Rev. Adv. Mater. Sci. 31 (2012) 19-24

DEVELOPMENT OF ULTRAFINE-GRAINED ZINC-FERRITE-STRENGTHENED ALUMINUM ALLOYS BY HIGH-ENERGY MILLING

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Received: April 20, 2012

Abstract. The present paper introduces the production route of a new ultrafine-grained zink-ferrite-reinforced aluminium alloy. By high-energy ball milling (Simoloyer ®), a powder mixture consisting of commercial 5083 aluminum and zinc ferrite ($ZnFe_2O_4$) was mechanically alloyed. The resulting composite flakes contain the zink ferrite as small precipitates. After direct hot extrusion compact cylindrical rods were obtained of approximately 200-250 nm grain size. First results of mechanical testing reveal the potential of this kind of ultrafine-grained Al alloys: The yield strength was increased up to 500 MPa at reasonable ductility values (elongation to fracture between 5 and 9%). It is believed that the fine-dispersed ceramic particles stabilize the microstructure even at elevated temperature, allowing for production of high-strength creep-resistant aluminium alloys.

1. INTRODUCTION

Due to the excellent stiffness-to-density ratio, the corrosion resistance and the susceptibility to different kinds of precipitation strengthening, aluminium alloys are the most important light-weight materials in aerospace and automotive industries. However, due to the low melting point aluminium alloys are prone to creep damage at temperatures as low as 100 °C. Above 200 °C, grain growth and coarsening of strengthening phases causes a softening effect and a dramatic loss in creep resistance. MMC alloys (metal matrix composites) produced, e.g., by spray forming [1] or high-energy milling [2,3], may exhibit a stable microstructure when growth of the dispersoids is suppressed by maintaining a low amount of dissolved oxygen or carbon, respectively. Due to the achievement of long-term mechanical strength at elevated temperatures, ODS aluminium alloys (oxide dispersoid strengthened), usually produced by mechanical alloying, are candidate materials for structural light-weight applications, e.g., compressor blades of gas turbines and aeroengines, pistons and con-rods of internal combustion engines as well as bolts, rollers and shafts.

Originally, mechanical alloying was developed to optimize the high-temperature strength of Ni-based superalloys resulting from a combination of the coherent γ' phase and fine-dispersed oxides [4]. During mechanical alloying using the process of high-energy ball milling, the powder mixture of the alloy constituents is exposed to collisions with hardened steel or zirconia balls that are brought in motion by rotating rotors. Fig. 1a shows an example of an operating model ball-milling device (Simoloyer ®) with

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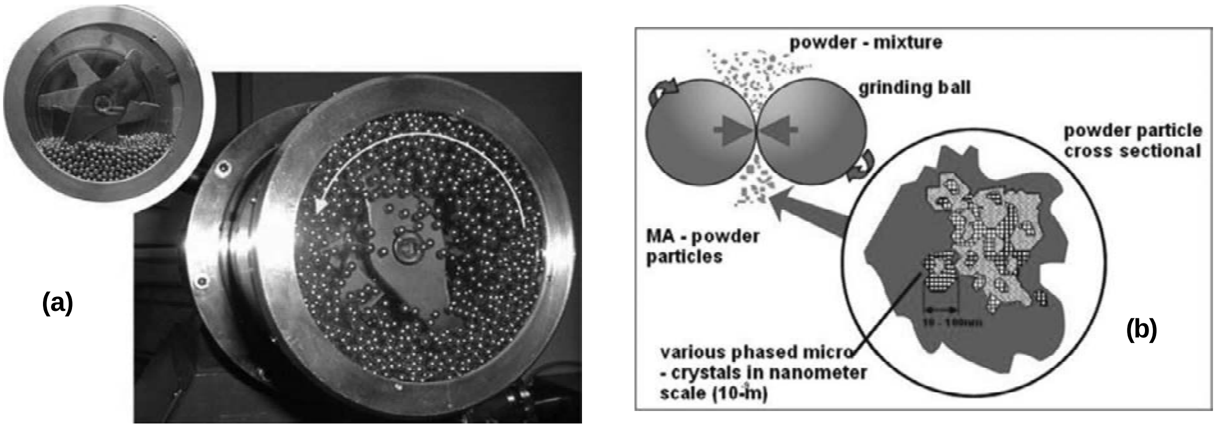


