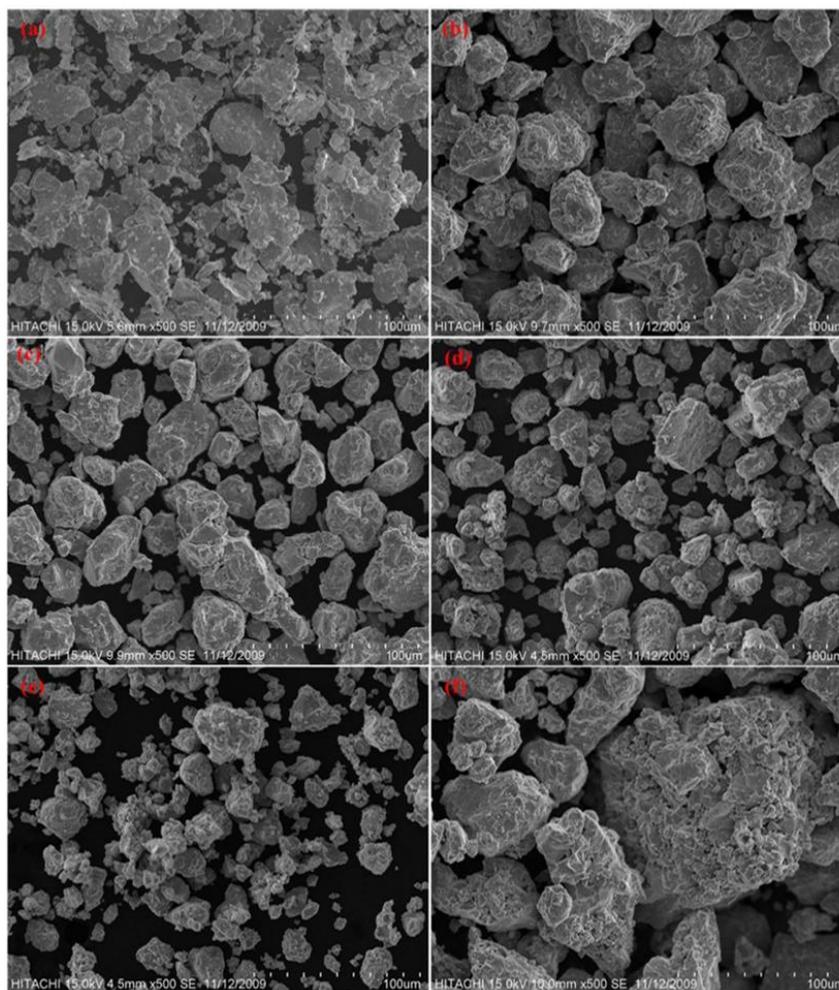
parameters of the powder [14,15]. However, at 40h of milling, it is shown that the internal strain decreases. This was most probably caused by the occurrence of annealing effect during milling process. Since the crystallite size almost reached its saturation value at 20h of milling and above, the impact produced by MA was to anneal the high amount of stress within the Ni<sub>3</sub>Al particles, thus decreasing the lattice strain [15,19].



