Ex situ Al–Al_2O_3 ultrafine grained nanocomposites produced via powder metallurgy

R. Casati [a,*], F. Bonollo [b], D. Dellasega [c], A. Fabrizi [b], G. Timelli [b], A. Tuissi [d], M. Vedani [a]

[a] Department of Mechanical Engineering, Politecnico di Milano, Via La Masa 1, 20156 Milano, Italy
[b] Department of Management and Engineering, Università di Padova, Stradella S. Nicola 3, 36100 Vicenza, Italy
[c] Department of Energy, Politecnico di Milano, Via Ponzio 34, 20133 Milano, Italy
[d] CNR-IENI, Corso Promessi Sposi 29, 23900 Lecco, Italy

Available online 11 November 2013

1. Introduction

Metal Matrix nano-Composites (MMnCs) are considered promising materials as they exhibit much higher strength than the base metal with a small drop in toughness [1,2]. They are generally made up by a ductile metal matrix reinforced with hard and thermodynamically stable nano-particles (NPs). Nano-reinforcements confer higher strength to the matrix because they are able to obstruct the movement of dislocations (Orowan strengthening) [3]. Moreover, they increase the dislocation density of the metal matrix since they are responsible of the formation of geometrically necessary dislocations due to the mismatch in coefficients of thermal expansion and elastic modulus between the nano-particles and the matrix (work hardening) [4–6]. Besides, as in all polycrystalline metallic materials, grain-boundary strengthening (also known as Hall–Petch strengthening) is a further suitable method to increase the strength of MMnCs [7]. Ultra-fine grained (UFG) materials, processed by severe plastic deformation methods, such as equal channel angular pressing (ECAP) or high pressure torsion, have attracted growing interest because of their unique physical and mechanical properties [8].

Nano-composites retain higher toughness than conventional composites because the enhancement in strength is achieved by using a lower amount of reinforcement than that required to reach the same strength level in conventional composites [1–6]. Formation of clusters must be avoided during preparation process of MMnCs and NPs must be homogeneously dispersed as well; however, the high surface area to volume ratio and the low wettability of ceramic compounds make these points big issues to be faced [1]. To overcome these problems, several non-conventional methods have been proposed to disperse discrete NPs produced in situ [9,10] or ex situ [6,11–15] in the matrix. Powder metallurgy routes [6,11–13], ultrasound assisted casting [14], disintegrated melt deposition [15,16] are some of the processes recently developed to produce MMnCs.

In this work, UFG–MMnCs have been prepared by powder metallurgy route in order to exploit both nano-sized particles and grain boundaries strengthening capability. Aluminum and alumina powders were ground by high-energy ball milling (HEBM) and consolidated by ECAP. Investigation on NPs dispersion was carried out by scanning electron microscopy (SEM) and grain size was determined by electron back-scatter diffraction (EBSD) technique. The mechanical behavior of the materials was finally estimated by hardness tests.

2. Materials and experimental methods

Commercial purity Al powders with average size of 20 μm, supplied by ECKA Granules, and an isopropanol dispersion of Al_2O_3, with particles size lower than 50 nm, were mixed and dried in order to prepare a mixture of Al-2 wt.% Al_2O_3 composite powder. The blended powders were then subjected to HEBM to break the oxide layer which covers the Al powders into nanosized fragments and to embed the hard alumina nano-particles in the ductile metal matrix. A Vario-Planetary Mill Pulverisette 4 equipped with tempered steel bowls and balls (10 mm in diameter) was used. About 1 vol.% of ethanol was added as process control agent (PCA) to avoid excessive cold welding and agglomeration of Al powders. The bowls were packed and closed in argon atmosphere within a glove box to prevent further

* Corresponding author. Tel.: +39 02 2399 8638.
E-mail address: riccardo.casati@polimi.it (R. Casati).

