

NANOSTRUCTURED ALLOYS AND MECHANICAL ALLOYING

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ABSTRACT

NANOSTRUCTURED ALLOYS AND MECHANICAL ALLOYING. This paper reviews the formation of nanostructured alloys, recent development of nanocrystalline magnesium alloys and their nanocomposite synthesized via mechanical alloying. Though mechanical alloying was developed for the processing of oxide dispersion strengthening super-alloys, this technique offers the possibility of producing very fine crystallite size down to the nano-scale with flexibility in alloying so that the mechanical properties of the final composite can be tailored.

Key words : Nanostructured Alloys, mechanical alloying.

ABSTRAK

PADUAN BERSTRUKTUR NANO DAN PEMADUAN MEKANIK. Makalah ini membahas pembentukan paduan berstruktur nano, perkembangan mutakhir paduan magnesi-nano-kristalin dan nanokomposit yang dibuat dengan teknik pemaduan mekanik. Dengan teknik ini dimungkinkan untuk membuat bahan berukuran butir nano dengan komposisi pemaduan yang diinginkan, sehingga sifat mekanik komposit yang dihasilkan dapat direkayasa sesuai kebutuhan.

Kata kunci : Paduan berstruktur nano, pemaduan mekanik

INTRODUCTION

The mechanical alloying process was invented at INCO's Paul D. Merica Research Laboratory around 1966. The initial attempt was to develop a material by combining oxide dispersion strengthening with gamma prime precipitation hardening in a nickel-based superalloy for gas turbine applications and other heat resistant alloys [1-10]. As the oxides could not be dispersed in the liquid phase, a solid state processing technique was therefore needed. In the early 1960s, INCO's Paul D. Merica Research Laboratory had successfully coated nickel onto graphite surface using this technique. The coated graphite particulates were injected into molten aluminium alloys using an argon sparging gas [11]. At this stage, this process was referred to as "milling/mixing". The term "mechanical alloying" was later introduced by E. C. MacQueen in the late 1960's [12]. The method has also been recognized as one of the novel techniques in the synthesis of new alloys. Since the discovery of formation of amorphous materials by Koch *et al.* [13], it is the first time that such alloys were produced when a mixture of elemental metal powders was mechanically alloyed in an inert gas atmosphere.

Recent years mechanical alloying has been applied to the magnesium alloys since they are the lightest metallic materials. However, as a result of the nature of its hexagonal close-packed structure, ductility of Mg is generally low. Improvement in ductility is hence a pressing necessity to enable Mg alloys to be acceptably used in structural applications. It has been known that ductility of Mg alloys is affected by grain size. Higher ductility and strength can be obtained when the grain size is reduced typically to less than about 10 μm [14].

Several methods such as mechanical alloying or mechanical milling, vapour deposition, equal channel angular deformation and recrystallization of amorphous can be used to produce the nanostructured materials. Among these techniques, reduction in grain size through mechanical milling has so far been most impressive [15-17]. Studies have demonstrated the possibilities of forming different nanocrystalline materials via a simple mechanical alloying technique [18-23].

This paper intends to review the current status of mechanical milling in the synthesis of Mg alloys and composites.

PROCESSING CONTROL AGENT

One of difficulties in processing Mg alloys via the use of MM is oxidation whereby the materials may catch fire or even explode. Protection from oxidation in the process is essential. Milling of Mg alloys is generally carried out in an Ar or vacuum chamber or milling jars. Powders are loaded into the milling jar under the protection of Ar.

Process control agent (PCA) must be used to prevent excessive cold welding. The amount of PCA required depends on the chemical composition of the materials and speed of milling. The amount determines the size of the powder particles and reaction rate of the milling process.

