Improvement of the properties of light metal matrix Micro/Nanocomposite Materials: myth or reality?

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Abstract
The use of materials reinforced by micro-nanoparticles (MMC) is more and more widespread. According to recent studies, the addition of micro-particles in solid materials (polymers, concrete or metal alloys) gives them interesting properties in terms of thermal conductivity, electrical conductivity and mechanical resistance. These properties open new perspectives in terms of environmental consequences. They allow for example to lighten structures while improving their mechanical characteristics, to increase the performance of electrical conductors by reducing energy losses. We provide an example related to light metal alloys widely used in automotive industry and aeronautics. However, the introduction of particles presents several difficulties. The efficiency of particle addition at liquid state depends on many factors, like their dimension, the type of sedimentation forces and the chemical composition of both liquid alloys and particles:
(i) at the metallurgical level, the particles are often very reactive and may modify the composition and the micro-structure of the alloy, which can be sometimes beneficial and sometimes damaging,
(ii) in terms of scale-up and development of actual processes, the introduction of micro- and especially nanoparticles in liquid phase is a very difficult operation to achieve. Many types of devices are proposed but none is really satisfactory, especially regarding the homogeneity of the materials.
We present some application cases related to magnesium alloys that perfectly illustrate the advantages and disadvantages of MMCs.

Key words : metallic-matrix composites, nano-particules, dispersion of particules, magnesium alloys, electromagnetic stirring

The majority of modern technologies for the production and processing of materials utilize diverse methods to tailor and optimise their properties using suitable volume or surface treatments. It has been recently shown that nano-particles dispersed in a metal could lead to superior properties of materials for electro-technical or mechanical applications. The impact expected from those materials is of major importance, namely (i) substantial enhancement of material properties, e.g. shaping of magnetic hysteresis loops, decrease of magnetic coercivity, increase of yield strength, ductility, surface hardness of metallic sheets, extension of lifetime, increase of operating temperature ranges, and/or (ii) new microstructures via processing of e.g. polymers in electric fields, including controlled dispersion of fillers, and/or (iii) reduction of costs. The dispersion of ceramic particles of micro and nanometric size in metals is a promising method to potentially provide composites with enhanced mechanical properties. Materials reinforced with ceramics, also called ceramic metal matrix composites (MMCs), present a tradeoff in properties due to the direct relation of stiffness and/or strength to the increase of volume fraction of reinforcement particles. For example, studies carried out by Nikhilesh Chawla and Yu-Lin Shen[1] on Al-Cu-Mg (2080) reinforced with SiC particles showed that ductility can decrease significantly when higher percentages of particles are incorporated. Their studies also showed that at same volume fraction the reinforced material presented a better ductility when smaller particles were used. The spatial distribution of the particles plays an important role in the improvement of the mechanical properties of composite materials, and significant improvements in tensile strength and hardening rate may obtained when the particles were well dispersed [1,2].

Various methods are used in order to elaborate composite materials. Elaboration of MMCs faces several major issues like introduction and dispersion of particles, chemical reaction with the alloy elements etc. The introduction of particles into a matrix remains a difficult problem. This is why various solutions are used. For example, the production of so-called ODS steel is achieved at solid state from a mixture of steel powders and particles[3]. The mixture is then compacted and sintered by rolling. Introduction of particles may also be achieved by injection into the liquid matrix. The latter operation is not always efficient since the crossing of the liquid free surface by particles is often difficult[4]. As far as nanoparticles are concerned, an additional issue comes from the trend of those particles to form clusters which are very difficult to de-agglomerate. Furthermore, elaboration of MMCs at liquid state requires an efficient dispersion of particles which conditions the performances of the material. That problem increases when the scale of the process becomes larger and larger. Accordingly, efficient stirring devices are necessary. They may use mechanical stirring, electromagnetic one and/or ultra-sound devices which are efficient to de-agglomerate nano-clusters [5-7].

The electromagnetic stirring provided by a travelling magnetic field (TMF) applied during melting of metals generates a flow that can be controlled in direction and intensity[6]. In principle, particles of different sizes and compositions can be accurately dispersed by controlling the metal flow. The control of the flow can be achieved by modifying the current applied to the electromagnet. However, for micro-particles both gravitational and electromagnetic sedimentation forces lower the ability of such device to produce a satisfactory dispersion. This was shown by experiments dedicated to mixing SiC macro-particles under the influence of TMF in pure magnesium and industrial magnesium alloy AZ91[6].

When industrial alloys are used, the particles may react with the various components. For example, Magnesium alloy AZ91 inoculated with Al_2O_3 particles presented an increase of the number of Al_8Mn_5 intermetallic particles in the alloy which suggest that Al_2O_3 particles served as nucleants for these intermetallic compounds[4]. Moreover, the Al_2O_3 particles react with the matrix material to form magnesium oxide MgO and other intermetallics precipitates like Al_8Mn_5. It turns out that refinement of the sample was obtained thanks to the presence of the bi-product MgO, which acts as a good grain refiner, and not Al_2O_3 particles directly. In that case mechanical tests showed that the presence of Al_2O_3 particles did not improve the hardness nor the tensile strength of the inoculated alloy.