oxidation of the powder during the whole process. HEBM was performed for 16 h with ball-to-powder weight ratio of 10:1. The milling was interrupted each 30 min for 10 min to avoid excessive raise of temperature. The speed of the main disk was set to 250 rpm clockwise whereas the speed of the planets was set to 200 rpm counter-clockwise. Powder-in-tube ECAP compaction with Al cans [12] was carried out on *as received* Al powder, on ball milled Al powder and on ball milled composite powder. The ECAP die is characterized by an angle between the intersecting channels of 110° and channels diameter of 10 mm. The temperature of the die was set at 400 °C, by using four resistance heaters (800 W each) placed in the ECAP die. The process was performed following the route Bc (rotation by 90° clockwise) from 1 to 12 passes at constant speed of 10 mm/min. Vickers microhardness (HV) was measured using Future Tech Corp. FM-700 tester applying 2 N for 15 s. For the microstructural investigations, samples were drawn from the cross section of the ECAP-processed materials. The specimens were prepared to a 1-μm finish with diamond paste and, finally, polished with a commercial 0.04 μm colloidal silica suspension. The samples were also polished by low-angle ion milling to ensure an improved EBSD signal acquisition. Microstructural characterization was carried out after chemical etching with Keller's solution by scanning electron microscope (SEM, Zeiss Supra 40) equipped with In-lens detector using an accelerating voltage of 5 kV. The EBSD analysis was performed by using field emission gun scanning electron microscope (FEG-SEM, FEI Quanta 250) equipped with automatic OIM (orientation imaging map) software from TSL. EBSD maps were taken at the centre of the samples; the step size and scan area for mapping were 0.05 μm and 15 × 20 μm, respectively. The grain size was determined by the grain reconstruction method in EBSD maps, considering only high-angle grain boundaries (HAB, $\theta > 15°$).

3. Results and discussion

Ground powders were successfully compacted by ECAP. One ECAP pass at 400 °C revealed to be able to consolidate both Al and composite powders. The compacts were near-fully dense. The density of commercial purity (CP) Al and composite after consolidation were 2.7 g/cm^3 and 2.71 g/cm^3, respectively. SEM analysis showed that the CP Al samples contain small aluminum oxide in the form of fine particles (<50 nm), which appear as discrete and well scattered in the metal matrix (Fig. 1a). HEBM led to the fragmentation of the oxide layer that covered the Al powder and favored the embedding of these oxide NPs in the Al matrix. When compared with other data given in literature, the size of the reinforcing particle is larger; this feature is supposedly due to thicker thickness of the native oxide layer of the Al powder [17,18].

In contrast, the Al-2 wt.% Al_2O_3 showed some small clusters of alumina as shown by the microstructure of Fig. 1b. The pores noticeable in the micrograph of Fig. 1b are due to the chemical etching; indeed they were not detected in the unetched samples (here not reported). In order to break these particles' agglomerates and to improve NPs dispersion throughout the metal matrix, the specimens were subjected to an increasing number of ECAP passes from 1 to 12. The microstructure of transversal sections of pure Al and MMnC specimens processed through 1 and 12 ECAP passes was analyzed by means of EBSD technique. An ultra fine equiaxial grain structure (UFG) was observed both in composite and commercial purity Al samples after 1 ECAP pass. In Fig. 2, the EBSD inverse pole figures (IPF) are reported for the nano-composite after 1 and 12 ECAP passes. These figures show no texture or preferential grain orientation in the specimens.

The graph represented in Fig. 3 illustrates the distributions of the grain size, estimated by EBSD analysis, with the corresponding log-normal fitting curves. It is revealed that 12 ECAP passes at 400 °C led to a slightly coarser grain structure that is supposed to be due to the annealing effect caused by the high processing temperature, which is only partially hindered by the refining effect caused by SPD induced by ECAP. HEBM induces defects in the crystal lattice of powders and leads to a raise of internal stresses, thus the metallic particles become less prone to be deformed and compacted. For this reason, in order to achieve a good compaction and to avoid cracks, ECAP had to be performed at high temperature (400 °C). No structural modification effect due to the Al_2O_3 ceramic reinforcement on the microstructural scale was achieved. Comparing the different materials, the grain size distributions are almost equal. By increasing the number of ECAP passes, the distribution

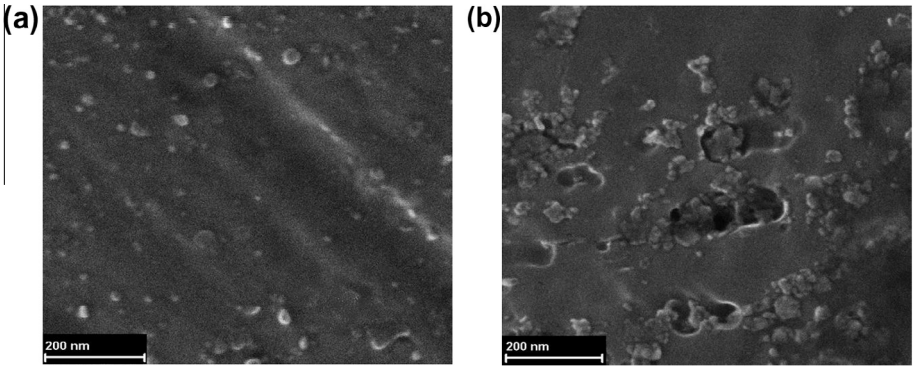

Fig. 1. Microstructure of the (a) commercial purity Al sample and (b) of Al-2 wt.% Al_2O_3 after 1 ECAP pass.