Fig. 1 shows the change in powder particle size of Mg as a function of the amount of stearic acid which is the most commonly used PCA. It can clearly be seen that the higher the amount of PCA, the smaller the Mg particle size. Although high percentage of PCA may effectively reduce the particle size, it also lowers the reaction rate. Fig. 2 shows the change in particle size using polyethylene glycol as PCA. The efficiency of

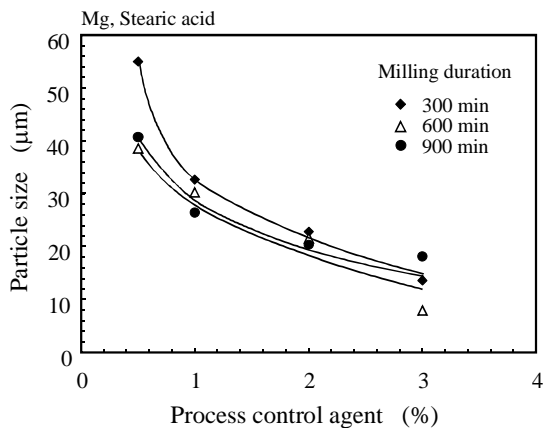


Figure 1. Average Mg particle size using stearic acid [25].

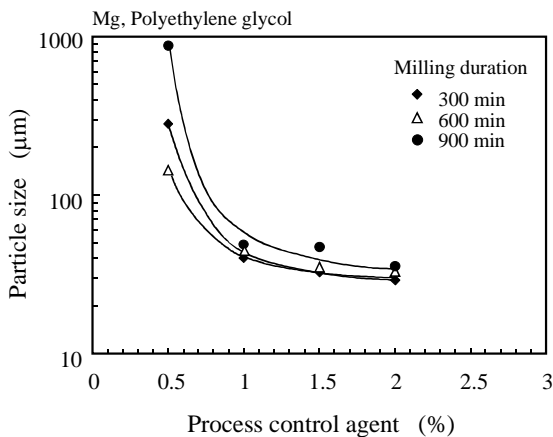


Figure 2. Average Mg particle size using polyethylene glycol [25].

polyethylene glycol is much lower in comparison with stearic acid.

FORMATION OF NANOSTRUCTURED MATERIALS

Transmission electron microscopy study has shown that crystals in the deformed powder particles are heavily strained in a rather inhomogeneous manner. Shear bands which are typical of deformation mechanism occurring at high strain rates in contrast to slip and twinning mechanisms at low and moderate strain rates have been observed. These shear bands, separated by areas of similar lateral dimensions in the micron range, have low defect densities consisting of individual grains with a diameter of 20 nm and are slightly rotated with respect to each other at a rotation angle of less than 20° [24]. The elemental processes of mechanical alloying leading to grain size refinement include the following three basic stages [24]:

- The deformation is localized in shear bands consisting of an array of dislocations with high density. This is accompanied by atomic level strains which may increase up to 3% for the compound phases.
- At a certain strain level, these dislocations annihilate and recombine as small angle grain boundaries separating the individual grains. The subgrains formed via this route are in the nanometer size range. During further collision the column having small grains extends throughout the powder particles.
- The orientations of the grains with respect to their neighbouring grains become completely random.

Coarse grained structures may be refined into very fine crystalline structure by a special treatment called hydrogenation, disproportionation, desorption and recombination process (HDDR) [31-34]. In the original HDDR process, nanocrystalline materials may be synthesized through two steps:

- decomposition of the intermetallic compound $A_{1-x}B_x$, where A and B are a hydride former and a non-hydride former respectively, into a hydride AH_x and the other B-rich $A_{1-x-y}B_x$ compound or pure element B via hydrogenation;
- realloying between element A produced by the decomposition of AH_x , and B-rich $A_{1-x-y}B_x$ compound or pure element B.

These two steps can be completed via mechanical alloying and a suitable thermal treatment [35].

