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Mesoscopic Material Design for Environmentally Benign Manufacturing and Materials Processing

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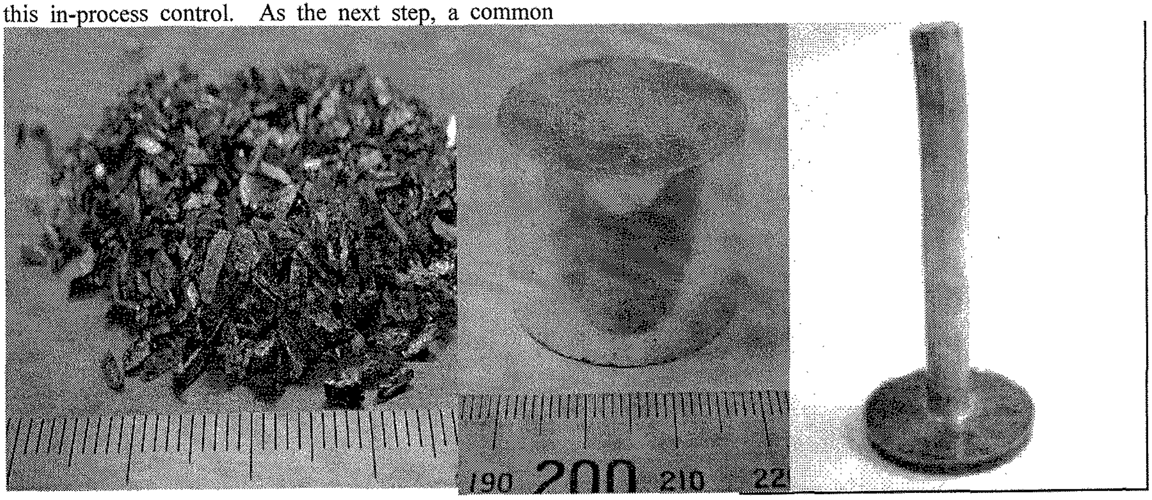
Maximization of materials efficiency is one of goals for the environmentally benign manufacturing and materials processing. Key essential items in the mesoscopic design are considered as a common knowledge base to develop the material circulation processes for ecomaterialization. In-process grain size refinement is the first item to have a unique microstructure for enhancement of deformation, stress transfer and solid state synthesis. As the second item, secondary phase materials are in-situ synthesized in sold for strengthening without loss of ductility. Fine, homogeneous distribution of these secondary-phase precipitates is favored for up-grade recycling to targeting products. In the case study, magnesium alloy chips together with pure silicon dusts are employed as a recyclable material model. Through the solid state recycling, fully dense magnesium alloy billets, bars and pipes are produced as Mg_2Si reinforced composite with high strength and ductility.

Key words: Environmentally benign manufacturing, Mescoscopic material design, In-process grain refinement, Solid state synthesis of secondary phase, Fine homogeneous distribution of precipitates, Solid state recycling

1. INTRODUCTION

In the conventional recycling, separation of contaminants, refining and purification become essential process. The can-to-can is a typical phrase to represent the material circulation through recycling. As have been discussed in Refs. [1], the grade of recycled materials is usually deteriorated even in one recycling circulation so that minimization of waste emission should be difficult without in-process improvement of material properties in recycling [2]. Hence, the conventional materials processing or manufacturing are in vain for high qualification to yield the products having higher value. The environmentally benign manufacturing stands on the in-process microstructure control to improve the functional quality in the final products [3]. Saving the energy consumption and reducing the alloying elements become the first step in this in-process control. As the next step, a common in-process microstructure control to various recyclable materials must be developed to enlarge the material selection. To satisfy the quality demand as a product, new method is necessary to improve the strength without significant loss of ductility and toughness only by using the starting materials.

In the present paper, mesoscopic materials design for upgraded recycling is proposed to accept recyclable chips and dusts as a starting material and to fabricate the bulk billets and rods with controlled microstructure for secondary forming to small-sized parts and components. Grain size refinement is a common step to preserve the ductility by grain boundary sliding mechanism at low temperature [4]. In-process solid-state synthesis of secondary phase is the second item to improve the strength without loss of ductility by its fine, homogeneous distribution in the matrix [5].



a) b) c)

Fig. 1: Our developed solid state recycling: a) Starting materials (chips), b) High density powder compact (dense green compact), and c) Final product after secondary process (extruded bars).

