NANOPARTICLES DISTRIBUTION AND MECHANICAL PROPERTIES OF ALUMINUM-MATRIX NANO-COMPOSITES TREATED WITH EXTERNAL FIELDS

J. Tamayo-Ariztondo, S. Vadakke Madam, E. Djan, D.G. Eskin, N. Hari Babu, Z. Fan

BCAST, Brunel University, UB8 3PH, United Kingdom

Keywords: Metal Matrix Composites, Nanoparticles, Ultrasonication, Aluminum Alloys

Abstract

Aluminum-matrix nano-composites have been produced after incorporating various hard ceramic nanoparticles (Al_2O_3, AlN and SiC) and Al_2O_3 microparticles into liquid metal by mechanical stirring. The mechanical stirring process is optimized to obtain distribution of nanoparticles in entire volume of the liquid. However, locally, nanoparticle clusters have been found. Application of the ultrasound to the slurry containing nanoparticles resulted in significantly improved particle dispersion and reduced nanoparticle clusters density. Nano-composites have been characterized by optical and scanning electron microscopy to see dispersion enhancement. Hardness was measured to study the local mechanical properties of these composites.

Introduction

Metals and metal alloys play a very important role in the technological development over thousands of years. Metallurgy has become one of the most significant branches of physical and processing sciences. Moreover, it has become a sophisticated research field that has impact on energy, environment, aeronautics, automotive, space, chemistry, construction, computing and health.

The key technical topic that supports the areas of alloying and alloy recycling is solidification, provided that 97% of all metal products are manufactured with at least one solidification processing stage. Light metal alloys (based on magnesium and aluminum) have become increasingly important in materials selection and technology. Many of steel components can be replaced by magnesium- or aluminum-based lighter components, which in the transport sector leads directly to less fuel consumption and reduced CO_2 emissions to the atmosphere. Thus, it implies that light allows are environmentally and economically friendly materials.

Composite materials offer next step in metallic material development that combines benefits of light weight with improved and sometimes unique properties. In last two decades there have been many advances in aluminum and magnesium matrix composites manufacturing technology, in order to enhance mechanical properties of the materials [1, 2]. Orowan strengthening [3–5] as well as grain refinement (Hall–Petch relationship) and the dislocation density (Taylor relationship) [6] is believed to be responsible for improved mechanical properties in nano-composite materials, as compared to conventional composite materials where grain-boundary pinning and structure modification are main strengthening mechanisms.

Aluminum- and magnesium-based composites became a major research topic, especially relevant to saving weight in aerospace and automotive components. Powder metallurgy and other solid-state processing routes are widely used yet have limitation in shapes and volumes of final parts. That is why a liquid-metal route when a composite is first prepared in the liquid state and then cast into a billet or in a final shape is technologically most promising though very challenging. Mechanical stirring is a usual way of introducing the reinforcement into the melt, but the particles, especially of small size, are clustered [7].

The great challenge of the metal matrix composites is to achieve a good dispersion of the reinforcements throughout the bulk composite. Ultrasonic cavitation and streaming are identified as one of the most promising external fields for improving the dispersion of reinforcing particles in the liquid state [8–13].

The development in nanoparticles manufacturing technology has had considerable breakthroughs in the recent years. Addition of hard nano-ceramics can give dramatic increase in strength of light-metal matrix [6, 14–17]. In this case, the ultrasonic technology plays an important role as it may enhance the wettability of the nanoparticles with the matrix metal [15, 19], in addition to a proper dispersion of the nanoparticles into the melt [15, 17, 20-21].

The real challenge in the current state-of-the art is the upscaling of the nano-composite technology. Most of the published studies report results obtained on 100–150 g of melt treated with ultrasonic cavitation for up to 45 min. Obviously, this is not a technological approach – whatever good results have been produced. Therefore in our research, we intentionally limit the time of processing simultaneously increasing the treated melt volume.