**Figure 2.** Internal strain and crystallite size of Ni<sub>75</sub>Al<sub>25</sub> as a function of milling duration

### 3.2. SEM Analysis

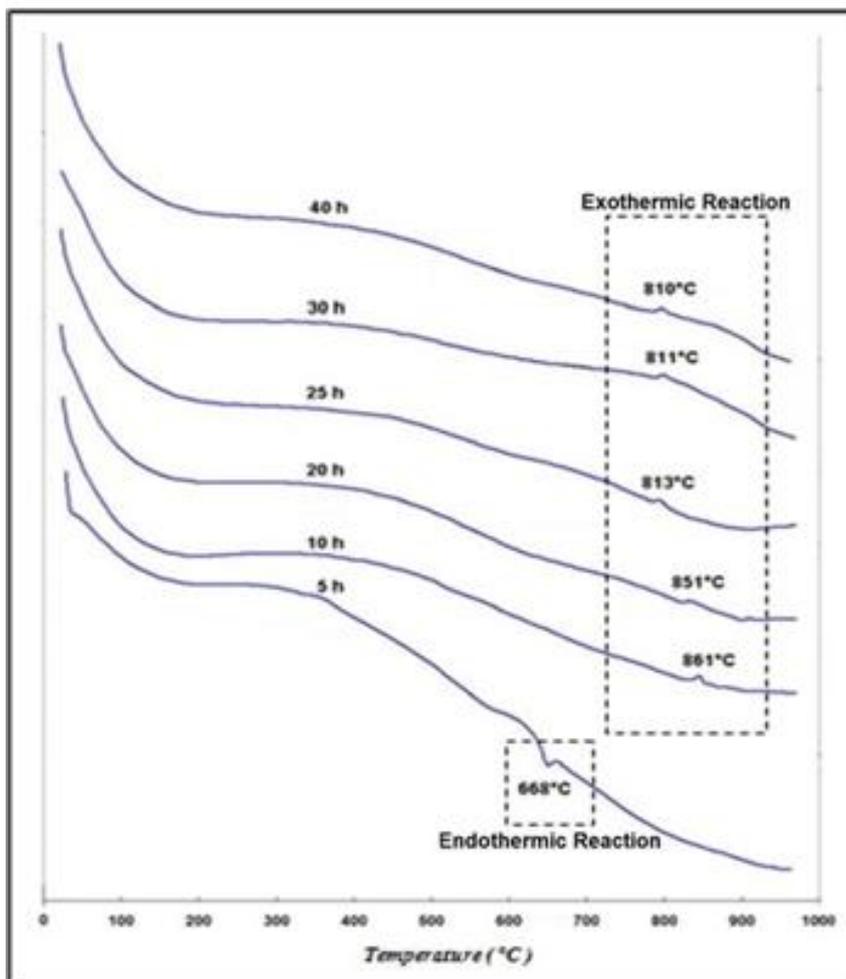
Figure 3 shows the morphological images of powder particles after different milling durations, from 5 to 40h. A typical coarse flaky and plate-like structure was observed for powder milled for 5h (Figure 3(a)), as previously reported [20]. As milling time increased, the powder particles exhibited increasing spherical equiaxial morphology as shown in Figures 3(b)-(e). The size of powder particles also reduced gradually with increasing milling hour, in accordance with previous studies [10,20,21]. After 40h of milling, large agglomerates consisting of very fine particles were observed. During MA, both the welding and microforging processes occurred in the initial stage of milling. Since Ni and Al are ductile materials, their powders had been conveniently compressed and flattened by the impact from the milling medium [20]. Besides welding, the process of fracturing within the powder particles also occurred during collisions between the balls and powder particles. The powders were extensively mixed and subjected to repetitive action of plastic deformation under impacts, welding in sandwiches between two elemental components and subsequent breaking. Therefore, the powders became layers with extremely low thickness and facilitated solid state reaction to occur [21-22]. As the extent of milling increased, the particle size decreased. Finally, both rewelding and autoadhesion processes took place within the particles [24]. The whole MA process may be described as having two consecutive steps: progressive refinement of Ni and Al particles within the spherical microstructure, followed by Ni<sub>3</sub>Al formation, presumably at the interfaces between Ni and Al grains [22].



**Figure 3.** SEM images of Ni<sub>75</sub>Al<sub>25</sub> powder particles milled for different milling times (a) 5h (b) 10h (c) 20h (d) 25h (e) 30h (f) 40h

### 3.3. Thermal analysis

The SDTA traces of the as-milled powders can be characterized by the presence of two different peaks, one endothermic and another exothermic (Figure 4). There was only one endothermic peak present at 668°C for 5h of milling, which resulted from the melting of aluminum [20]. This was confirmed by the XRD result as shown in Figure 1 since the peak due to Al phase had been detected. It was suggested that a small portion of element Al phase had not mechanically reacted with Ni phase and still remained in the Ni-Al mixture for the early stage of milling. Since the melting temperature of Ni element was more than 1000°C, the formation of endothermic peak that was attributable to the melting of Ni was not possible. However, no endothermic peak was observed in the SDTA curves at the beginning of 10h of milling. The Al phase probably had completely reacted with Ni phase to form Ni<sub>3</sub>Al intermetallic compound. This observation was in good agreement with the XRD result in Figure 1 that showed no Al phase was present at the beginning of 10h of milling.



**Figure 4.** SDTA traces of  $\text{Ni}_{75}\text{Al}_{25}$  powder for different milling times

The corresponding temperatures of the exothermic peaks in the range of 800-870°C at the beginning of 10h of milling could be due to the formation of  $\text{Ni}_3\text{Al}$  phase during heating [20]. The temperature of the exothermic peaks decreased with increasing milling times, due to the gradual increase of strain energy introduced into the Ni-Al mixture by mechanical alloying [18].

#### 4. CONCLUSIONS

Powder mixtures with  $\text{Ni}_{75}\text{Al}_{25}$  (at %) composition have been mechanically alloyed in a planetary ball mill.  $\text{Ni}_3\text{Al}$  intermetallic compound was successfully formed after 10h of milling with the absence of Al phase. XRD patterns have revealed refinement of crystallite sizes and gradual increase of internal strain in the milled powder with increasing milling duration. The nanocrystalline  $\text{Ni}_3\text{Al}$  with its crystallite size of 12.6nm was formed after 40h of milling. The resulted morphology of the milled powder shows a reduction of particles size which is in accordance with the XRD patterns. The particles have changed from flaky to equiaxed morphology and agglomerated at final stage of

milling. The particles have undergone incidents of welding, microforging, fracturing, rewelding and agglomeration. Formation of Ni<sub>3</sub>Al was an exothermic process whereby Al element has fully reacted with Ni element to form this intermetallic compound via a spontaneous reaction. The gradual decrease of temperature of all exothermic peaks as a function of milling time is due to the increase of strain energy introduced into the Ni-Al mixture during MA.

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