In order to demonstrate the effectiveness of the above mesoscopic design frame, the solid-state recycling is employed. The magnesium alloy chips as well as the silicon dusts are selected as a starting material to yield the high strength magnesium base bars. Figure 1 illustrated a typical procedure of the solid-state recycling. During fine mixing and refining by application of repeated intense straining in the bulk mechanical alloying, both magnesium chips and silicon dusts are forced to reduce their size and shaped to high dense green compact. In this solid state recycling, reinforcing precipitates of Mg_2Si are in-situ synthesized. Since these precipitates distribute finely and homogeneously in the matrix, the net-shaped products have higher strength.

2. KEY MESOSCOPIC DESIGNS

Three key mesoscopic design items are selected for the environmentally benign manufacturing and materials processing (EBM). After physical separation, the recyclable wastes have various shapes or morphology. In EBM, reduction of constituent structure size is the first way to be done after separation. Being free from oxidation or inflammation, this grain-size reduction process might well be done in high dense solid.

Consider the case of EBM for magnesium alloys. A single crystal magnesium material has hcp structure with large difference of critical resultant shear stress on the basal and non-basal planes. Hence, polycrystalline magnesium alloys are thought to have insufficient degrees of freedom in kinematics at the room temperature. Being pointed out in Ref. [6, 7], the above mechanically subsidiary conditions change themselves with reducing the average grain size (d).

According to the Hall-Petch relation, strength is improved by decreasing d: $\sigma = \sigma_0 + \kappa \cdot d^{-1/2}$, where σ_0 is the intrinsic strength and κ, the constant which is dependent on the texture. In particular, since the texture advances with grain size refinement, κ for magnesium becomes much higher than that for aluminum. Much importance must be placed on the deformation mechanism change by grain size reduction. That is, the grain boundary sliding mechanism, as well as the non-basal sliding ones, work even at the room temperature. Since the strain compatibility across the grain boundaries is satisfied, fine-grained magnesium alloys have sufficient workability for various metal forming. That is, reduction of constituent size can afford to fix the subsidiary conditions in kinematics of recyclable materials.

In-process solid-state synthesis of secondary phase compounds becomes the second mesoscopic design item. For an example, consider the processing to accept the mixture of two elements (A+B) as an input. Usually, relatively high temperature is necessary to ignite the reaction in processing. In fact, reaction in the self-heating synthesis commences just below the melting temperature of either A or B. Noticeable amount of melts is always generated, so that microstructure of wrought materials is coarsened in the final product [8]. The onset temperature of reaction reduces with grain size refinement, since the fresh interface area between A and B elements, enlarges in the dense material. In other words, homogeneous refining in the microstructure leads to significant reduction of onset temperature for solid-state synthesis.

Homogeneous mixing refining in reducing the microstructure results in fine, homogeneous distribution of in-situ synthesized secondary phase. This microstructure modification is favored for high strengthening. In the case when the nano-sized clusters precipitate in the matrix, their strengthening effect is much enhanced to improve the wear and fatigue resistance. In fact, as discussed in Ref. [9], surface structuring via plasma nitriding succeeded in fine precipitation of CrN nano-particles in the high chromium steel parts, resulting in high surface hardening and strengthening. These precipitates must be easily separated in recycling; since the density of Mg_2Si is 1.9 to 2.0 Mg/m^3, it can be separable from magnesium alloy melts not to increase the amount of contaminants in the starting magnesium alloys.