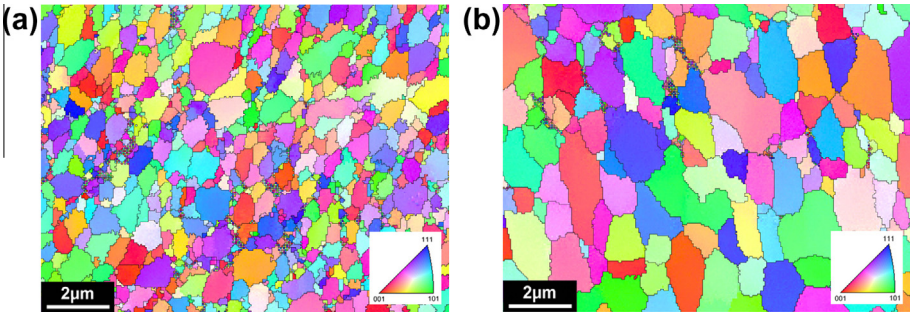

Fig. 2. EBSD inverse pole figure of the Al-2 wt.% Al_2O_3 sample after (a) 1 ECAP pass and after (b) 12 ECAP passes.

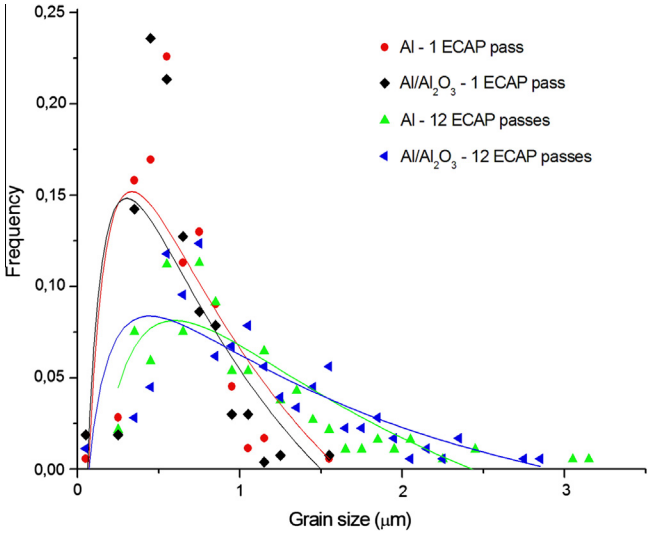

Fig. 3. Distributions of the grain size, estimated by EBSD analysis, with the corresponding log-normal fitting curves for composite and commercial purity Al samples after 1 and 12 ECAP passes.

of the grain size becomes more spread. The equivalent diameter of grains with the maximum frequency shifts towards higher values and the absolute value of the maximum frequency decreases. The average grain size increases from 0.6 to 0.9 μm when moving from 1 to 12 ECAP passes.

The results obtained by microhardness tests, depicted in Fig. 4, show a reduction in hardness with increasing number of ECAP passes. The hardness decrease of commercial purity Al specimen is significantly more drastic than that of the composite. After the first pass, the hardness Vickers number (HVN) of commercial purity Al and nano-composite was 107 and 117, respectively; while, after 12 passes, it decreased to HVN 76 and 111. In the composite, the limited reduction of hardness is apparently in contrast considering the potential loss in the Hall–Petch contribution due to coarser grain size. This conflict was supposed to be due to the improved dispersion of the alumina NPs that increased the composite strength mainly by the Orowan mechanism. Indeed, the nanocomposite subjected to 12 ECAP passes showed a better dispersion of nanoparticles, although some small sub-micrometric clusters were still noticeable.

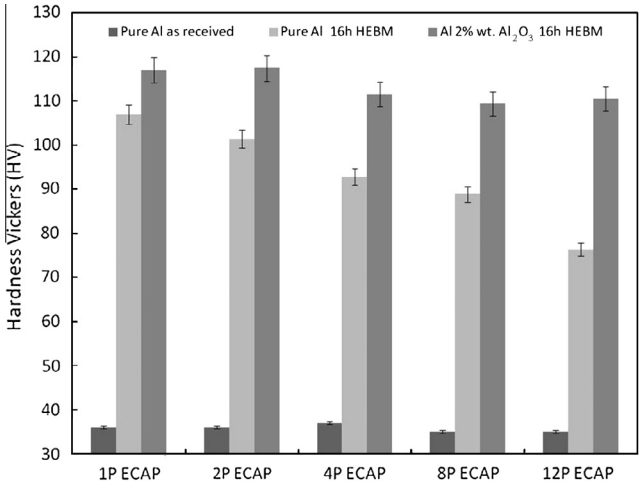

Fig. 4. Microhardness results for composite and commercial purity Al samples after different ECAP passes.