Fig. 1. High energy ball milling: (a) model attritor showing the rotor and the moving steel balls, (b) schematic representation of the fragmentation process during mechanical alloying, replotted from [5].

the flying steel balls being visible through a PMMA window [5]. During the milling process the powder particles experience continuous fracture, work hardening and cold welding, ending up in a steady state process, where the particles have grown to relatively large flakes that contain small precipitates of the strengthening phase, cf. [3,4]. To control fracture and cold welding the milling process can be carried out within a slurry of liquid nitrogen (cryomilling [6,8]) and the addition of approx. 0.2 wt.% stearic acid [3,6,8].

As a second process step, the alloy flakes are hot degassed and consolidated by hot isostatic pressing (HIP), cf. [3,6]. The simultaneous application of high temperature and high pressure (e.g. cryomilled Al5083 [6]: p = 172 MPa and T = 623K) causes closing of the inter-particle porosity by interface diffusion while the occurrence of grain growth is suppressed [8]. As a last step, the material is hot-extruded. Depending on the substrate alloy, both the material's strength and ductility can be further improved by heat treatment, cf. [3]. In general, mechanical alloying is not limited to a certain material combination. Hence, a great variety of commercial aluminium alloys can be strengthened, by e.g., SiC, TiC, VC, $MgAl_2O_4$ or Al_2O_3 dispersoids, cf. [2,3,7].

In addition to establishing a thermally stable distribution of small dispersoids, mechanical alloying results in the formation of a nanocrystalline microstructure. Continuous fracture and cold welding of the powder particles during high-energy milling causes gradual grain refinement. This is schematically shown in Fig. 1b.

According to the Hall-Petch relationship

$$\sigma_Y = \sigma_0 + \frac{k}{\sqrt{d}} \tag{1}$$

with k being the Hall-Petch constant, the decrease in the grain size d is the most effective way to increase a material's yield strength σ_Y (with respect to the friction stress σ_0 of the respective singly crystalline material) without a significant loss in ductility. Since the grain boundaries of mechanically alloyed materials are stabilized by the dispersoids or thin oxide bands that are formed during the milling process, grain growth can be hindered effectively, even at elevated temperatures, cf. [8].

The mechanical behaviour of MMCs at elevated temperatures depends strongly on the grain size as well as on the shape, the strength, and the size of the dispersoids. While large mm-sized dispersoids contribute to creep resistance by load sharing (cf. [1]), the smaller nm-sized dispersoids are effective by Orowan strengthening (direct strengthening) and by maintaining a nanocyrstalline microstructure by grain-boundary pinning (indirect

Table 1. Chemical composition (wt.%) and particle size distribution of the as-received Al5083 powder.

Al 5083:	Mg 4.83	Cr 0.2	Mn 0.8	Al bal.
particle size:	>100 μm 6%	>63 μm 35%	>45 μm 24%	<45 μm 35%