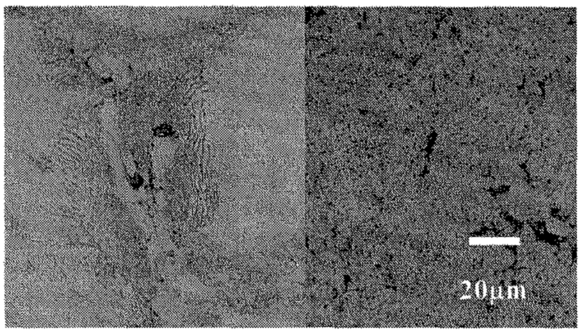
3. CASE STUDY

Solid-state recycling is employed as EBM to accept magnesium chips as well as silicon dusts as a material waste model. Most of magnesium alloy wastes are often crushed to chips or platelets through fragmentizer or crusher. Hence, the chips are the most common morphology of recyclable metallic materials after separation. On the other hand, the wastes coming from silicon wafer have various morphologies: e.g., block, wire, plate or flaky dusts. Most of bulky silicon wastes are frequently recycled to silicon-ingot making or used as an additive in alloying. Silicon flaky dusts have no use in the present recycling market. AZ31 alloy chips and silicon flaky dusts are selected as a starting material for the present experiments in order to demonstrate that mesoscopic material design should be an essential compass for solid-state recycling.

At the presence of aluminum in AZ31 alloy, $Mg_{17}Al_{12}$ intermetallic compounds precipitate as a net-work structure along grain boundary or as a lamellar structure in grains. In the conventional melting and solidification processes, these precipitates grow to deteriorate the mechanical properties. Homogeneous refining of this precipitate phase must be accompanied with the grain size refinement.

As illustrated in Fig. 1, the developed solid recycling has two stages: green-forming process and hot shaping process. In the former, the bulk mechanical alloying (BMA) is used for homogeneous mixing and refining. Different from the conventional ball-milling or attriting, the starting materials are poured into a die cavity and subjected to cyclic loading. One pass schedule has two compression modes and one forward extrusion mode. In this repeated plastic working, the starting materials are forced to elongate or fracture into fragments and to recombine into solid. This intense straining takes place in the inside of a die cavity although the process so that the refined magnesium alloys should never be inflammable. Final product after BMA is a high dense powder compact or green body with the relative density of 85 to 90 % T.D.

Figure 2 depicts the variation of microstructure with increasing the number of cycles (N) in this process. Since intense plastic straining is applied in the repeated manner during the process, the original microstructure of AZ31 alloy with $Mg_{17}Al_{12}$ precipitates are fractured and refined with N. The characteristic peak intensity to $Mg_{17}Al_{12}$ also decreases with N; a part of intermetallic compounds resolved into matrix.



a) N = 0 b) N = 500

Fig. 2: Homogeneously refining of microstructure with increasing the number of cycles in BMA.

The above refinement of $Mg_{17}Al_{12}$ precipitates or partial solid solution of $Mg_{17}Al_{12}$ into matrix, reflect on the variation of strength or hardness with increasing the number of cycles. Figure 3 depicts the variation of measured hardness with increasing N. When N = 0, since the original microstructure is heterogeneous, high hardness is experienced for $Mg_{17}Al_{12}$ compound layer but lower hardness is measured in the matrix. This difference in hardness disappears when increasing the number of cycles up to N = 100. Abrupt increase of hardness comes from the homogenous refinement of intermetallic compounds. Gradual increase of hardness after N $\geqq$ 100 is attributed to solid solution of $Mg_{17}Al_{12}$ into matrix as well as its refining in matrix.

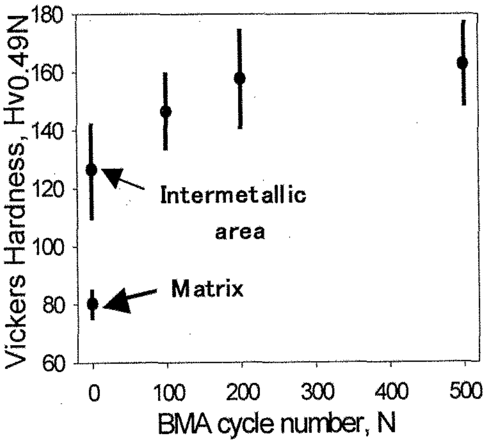


Fig. 3: Strengthening of refined AZ31 alloy with increasing the number of cycles in BMA.