Another method to fabricate more stable nanocrystalline phase is to anneal the amorphous structure at around the glass transition temperature or to mechanically crystallize the amorphous phase. The most important consideration here is to control grain growth rate of crystallized structure.

$$f_v = N_v \frac{D_n}{a^2} \exp\left(\frac{Q}{kT}\right) \quad (1)$$

where Q is the activation energy for the formation of a nucleus of critical size, D_n , diffusivity, a , the size of the particle and N_v , the number of atom per unit volume. Activation energy can be calculated using:

$$Q = \frac{16\pi}{3} \frac{\gamma_{a \rightarrow c}}{\Delta G_{a \rightarrow c}} \quad (2)$$

where $\gamma_{a \rightarrow c}$ is the amorphous-crystal interfacial energy and $\Delta G_{a \rightarrow c}$, the free energy difference between amorphous and crystal phase.

STRUCTURAL EVOLUTION DURING MECHANICAL ALLOYING

Structural evolution of powder is usually characterized by X-ray diffraction technique, such as shown in Fig. 3 of the XRD diffraction spectra of the simple Mg5wt.%Al system after 10 and 20 hours of milling. Broadening of the Mg peaks indicate a reduction in the crystalline size as the milling process progresses. Formation of $\text{Al}_{12}\text{Mg}_{17}$ can be observed after a short time of milling. However, it disappears after 20 hours of milling.

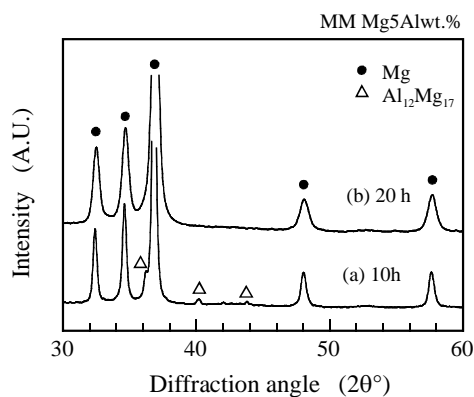


Figure 3. XRD spectra of Mg5%Al.

Crystalline size can be found based on the concept of x-ray line broadening. Peak broadening at half height intensity of the x-ray diffraction patterns is induced by a reduction in crystalline size, faulting and microstrains within the diffracting domains. In mechanical alloying or milling, the powder particles are subjected to plastic microforging. Fig. 4 shows an example of a broadened x-ray spectrum

One method to estimate crystalline size is to use the Scherrer equation [26]:

$$\beta = \frac{\zeta\lambda}{d_c \cos \theta} \quad (3)$$

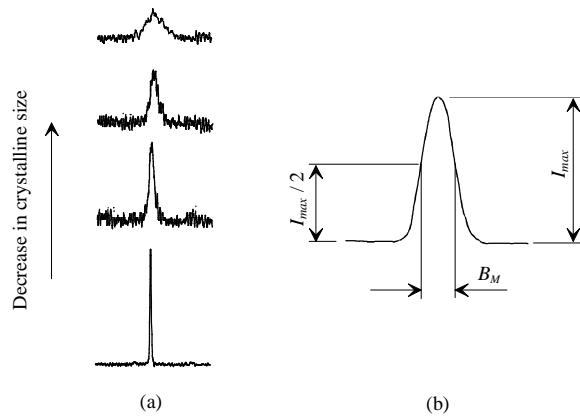


Figure 4. Broadened x-ray spectrum [25].

where β [rad] is the broadening of the diffraction peak due purely to crystalline size measured at half its maximum intensity, d_c , diameter of crystalline size and ζ , constant. The constant ζ depends mainly on the crystalline shape and the indices. It has a value of about 0.9. The validity of Scherrer's equation has been subsequently borne out by different investigators [27-29]. In recent years, this equation is widely accepted for the evaluation of crystalline size down to nanometer.

STRUCTURAL EVOLUTION DURING MECHANOCHEMICAL MILLING

McComic [36] first used mechanochemical milling to reduce Cu from CuO through displacement. The work has been extended to different metallic and non-metallic materials.