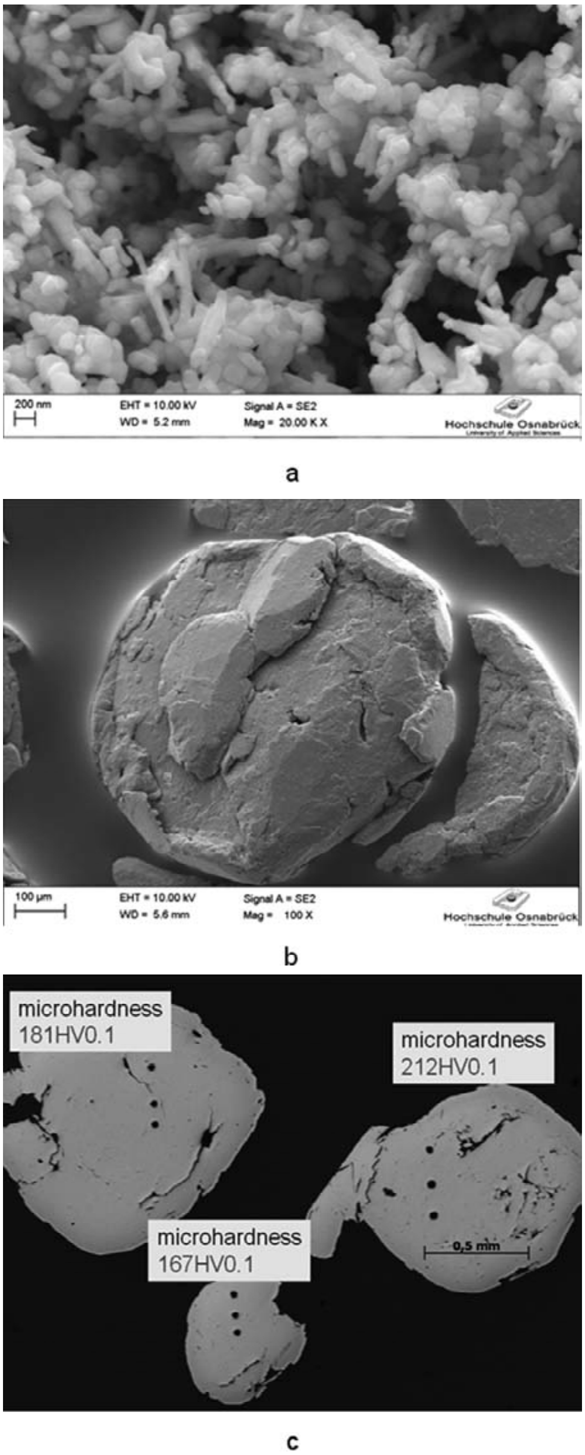


Fig. 2. Powders: (a) $ZnAl_2O_4$ spinel particles, (b) composite flakes after ball milling, and (c) cross section of the composite flakes.

strengthening). According to Schneibel *et al.* [10], nanocrystalline materials exhibit a pronounced decrease of the yield strength when exceeding a certain transition temperature. This effect can be attributed to the thermally activated absorption of dislocations at the grain boundaries and an increase in the contribution of grain boundary diffusion creep (Coble creep) due to the high fraction of grain boundary volume with respect to the total volume.

Aim of the present work is the development of a new nanostructured aluminium material that is high-energy milled in combination with zinc-ferrite spinel powder ($ZnFe_2O_4$), which is available as a cheap side product from steel production, and which shall provide an effective disperspoid strengthening phase and a nanostructure stabilizer. $ZnFe_2O_4$ is considered as an efficient alternative to $MgAl_2O_4$, which is used as a reaction product between Al_2O_3 particles and the alloying element Mg and considered to increase the yield strength and the creep resistance [11].