In this work, two types of aluminum alloys have been used as matrices and the distribution of several types of nano- and microparticles has been studied by microscopy. Also, the mechanical properties of these composites were assessed by Brinell.

Experimental Procedure

Two different aluminum alloys were used in this work as matrices: a commercial 6XXX-series wrought alloy and a model Al–10% Cu–2% Mg alloy. These alloys belong to different types, i.e. a low-alloyed solid-solution type (6XXX) and a high-alloyed hypoeutectic type (Al–Cu–Mg).

Different nano- and microparticles were used as reinforcements as listed in Table 1. The selection is quite typical for reinforcement of aluminum alloys. The percentage of addition has been either 0.5 or 1 wt%. Al_2O_3 and AlN nanoparticles have been supplied by Tomsk State University, SiC nanoparticles by Electro Abrasives, and Al_2O_3 microparticles by Alpha Aesar.

Addition of the nanoparticles and initial mixing was performed with a titanium impeller powered by a stirrer (IKA Eurostar 60) at 300–400 rpm. Ultrasonic processing was performed by submerging a Nb horn in the melt. The working amplitude was 30–35 μm at 17.5 kHz and a Reltec water-cooled magnetostrictive transducer fed from a 5-kW ultrasonic generator was used. The processing was performed in a 1-kg melt volume inside a clay-graphite crucible with subsequent casting in a steel book mould.

The processing conditions were varied depending on the alloy, with the aim to optimize processing parameters.

Table 1. List of reinforcements used in this work**.**

Particle type	Maximum particle size, nm
Al_2O_3	<100
AlN	<100
SiC	<700
α-Al_2O_3	1000

Tables 2 and 3 summarize the processing parameters for 6XXX and Al–Cu–Mg composite alloys, respectively. The reference samples without reinforcement were also produced using the same process parameters.

Table 2. Processing stages and temperatures for 6XXX-based composites.

Reinforcement	Addition+mixing (ºC)	Ultrasound (5 min) (ºC)	Cast (ºC)
Reference	755	720	700
Al_2O_3	740–677	715	700
AlN	755–705	725	700
SiC	755–706	735	700

Table 3. Processing stages and temperatures for Al–Cu–Mg-based composites.*

Reinforcement	M1 (ºC)	US1 (ºC)	M2 (ºC)	US2 (ºC)	Cast (ºC)
Reference	630	700	720	700	690
Al_2O_3 (1% wt)	680-620	700	720	710	685
Al_2O_3 (0.5% wt)	660-630	685	700	730	720
AlN (1% wt)	660-620	710	720	740	730
AlN (0.5% wt)	630-620	725	715	750	728
α-Al_2O_3 (1% wt)	630-620	700	710	735	730
α-Al_2O_3 (0.5% wt)	657-620	690	725	735	730

* M1: Addition + initial mechanical mixing; US1: Ultrasound 5 min; M2: additional mechanical stirring; US2: Ultrasound 5 min.

Note that addition of the particles was done at different conditions of the melt. In the case of 6XXX matrix, particles were added in the superheated liquid; while in the case of the model Al–Cu–Mg alloy, this was been in the semi-solid state. Moreover, in the case of the Al–Cu–Mg alloy, ultrasonic processing was performed twice, in order to improve the dispersion enhancement. In both cases, melts were cast in the same steel mould.

Optical microscopy (Zeiss Axioscope A1) was used for characterizing the produced composites. Scanning electron microscopy (Zeiss Gemini Supra 35VP SEM) was utilized to have a better idea of how nanoparticles are distributed. Samples were ground by 2500 grid size SiC, polished with OPS and cleaned in an ultrasonic bath to have a clean surface for characterizing properly.