Other tests were performed with a second industrial magnesium alloy: Magnesium ELEKTRON 21. Mg EK21 is a high strength fully heat treatable magnesium based alloy designed to be used for lightweight structural applications subjected to high temperature. Its excellent mechanical properties make this light alloy widely used in automotive and aerospace applications. The composition of magnesium EK21 contains rare earths such as neodymium and gadolinium which provide high strength at high temperatures and also a great potential for precipitation strengthening. Zirconium is also present in its composition and serves as grain refiner, which improves its mechanical properties at ambient temperature and enhances its corrosion resistance. Dispersion-strengthening using ceramic nanoparticles which are theoretically stable at high temperatures, holds a high potential as a method to improve high-temperature properties of magnesium alloys. The reinforcement of metal matrices using ceramic nanoparticles effectively dispersed can be achieved by different mechanisms, such as Orowan pinning of dislocations or by restricting grain boundary sliding[8]. For instance, the dispersion of SiC nanoparticles in pure magnesium using ultrasounds stirring system was carried out by Dieringa[9] produced the improvement of its creep resistance. This feature was related to Orowan strengthening and dislocation generation. Liu *et al*[10] demonstrated that dispersion of nanoparticles of aluminium nitride (AlN) into nanocrystalline aluminium enhanced its elastic modulus and hardness. One of the particularities presented by AlN particles is its lattice parameter which is similar to the one presented by pure magnesium. This feature makes this particle a potential grain refiner for magnesium matrices. Different authors demonstrated that improvement of mechanical properties of particulate reinforced composites highly depends on the good dispersion of the particles within the matrix material[11]. We have carried out a microstructural and mechanical analysis of magnesium EK21-based samples in which nano- particles of AlN were electromagnetically dispersed using a travelling magnetic field. Among the different advantages offered by electromagnetic stirring, the contact-less interaction with the melted material, is of utmost importance in order to avoid melt contamination. Moreover, the sedimentation effects on nano-particles are weak. The capacity to monitor the direction of the flow and therefore the particle distribution patterns as well as the capacity to maintain the stirring until the end of the solidification stand also as decisive assets.

The addition of AlN nanoparticles to magnesium EK21 produces measurable changes in the microstructure and mechanical properties of the material. The first effect observed is an unexpected increase in grain size with respect to the pure material processed under the same casting conditions. The reinforced material presents an average grain size 200% bigger than the average grain size of pure magnesium EK21. The study of the equilibrium reactions of AlN with pure magnesium shows that an amount equivalent to 0.3% in weight of aluminium is released into the magnesium matrix under the casting conditions applied during the experiments. The aluminium dissolves in the melted magnesium and tends to react with the available elements in the alloy such as zirconium which is used in this alloy as grain refiner. The reaction between zirconium and aluminium produces different compounds such as AlZr. The lattice mismatch between zirconium and magnesium is reported to be less than 1%[12] , whereas the lattice mismatch between AlZr and magnesium is approximately 4% which suggest that this particle is not well adapted as a grain refiner of magnesium matrices. The formation of this particle is suspected to reduce the grain refinement effect of zirconium and consequently to be responsible for the increase of the grain size observed. Aluminium was also found in the intermetallic phase rich in Gadolinium and Neodymium. The high difference of electronegativity between aluminium and rare earths leads to a high tendency to form Al-RE compounds. Aluminium compounds containing rare earths such as Al_3Zr have been related to the enhancement of creep strength on different alloys such as Mg-Li-Al[13]. The formation of $AlNd_2$ compounds was predicted by thermodynamic calculations and confirmed during XRD analysis of the materials produced. The presence of aluminium in the intermetallic phase can be also related to the presence of AlN nanoparticles rejected to grain boundaries during solidification. The presence of AlN nanoparticles in grain boundaries has been detected showing that despite of the partial dissolution of the particles during material processing, most of the nanoparticles survived. The presence of particles in the intergranular space could have contributed to the reinforcement of the material related to intergranular reinforcement. Signs of interaction between particles and dislocations, presented as stress variations at the end of the tests, were observed during the compression tests of the samples containing nanoparticles. Finally, the compression tests put in evidence the decrease of the dynamic recovery in the materials reinforced with nanoparticles. This could be a possible evidence of the reduction of annihilation of dislocations by the presence of the particles which could have acted as obstacles for the moving dislocations during recovery. The effects produced in the microstructure and creep resistance by the incorporation of AlN nanoparticles into magnesium EK21 matrices has been assessed. The following conclusions can be drawn: The creep threshold of the samples containing nanoparticles increased with respect to the pure alloy, and the flow stress rose up by 20 % to 50% which supports other studies found in literature.

In conclusions, the development of liquid phase MMCs with good particle distribution homogeneity is a real challenge, especially for large size processes. This partly explains why the performances of these materials are contrasted. In addition to the difficulty of injecting the particles into a liquid metal, the addition of particles does not always lead to any improvement in the performance of the material, as our experiments showed. Finally, as far as industrial alloys are concerned, the particles react chemically with the elements of the alloy and cause unexpected effects.

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