Recent two examples of mechanochemical milling of Mg based alloys are the in-situ TiC [37] and MgO nanocomposites. In-situ TiC was formed during mechanochemical milling of Mg-Ti-C. Very fine TiC particles were embedded in the Mg nanograins. It was found that although the mechanically milled Mg and TiC composite has slightly higher yield stress, its ductility is very low compared to in-situ Mg-Ti-C nanocomposite.

Formation of nanocomposite via reduction of TiO_2 by Mg has been successfully carried out by the present authors. Fig. 5 shows the XRD spectra of the powder mixture with stoichiometric composition after different durations of milling [21]. After 10 hours of ball milling, as shown in Fig. 5 (b), the diffraction peaks of TiO_2 and Mg have been reduced significantly. Peaks of MgO at the same time start to appear. Since the MgO peak is broad, it is suggested that fine MgO crystallite has been formed. After 20 hours of milling, almost no TiO_2 peaks could be detected as shown in Fig. 5 (c). This implies that all the TiO_2 present in the reactant mixture has been reacted. Concurrently, Mg peaks start disappearing even though the (101) Mg peak is still visible

and peaks of MgO are observed to increase in intensity suggesting that some amount of Mg is reacting with TiO₂. There is no significant difference in the diffraction spectra of the powder mixtures mechanically alloyed for 30 to 60 hours (Figs. 5 (d) to (f)). Grain size of Mg decreases to about 30 nm after just 10 hours of milling. About 20 nm size has been achieved after 20 hours of milling. Although TiO₂ is more or less fully reduced, no Ti diffraction could be seen from the figure. It is possible that Ti exists but without crystallinity or its particle size is too fine to be detected by XRD.

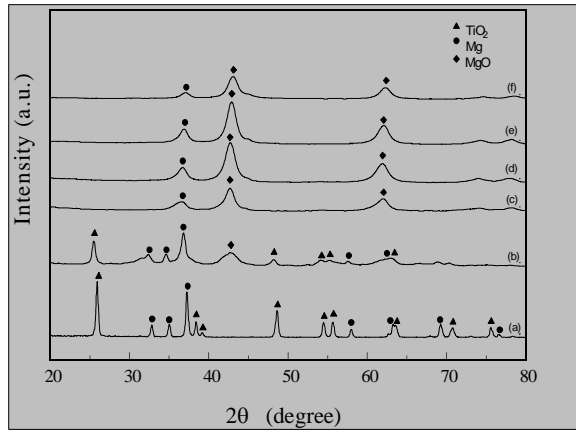


Figure 5. XRD spectra of powder mixture with stoichiometric composition after different durations of milling

CONCLUSIONS

Mechanical alloying has now been recognized as a unique technique. It has been utilized in different areas of material processing and applied to many different material systems. Oxide dispersion strengthened materials, composites, amorphous, nanocrystalline alloys, intermetallic compounds, non-equilibrium materials and ceramics have all been successfully synthesized, an achievement not possible by means of traditional techniques.