Brinell hardness tests have been conducted after milling of the surface and polishing with 4000 grid size SiC paper. Samples were tested in a Brinell Hardness Tester BH3000, using HBW DM:7.105, application time 5 seconds, dwell time 15 seconds with a 10-mm indenter. A force of 9.8 kN has been applied. Four measurements were taken for Al-Cu-Mg-based composites and 16 – for 6XXX-series composites. Statistical analysis has been performed and average values are reported.

Results and discussion

Characterization of 6XXX-based nanoparticles composites

Figures 1 to 3 show optical microstructures 1 wt% Al_2O_3-, AlN- and SiC-nano-reinforced 6XXX-based composites.
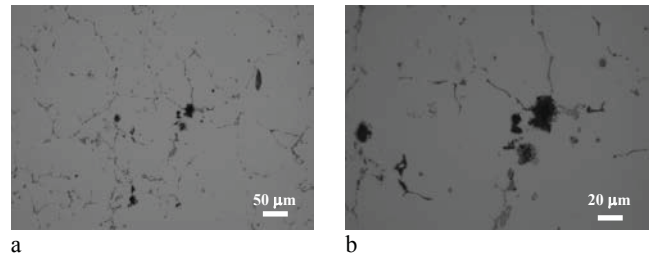

a   b
Figure 1. Optical images at different magnifications of a 6XXX–Al_2O_3 composite.

Clusters of Al_2O_3 nanoparticles are found in the 6XXX–Al_2O_3 composite, ranging from 5 to 25–30 μm in size. There is some evidence that clusters are not totally compact, i.e. some aluminum matrix is inside the clusters.
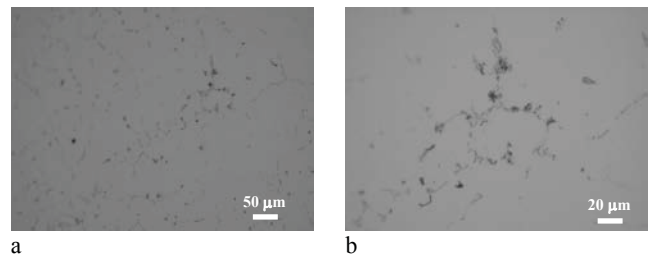

a   b
Figure 2. Optical images at different magnifications of a 6XXX–AlN composite.

Figure 2 shows that there are less clusters of AlN particles in the aluminum matrix. The observed clusters were 5 to 15 μm in size. It whould be noted that addition of AlN nanoparticles to the molten metal was difficult with some portion of the particles being rejected to the melt surface and burned. As are result, a lesser amount of particles (than nominal 1 wt%) was introduced in the composite. Summarizing, less particles have gone into the melt, but their dispersion is better.
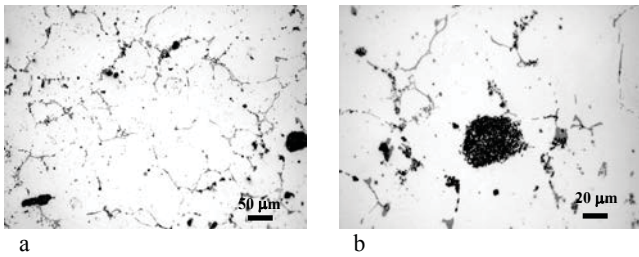
a   b

Figure 3. Optical images at different magnifications of a 6XXX–SiC composite.

In Figure 3, SiC clusters can be clearly seen in the images. A big scatter in the cluster size in the 6XXX–SiC composite is revealed, with clusters ranging from 5 to 60 μm. The aluminum matrix is clearly present inside the clusters.

A common feature found in all the three types of nano-composites: clusters are formed near intermetallics, in this case (AlMnFeSi) and Mg_2Si. Scanning electron microscopy was used to confirm this observations, and for characterizing clusters and nanoparticles.