2. EXPERIMENTAL

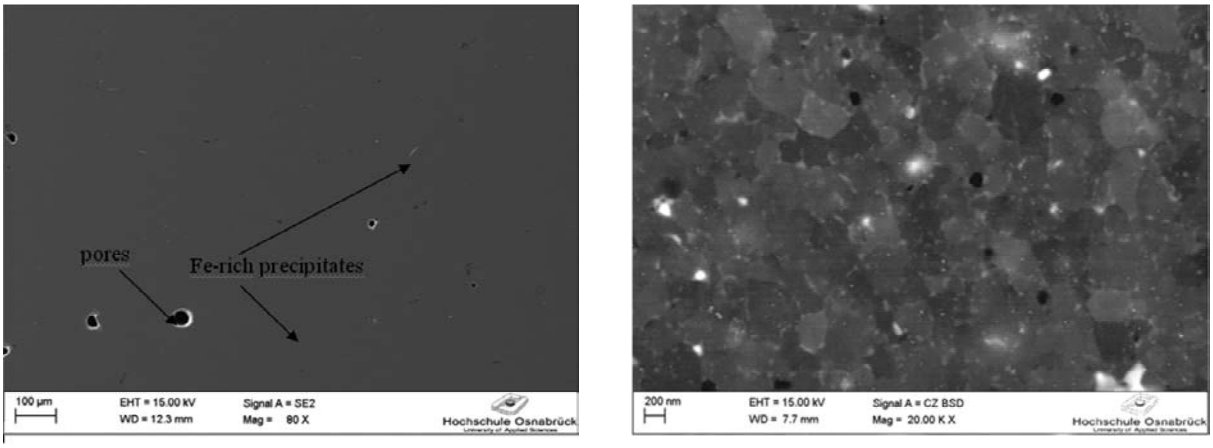
Commercial 5083 aluminum powder (Ecka Granules), of the chemical composition and particle size distribution as given in Table 1, in combination with zinc ferrite spinel ($ZnFe_2O_4$, Ferro GmbH) of density ρ = 4.6 g/cm³ and mean particle size of 600 nm were used as starting material. The zinc ferrite spinel particles consist of an agglomeration of nano-sized needles as shown in Fig. 2a.

The powder mixture (batch size: 200 g Al5083 with 0.5 wt.% $ZnFe_2O_4$) was mechanically alloyed by high-energy ball milling using a Zoz Simoloyer ® in combination with 100Cr6 steel balls as grinding media under inert Ar atmosphere for a 2 h processing time. Fig. 2b shows the resulting product; mechanically alloyed flakes of a size between approximately 200 μm and 500 μm.

Different to the conventional production sequence for ODS alloys, the flakes were directly hot extruded, using a slow extrusion speed (<3.7 mm s^{-1}), a pressure of 1050 MPa at 663K and 613K, respectively. The resulting cylindrical rods of a length of 500 mm and a diameter of 15 mm were cut in small pieces for metallographic analyses and machined to produce tensile, fatigue and creep specimens.

As subject of this study, only tensile tests at room temperature were carried out to reveal the state and the general potential of the material development approach.

Metallographic cross sections were prepared by grinding with SiC paper and polishing with diamond suspension (1 μm). Finishing was done on a vibro polisher (Buehler) using 0.05 mm colloidal silica. The specimens were investigated by means of light microscopy and high-resolution scanning electron microscopy (SEM, Zeiss Auriga with Schottky field emitter).



a b

Fig. 3. SEM micrographs of the extruded Al-$ZnAl_2O_4$ composite (cross section with respect to the extrusion axis): (a) macroscopic view showing small pores and Fe-rich precipitates, (b) microscopic view of the ultrafine-grained microstructure with spinel dispersoids at the grain boundaries (ECCI).

3. RESULTS AND DISCUSSION

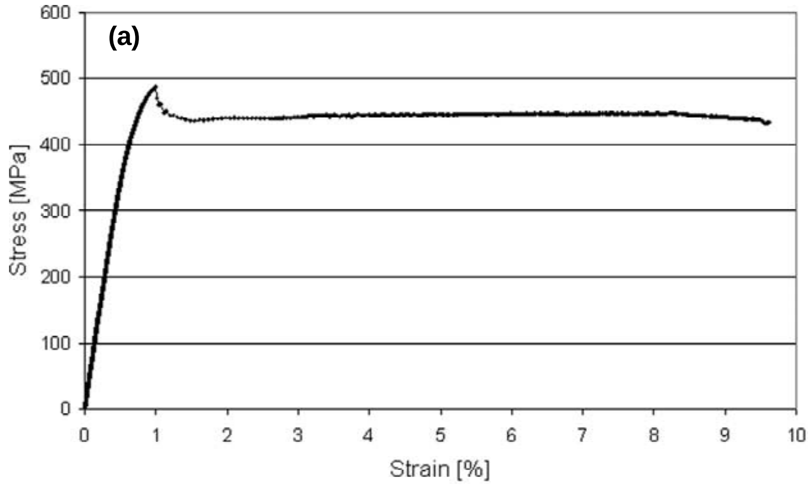
Large facetted flakes as shown in Fig. 2b were produced by the high-energy ball milling process. The flakes consist of pan-cake-shaped fragments of the strongly deformed Al and zinc-ferrite spinel powder particles that are packed in layers. The interface between the layers contains large cracks and oxide bands (cf. Fig. 2c). A substantial increase in Vickers hardness up to 210HV (corresponding to a tensile strength of approximately UTS = 735 MPa) was observed, as compared to approximately 100HV (UTS = 350 MPa) that can be reached for conventional wrought 5083 aluminum alloys.