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REFERENCES

- [1]. J.S. BENJAMIN, *Mechanical alloying-history and future potential, Novel Powder Processing Adv. In Powder Metall.*, **7** (1992), Proc. of the 1992 Powder Metallurgy, World Congr., San Francisco, CA, USA, 21-26 June (1992), Publ. Metal Powder Industries, 155-168.
- [2]. R.M. DAVIS and C.C KOCH, *Scripta Metall.* **21** (1987), 305.
- [3]. S. ZHANG, K.A. KHOR and L. LU, *J. Mater. Proc. Tech.*, **48** (1995), 779.
- [4]. R.M. DAVIS, B.T. McDERMOTT and C.C. KOCH, *Metall. Trans.*, **19A** (1988), 2867.
- [5]. D. LEE, J. CHENG, M. YUAN, C.N.J. WAGNER and A.J. ARDELL, *J. Appl. Phys.*, **64**, 4772.
- [6]. J.S. BENJAMIN, *Met. Constr. Mech.*, **104** (1972), 12.
- [7]. J.S. BENJAMIN, Dispersion-strengthened electrical heating alloys by powder metallurgy, US Patent #US3 660 049, May 2, 1972.
- [8]. J.S. BENJAMIN, Powder metallurgical products, British Patent #1 298 944, December 6, 1972.
- [9]. J.S. BENJAMIN, R.L. CAIRNS and J.H. WEBER, Hot working, heat resistant alloys, S. African Patent #7 104 328, February 21, (1972).
- [10]. J.S. BENJAMIN, Dispersion-hardened nickel-chromium-cobalt wrought alloy, German patent #2 223 715, December 21, (1972).
- [11]. J.S. BENJAMIN, *Mater. Sci. Forum*, **88-90** (1992), 1.
- [12]. J.S. BENJAMIN, New Materials by Mechanical alloying Techniques, DGM Confer., Calw-Hirsau (FRG), Oct. 1988, Ed. E. Arzt and L. Schultz, Informationsgesellschaft Verlag, 3.
- [13]. C.C. KOCH, O.B. CALVIN, C.G. MCKAMEY and J.O. SCARBROUGH, *J. Appl. Phys. Lett.*, **43** (1983), 1017.
- [14]. H. WATANABE and T. MUKAI, *Scripta Mater.*, **40** (1999), 477.
- [15]. C.C. KOCH and J.D. WHITTENBERG, *Intermetallics*, **4** (1996), 339.
- [16]. C. SURYANARAYANA, *Inter. Mater. Rev.*, **40** (1995), 41.
- [17]. Y. CHEN and J.S. WILLIAM, *J. Alloys Comp.*, **217** (1995), 181.
- [18]. D.G. MORRIS and M.A. MORRIS, *Mater. Sci. Eng.*, **A104** (1988), 201.
- [19]. G. COCCO, S. ENZO, L. SCHIFFINI and L. BATTEZZATI, *Mater. Sci. Eng.*, **97** (1988), 43.
- [20]. H.J. FETCH, E. HELLSTERN, Z. FU and W.L. JOHNSON, *Adv. in Powder Metall.-1989, Comp. T.G. GASBARRE and W.F. JANDESKA, Jr., Publ. Metal Powder Industries Federation*, Princeton, N.J., **2** (1989), 111.
- [21]. F.H. FROES and C. SURYANARAYANA, *JOM*, **41** (1989), 12.
- [22]. E. HELLSTERN, H.J. FETCH, C. GARLAND and W.L. JOHNSON, *Multicomponent Ultrafine Microstructures*, Ed. L.E. Mc. CANDLISH, D.E. POLK, R.W. SIEGEL and B.H. KEAR, *Publ. Mater. Res. Soc.*, Pittsburgh, PA, **132** (1989), 137.
- [23]. A.R. YAVARI, *Mater. Sci. Eng.*, **A179/180** (1994), 20.

L. PATTERSON, *Phys. Rev.*, **49** (1936), 884.
Lu, M.O. LAI, Y.H. TOH and L. FROYEN, *Mat.
i. Eng.*, in press.
K. MUKHOPADHYAY, C. SURYANARAYANA
and F.H. FROES, *Proc. of the 2nd Intern. Confer.
Structural Applications of Mechanical
Joining*, Vancouver, Canada, Ed. J.J. deBarladillo,
I. FROES and R. SCHWARZ, *Publ. ASM Intern.,
Materials Park*, 20-22 Sep. (1993), 131.
TAKESHITA and R. NAKAYAMA, *10th Intern.
Workshop on Rare-Earth Magnets and Their
Applications*, Kyoto, (1989), 551.
L. HARRIS and P.J. McGUINNESS, *J. Less.*