Figures 4 to 6 gives SEM images of nano-reinforced 6XXX-based composites.

b
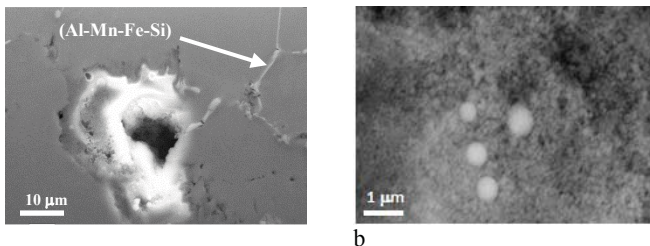
Figure 4. SEM images of the 6XXX–Al_2O_3 composite: a) an alumina cluster, next to intermetallics and b) individual alumina nanoparticles inside the cluster.

Figure 4 shows a cluster of Al_2O_3. The pore inside the cluster on the left-hand photo is a result of nano-particles being taken out during polishing. The photo on right is the same cluster at a higher resolution. One can see a heterogeneous particle size distribution in the cluster. There are many small particles, but there are also a few big particles which are more than 500 nm in size.

In all cases, the particles seem to be spherical. Finally, it is demonstrated that the cluster forms next to (AlMnFeSi) intermetallics, though in other cases these were Mg_2Si particles.
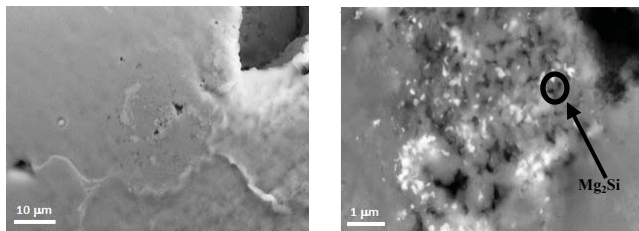

a

Figure 5. SEM images of the 6XXX–AlN composite.

As we already mentioned, the amount of AlN particles that were introduced into the melt was lesser than in the other composites. However, as Figure 5 shows, nanoparticles are present in the matrix. They seem to be smaller than the Al_2O_3 nano-particles

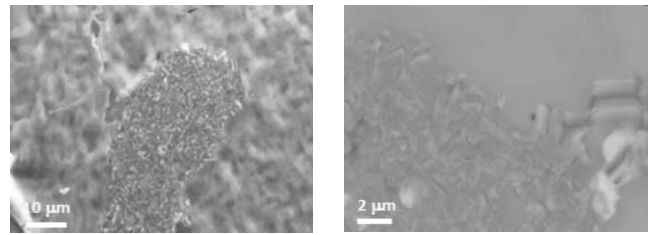and are also spherical. Mg_2Si particles were found between AlN particles.

Figure 6. SEM images of the 6XXX–SiC composite.

In the case of SiC particles (Fig. 6), clusters found are more compact than in the composite with Al_2O_3 nanoparticles. The particles are not spherical; they have a rather rod-like shape. Because of that, particles have a greater specific surface area than the spherical ones. The particle size is quite uniform. The clusters are formed close to (AlMnFeSi) intermetallics.

Characterization of Al–Cu–Mg-based nanoparticles composites

In the Al–Cu–Mg-based composites, similar clusters were observed, usually located next to Al_2Cu and Al_2CuMg intermetallics. Figures 7 to 12 show the microstructures of these composites.
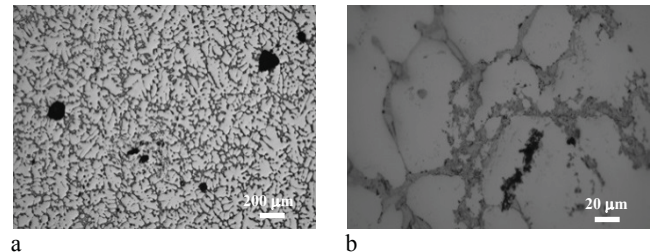

a   b

Figure 7. Optical images of (Al–Cu–Mg)–1 wt% Al_2O_3 composites. Clusters appear near the Al-Cu and (AlCuMg) intermetallics.