Certainly, there is a drop in hardness after the hot extrusion process to approximately 140-150 HV, which can be attributed to a decrease in the dislocation density caused by dynamic recovery. Dynamic recrystallization ends up in a ultrafine-grained microstructure as it is shown in Fig. 3b. The grain structure with an average grain size of approximately d = 250 nm became visible by electron chaneling contrast (ECCI) using the backscatter electron detector. The grain boundaries are decorated by tiny spinel dispersoids, probably $ZnAl_2O_4$, $FeAl_2O_4$, and $MgAl_2O_4$. Due to the element contrast they appear bright as compared to the "light" aluminium alloy grains, which appear in different grey colours.

While hot extrusion at high temperatures, above approximately 663K, caused hot cracks in the material, processing at 613K resulted in very homogeneous rods with some small Fe-rich precipitates (probably due to residues from the steel milling balls) and low porosity (less than 1%) with pore diameters between 5 and 20 μm. Fig. 3a shows a metallographic cross section of the material at low magnification.

First studies on the mechanical properties of the composite material reveals a slightly higher Young's modulus as compared to the wrought Al alloy Al5083 ($E \cong$ 70 GPa). Precise measurements using the resonance frequency damping analysis (RFDA) method yielded values between E = 73 GPa and E = 75 GPa. By tensile testing it was shown that the strength was significantly increased to yield strength values between R_e = 490 MPa and R_e = 510 MPa with a reasonable elongation to fracture of approximately A = 9%. Prior fracture, the specimens show necking within the gauge length. Fig. 4a shows an example of a stress-strain diagram obtained for the Al-0.5%$ZnFe_2O_4$ composite. It is obvious that the yield strength corresponds to the tensile strength, i.e., no work hardening was observed. According to [6], the abrupt drop in the stress level after reaching the yield point (see Fig. 4a) was considered as to be a result form the dislocation breakaway from strong pinning interactions with the small dispersoids. The small amount in work hardening can be attributed to dynamic recovery at the grain boundaries which might be classified as non-equilibrium grain boundaries (cf. Valiev *et al.* [12]).

Fig. 4b shows that the first results of the tensile tests of the Al-0.5%$ZnFe_2O_4$ composite fits quite well with the Hall-Petch data of the cryomilled Al5083 materials, according to [8]. The authors consider the results as promising in the sense that further development by modifying the alloy composition and the milling parameters may lead to a substantial further increase in the yield strength.



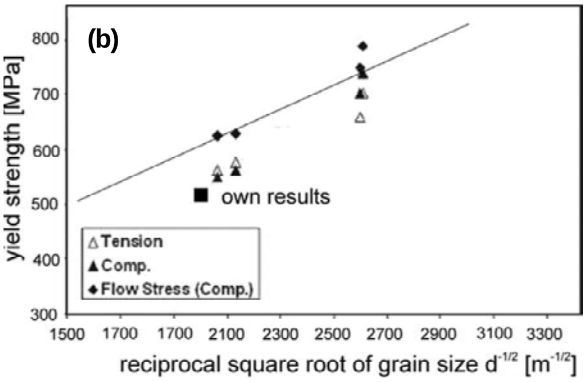


Fig. 4. Mechanical behaviour of the Al-$ZnAl_2O_4$ composite: (a) stress-strain diagram of one of the tensile tests and (b) comparison of Hall-Petch data from the literature [8] (yield strength vs. reciprocal square root of the grain size).