When starting from the AZ31 alloy chips, only grain size refinement takes place uniformly with increasing N. Without the secondary phase to be working as a pinning site, the refined microstructure could be coarsened easily at the elevated temperature. Self-heating synthesis (SHS) often takes place even in the room temperature for the nano-sized powder mixture. This type of SHS results in partial reaction into compounds because of insufficient heat conductivity among powder particles. In order that the solid-state reaction should be sustained in the whole materials, the solid medium has dense, fine-grained microstructure. In BMA, homogeneous mixing and refining advances with N, preserving high relative density. That is, the new fresh surface of particles is generated by the application of intense shear straining at the forward extruding stage of BMA, and, these refined particles with fresh surface are recombined into dense solid at the compression stage of BMA. Since the above process continues till the specified number of cycles, the fresh interface area between two elements increases with N.

As before mentioned, in the case of pure magnesium and silicon mixture, no reaction to Mg_2Si takes place below the melting point of magnesium. At the interface between refined magnesium and silicon particles, local reaction might be ignited at the lower temperature. Figure 4 shows the variation of DTA (Differential Thermal Analysis) diagrams with increasing N. When N = 0, the exothermic peak is present at the vicinity of melting point for magnesium but no peaks exist in the lower temperature side. Increasing the number of cycles up to N = 150, the exothermic peak shifts to the lower temperature side. XRD (X-Ray Diffraction) profile measured at 623 K reveals that only Mg_2Si is synthesized in the single phase. The calculated enthalpy ($\Delta H = 96$ kJ/mol) is in fairly good agreement with the reference data ($\Delta H = 89$ kJ/mol) for the reaction of $2Mg + Si \rightarrow Mg_2Si$. Solid-state reaction to Mg_2Si is ignited at 473 K from the BMA mixture of Mg and Si particles.

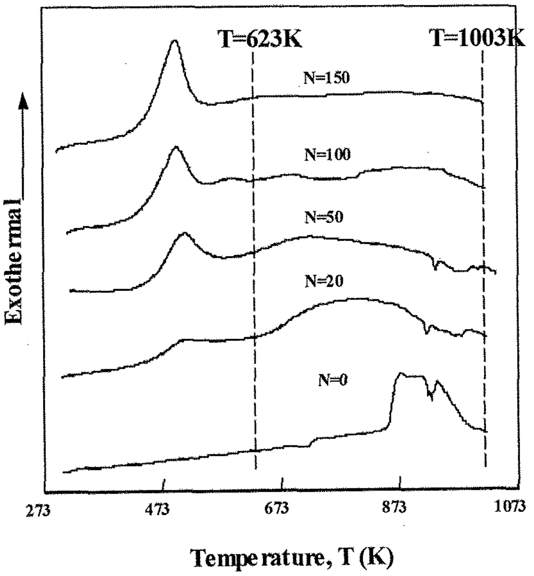


Fig. 4: Reduction of onset temperature for solid-state reaction in the system of Mg-Si.

This reduction of onset temperature for reaction is attributed to in-situ formation of Mg_2Si cluster, which plays as an intermediate phase to activate the solid-state reaction. As shown in Fig. 5, TEM micrograph reveals that these clusters with the size of 20-40 nm finely distribute to play as a nucleation site of reaction. With further increasing the number of cycles, simultaneous reaction could take place from these clusters in the matrix if the materials have enough thermal conductivity to sustain the reaction. More importance lies in the uniform, homogenous distribution of clusters. This cluster is synthesized to have nearly the same size of original silicon particle during the process. Hence, refinement of silicon particle size with increasing the number of cycles reflects on the fine distribution of Mg_2Si clusters.

Figure 6 depicts the variation of both the yield and ultimate strengths with increasing the number of cycles. When N = 0, Mg_2Si is synthesized but their size is coarsened partially because the reaction is accompanied with magnesium melts. In addition, these coarse Mg_2Si agglomerate and segregate into a block, which is easy to break away. Little strengthening is expected for this type of reaction even when starting from the fine magnesium and silicon powder mixture. On the other hand, the ultimate strength as well as the yield strength, increase with N; e.g., the ultimate and yield strengths reach 350 MPa and 300 MPa, respectively. This high strengthening is attributed to alignment of fine Mg_2Si precipitates along the extrusion direction.