For the composites with Al_2O_3, there is a difference in clustering behavior at different amount of added particles. In the case of 1 wt% (Fig. 7), particles big clusters of about 150 μm are observed while large clusters do not appear in the composite with 0.5 wt% particles (Fig. 8).
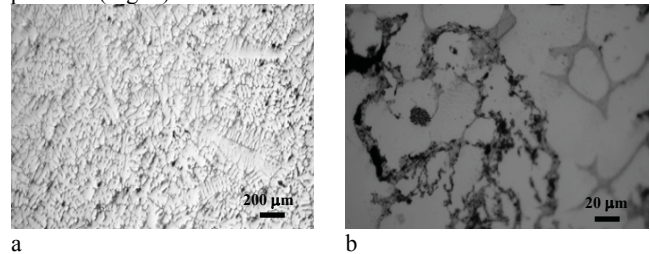

a   b

Figure 8. Optical images of (Al–Cu–Mg)–0.5 wt% Al_2O_3 composites.

Similar trend was observed no AlN-reinforced composites as illustrated in Figures 9 and 10.
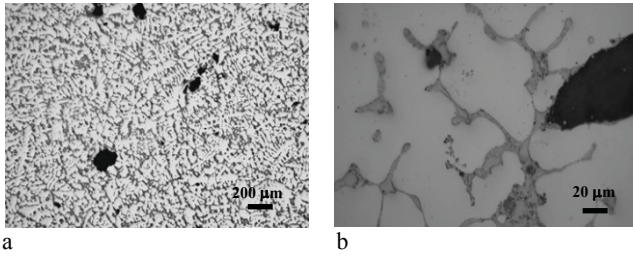
Figure 9. Optical images of (Al–Cu–Mg)–1wt% AlN composites.

As compared 6XXX-based composites, it seems that more AlN nanoparticles have been introduced into the Al–Cu–Mg matrix. This might be because of two reasons. The first reason is the processing conditions: in this second case nanoparticles were introduced into the semi-solid slurry rather than in the superheated melt. Nanoparticles might go into the bulk volume easier in this temperature range due to a larger viscosity and sticking of the particles to the solid matrix crystal.
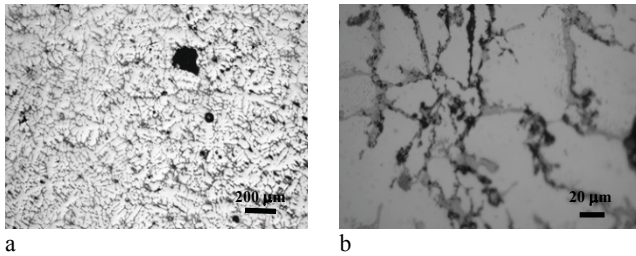

Figure 10. Optical images of (Al–Cu–Mg)–0.5 wt% AlN composites.

The second reason might be a greater volume fraction of eutectic liquid. The particles have tendency to be pushed by the solidifying solid phase to the dendrite boundaries. In the case of more eutectic liquid available, the particles have more opportunity of uniform distribution, sticking with the intermetallics.
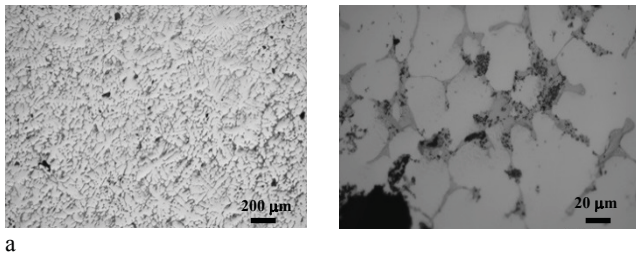

Figure 11. Optical images of (Al–Cu–Mg)–1 wt% α-Al$_2$O$_3$ composites.