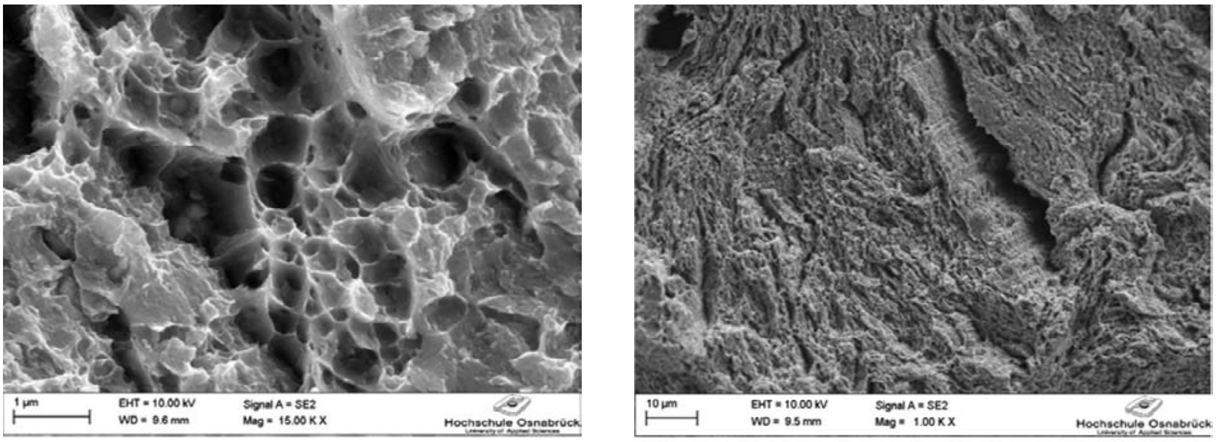


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Fig. 5. Fracture surface of the Al-$ZnAl_2O_4$ composite after tensile testing: (a) dimple fracture surface and (b) secondary cracks, resembling the oxide bands within the composite flakes after ball milling.

SEM analysis of the fracture surface supported the results of the mechanical testing where a remarkable amount of ductility was measured. The complete fracture surface shows small dimples (Fig. 5a) which are considered as a proof for ductile failure. At lower magnification (Fig. 5b) secondary cracks can be seen, which are probably due to the large oxide bands that are formed during the cold welding process of the pan-cake-shaped fragments, as mentioned above. The limitation of the ductility to elongation-to-fracture values below 10% is attributed to those secondary cracks.

The reasonable ductility of the Al-0.5%$ZnFe_2O_4$ composite is mainly due to the interrupted decoration of the grain boundaries by the dispersoids, prohibiting brittle intercrystalline separation. It is assumed that this effect is maintained even at elevated temperatures (cf. [10]). Creep and fatigue testing of the Al-0.5%$ZnFe_2O_4$ composite are subjects of current research work.

4. CONCLUSIONS

By high energy ball milling of 5083 aluminum powder in combination with 0.5wt.% $ZnFe_2O_4$ zinc ferrite spinel particles followed by hot extrusion, a new composite material was produced. High resolution scanning electron microscopy revealed an average grain size of approximately 250 nm. The grain boundaries are decorated by small spinel dispersoids. The composite material was shown to have a ductile deformation behaviour. No intercrystalline cracking was observed during tensile testing. Strength values of 500 MPa and more, as well as a Young's modulus that lies between 5 and 10% higher than that of conventional Al5083 alloys show that the processing route is promising in the sense to produce high performance aluminium alloys for structural applications in automotive, aerospace and energy technologies.

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