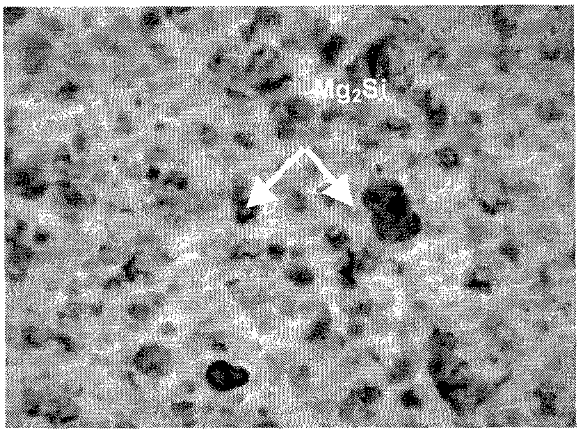


Fig. 5: Formation of Mg_2Si cluster as an embryo for nucleation of solid-state reaction.

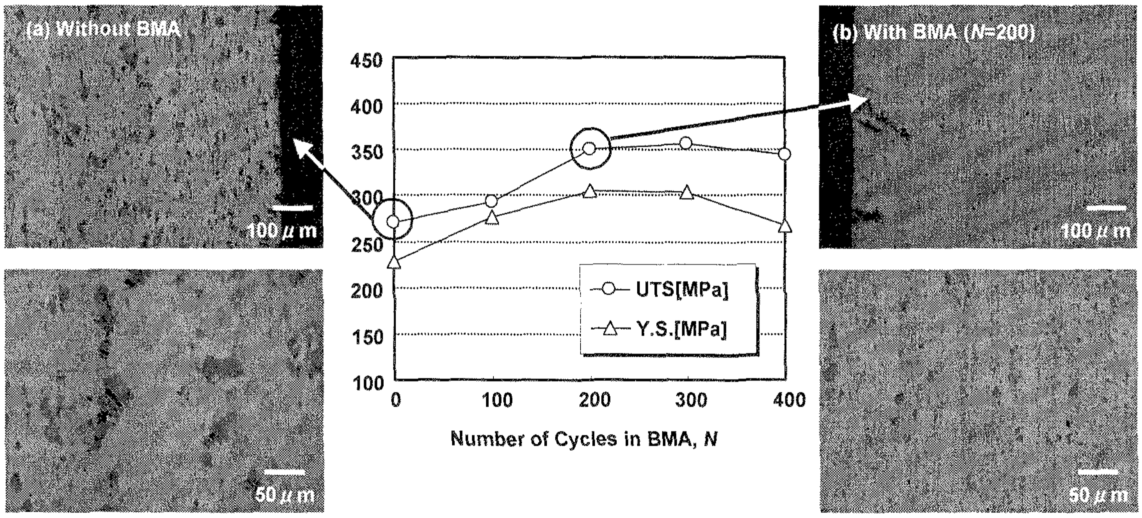


Fig. 6: Variation of the yield and ultimate strengths with increasing the number of cycles in the solid-state recycling.

4. CONCLUSION

On the basis of mesoscopic materials design, various recyclable wastes are accepted as an input for environmentally benign manufacturing and materials processing to fabricate the highly qualified structural parts and components. Success in solid-state recycling from magnesium chips and silicon dusts to yield Mg_2Si reinforced magnesium alloy billets, reveals that mesoscopic materials design should be a key to link the acceptable market demand with the recyclable materials.

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[References]

[1]T.G. Gutowski: Mater. Trans. 43 [3] (2002) 282-284.

[2]T. Aizawa, K. Halada and T.G. Gutowski: Mater. Trans. 43 [3] (2002) 390-396.

[3] K. Kondoh and T. Aizawa: Mater. Trans. 44 [7] Mater. Trans. 1276-1283.

[4] T. Aizawa, T. Luangvaranunt and K. Kondoh: Mater. Trans. 43 [3] (2002) 315-321.

[5] K. Kondoh, T. Luangvaranunt and T. Aizawa: Mater. Trans. 43 [4] (2002) 322-325.

[6] T. Aizawa and K. Kondoh: Proc. Int. Symp. Ecomaterials and Ecoprocess. COM-2003 (Vancouver, Canada, Aug. 27th, 2003) (in press).

[7] J. Koike: Private communication (2003).

[8] K. Kondoh, H. Oginuma, E. Yuasa and T. Aizawa: Mater. Trans. 42 [8] (2001) 1293-1300.

[9] N. Granito, H. Kuwahara and T. Aizawa: J. Mater. Sci. 37 (2002) 835-844.

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