Figures 11 and 12 shows optical images of Al–Cu–Mg-based composite with microscopic particles of α-Al$_2$O$_3$, also with 1 and 0.5 wt% reinforcement. The difference in the cluster size between the composites with different particle loading is not as noticeable as in the case of nano-composites.
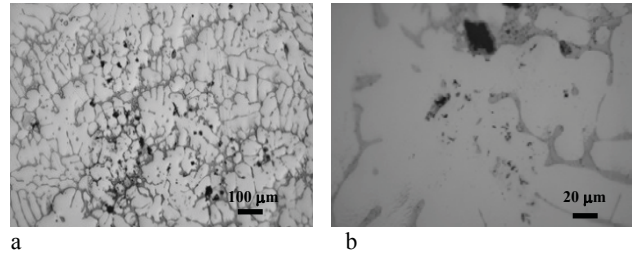

Figure 12. Optical images of (Al–Cu–Mg)–0.5 wt% α-Al$_2$O$_3$ composites.

Mechanical properties of nano-composites

Tables 4 and 5 exhibit the Brinell hardness of 6XXX- and Al–Cu–Mg-based composites, respectively.

Table 4. Brinell hardness 6XXX-based composites.

Reinforcement	Brinell Hardness (HB)
Reference	45±2
Al$_2$O$_3$	56±2.8
AlN	52±1.8
SiC	56±1.4

Comparing to the reference material, there is a sensible increase in hardness, especially with Al$_2$O$_3$ and SiC nano-reinforcement (Table 4). This may be due to the smaller amount of AlN nanoparticles which were introduced into the melt during the addition and mixing of the particles.
In the case of the Al–Cu–Mg composites, the Brinell hardness does not increase much with the addition of particles. This may reflect a more porous microstructure with also more intermetallic particles (Table 5).

Table 5. Brinell hardness of Al–Cu–Mg-based composites.

Reinforcement	Brinell Hardness (HB)
Reference	114±2.4
Al$_2$O$_3$ (1% wt)	122±4.4
Al$_2$O$_3$ (0.5% wt)	118±2.2
AlN (1% wt)	117±1.7
AlN (0.5% wt)	118±1.4
α-Al$_2$O$_3$ (1% wt)	122±1.5
α-Al$_2$O$_3$ (0.5% wt)	116±2.7

Conclusions

Nano- and micro particles were added to 6XXX and Al–10% Cu–2% Mg alloys using mechanical mixing and ultrasonic processing in a considerable volume of 1 kg of melt and with a relatively short processing time. Addition of the particles seems to be easier

in the semi-solid state, though it must be taken into account that addition of nanoparticles depends on the alloy structure. Further research in this matter is required.

Clusters of particles were found in all produced nano- and micro-reinforced composites. Besides, an association of cluster with intermetallics is consistently observed. There might be a preferential association of some particles with particular intermetallic phase.

Concerning mechanical properties, a slight enhancement has been achieved in Brinell hardness. This means that particles were introduced into the matrix, but better dispersion of them is needed along with the lesser porosity.

With taking into account the treated volume and short processing times the results seem to be promising and further optimization of the processing is underway.

Acknowledgement

References

[1] S.G. Tjong and Z.Y. Ma, "Microstructural and mechanical characteristics of in situ metal matrix composites". *Materials Science and Engineering R,* 29 (2000), 49–113.

[2] P.J. Li, E.G. Kandalova, V.I. Nikitin, A.G. Makarenko, A.R. Luts and Y.F. Zhang, "Preparation of Al-TiC composites by self-propagating high-temperature synthesis". Scripta Materialia, 49 (2003), 699–703.

[3] R.J. Arsenault, "The strengthening of aluminum alloy 6061 by fiber and platelet silicon carbide". *Materials Science and Engineering*, 64 (1984) 171-181.

[4] R.J. Arsenault and N. Shi. "Dislocation generation due to differences between the coefficients of thermal expansion". *Materials Science and Engineering*, 81 (1986), 175-187.

[5] R.J. Arsenault, L. Wang and C.R. Feng, "Strenghtening of composites due to microstructural changes in the matrix". *Acta Metallurgica et Materialia*, 39 (1991), 47-57.

[6] Y. Li, Y.H. Zhao, V. Ortalan, W. Liu, R.G. Zhang, R.G. Vogt, N.D. Browning, E.J. Lavernia and J.M. Schoenung. "Investigation of aluminum-based nanocomposites with ultra-high strength". *Materials Science and Engineering A*, 527 (2009), 305-316.

[7] I.A. Ibrahim, F.A. Mohamed and E.J. Lavernia. "Particulate reinforced metal matrix composites – A review". *Journal of Material Science*, 26 (1991) 1137-1156.

[8] G.I Eskin, Yu. P. Pimenov and G.S. Makarov. "Effect of cavitation melt treatment on the structure refinement and property improvement in cast and deformed hypereutectic alloys". *Materials Science Forum*, 242 (1997), 65-70.

[9] G.I. Eskin. "Broad prospects for commercial application of the ultrasonic (cavitation) melt treatment of light alloys". *Ultrasonics Sonochemistry*, 8 (2001), 319-325.

[10] G.I. Eskin and D.G. Eskin. "Production of natural and synthesized aluminum-based composite materials with the aid of ultrasonic (cavitation) treatment of the melt". *Ultrasonics Sonochemistry*, 10 (2003) 297-301.

[11] J. Campbell. "Effects of vibration during solidification". *International Metals Review*, 26 (1981), 71-108.

[12] O.V. Abramov. "Action of high intensity ultrasound on solidifying metal". *Ultrasonics*, 25 (1987) 73-82.

[13] L. Ma, F. Chen and G. Shu, "Preparation of fine particulate – reinforced metal-matrix composites by high-intensity ultrasonic treatment". *Journal of Materials Science Letters*, 14 (1995), 649-650.

[14] B.F. Schultz, J.B. Ferguson and P.K. Rohatgi, "Microstructure and hardness of Al_2O_3 nanoparticle reinforced Al-Mg composites fabricated by reactive wetting and stir mixing", *Materials Science and Engineering A*, 530 (2011) 87-97.

[15] Y. Yang, J. Lan and X. Li, "Study on bulk aluminum matrix nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy". *Materials Science and Engineering A*, 380 (2004) 378-383.

[16] X. Li, Y. Yang and X. Cheng, "Ultrasonic –assisted fabrication of metal matrix nanocomposites". *Journal of Materials Science*, 39 (2004), 3211-3212.

[17] J. Lan, Y. Yang and X. Li, "Microstructure and microhardness of SiC nanoparticles reinforced magnesium composites fabricated by ultrasonic method". *Materials Science and Engineering A*, 386 (2004), 284-290.

[18] T. Yamasaki, Y.J. Zheng, Y. Ogino, M. Terasawa, T. Mitamura and T. Fukami, "Formation of metal-TiN/TiC nanocomposite powders by mechanical alloying and their consolidation". *Materials Science and Engineering A*, 350 (2003), 168-172.

[19] H. Yoshiki, Y. Tsunekawa, N. Mohri, M. Okumiya and I. Niimi, "Influence of ultrasonic vibration on the wettability". *Journal of Japan Institute of Light Metals*, 43 (1993) 8-13.

[20] K. Akio, O. Atshushi, K. Toshiro and T. Hiroyuki, "Fabrication process of metal matrix composite with nano-size SiC particle produced by vortex method". *Journal of Japan.Institute of Light Met*als, 49 (1999) 149, 154.

[21] Cao G, Konishi H, Li X, "Mechanical properties and microstructure of SiC-reinforced Mg-(2,4)Al-1Si nanocomposites fabricated by ultrasonic cavitation based solidification processing". *Materials Science and Engineering A, 486* (2008), 357-362.