4. Conclusions

Powder metallurgy route, consisting in high energy ball milling and ECAP consolidation, is a suitable method to produce UFG aluminum based ex situ MMnCs. HEBM is the key process to promote the dispersion of nano-alumina into the aluminum matrix. Further, multi-pass ECAP enhances the dispersion of the reinforcement. The total amount of alumina experimentally found within the nanocomposite is the sum of the alumina deliberately added as reinforcement and of the aluminum oxide that naturally covers the Al powders. HEBM allows the fragmentation of the oxide layer into small pieces, which are able to further increase the strength of the material. The grain size after the first ECAP pass is in the range of about 600 nm, while 12 ECAP passes led to coarser grain structure. The final hardness of the Al-2 wt.% Al_2O_3 composite is higher than that of commercial purity Al, and it is more stable after multi-pass ECAP processing due to the beneficial contribution induced by NPs dispersion.

Acknowledgements

The authors acknowledge Dr. Gandin and ECKA Granules for material supplying.

References

[1] S.C. Tjong, Novel nanoparticle-reinforced metal matrix composites with enhanced mechanical properties, Adv. Eng. Mater. 9 (2007) 639–652.
[2] S.R. Bakshi, D. Lahiri, A. Agarwal, Carbon nanotube reinforced metal matrix composites – a review, Int. Mater. Rev. 55 (2010) 41–64.
[3] Z. Zhan, D.L. Chen, Contribution of Orowan strengthening effect in particulate-reinforced metal matrix Nanocomposites, Mater. Sci. Eng. A 483–484 (2008) 148–152.
[4] A. Sanaty-Zadeh, Comparison between current models for the strength of particulate-reinforced metal matrix nanocomposites with emphasis on consideration of Hall–Petch effect, Mater. Sci. Eng. A 531 (2012) 112–118.
[5] P. Luo, D.T. McDonald, W. Xu, S. Palanisamy, M.S. Dargusch, K. Xia, A modified Hall–Petch relationship in ultrafine-grained titanium recycled from chips by equal channel angular pressing, Script. Mater. 66 (2012) 785–788.
[6] R. Casati, M. Amadio, C.A. Biffi, D. Dellasega, A. Tuissi, M. Vedani, Al/Al_2O_3 nano-composite produced by ECAP, Mater. Sci. Forum 762 (2013) 457–464.
[7] R.E. Smallman, A.H.W. Ngan, Physical Metallurgy and Advanced Materials, seventh ed., Butterworth Einemann, 2007.
[8] R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, Bulk nanostructured materials from severe plastic deformation, Prog. Mater. Sci. 45 (2000) 103–189.
[9] L. Lu, M.O. Lai, Y. Su, H.L. Teo, C.F. Feng, In situ TiB_2 reinforced Al alloy composites, Script. Mater. 45 (2001) 1017–1023.
[10] J.P. Tu, N.Y. Wang, Y.Z. Yang, W.X. Qi, F. Liu, X.B. Zhang, H.M. Lu, M.S. Liu, Preparation and properties of TiB nanoparticle reinforced copper matrix composites by in situ processing, Mater. Lett. 52 (2002) 448–452.
[11] S. Goussous, W. Xu, K. Xia, Developing aluminum nanocomposites via severe plastic deformation, J. Phys: Conf. Series 240 (2010) 012106.
[12] R. Casati, M. Vedani, D. Dellasega, P. Bassani, A. Tuissi, Mater. Manuf. Processes. 4 (2013) 25–30.
[13] K. Xia, Consolidation of particles by severe plastic deformation: mechanism and applications in processing bulk ultrafine and nanostructured alloys and composites, Adv. Eng. Mater. 12 (2010) 724–729.
[14] X. Li, Y. Yang, X. Cheng, Ultrasonic-assisted fabrication of metal matrix nanocomposites, J. Mater. Sci. 39 (2004) 3211–3212.
[15] M. Gupta, M.O. Lai, M.S. Boon, N.S. Herng, Regarding the SiC particulates size associated microstructural characteristics on the aging behavior of Al–4.5 Cu metallic matrix, material research, Bulletin 33 (1998) 199–209.
[16] M. Shanthi, M. Gupta, A.E.W. Jarfors, M.J. Tan, Synthesis, characterization and mechanical properties of nano alumina particulate reinforced magnesium based bulk metallic glass composites, Mater. Sci. Eng. A 528 (2011) 6045–6050.
[17] M. Balog, C. Poletti, F. Simancik, M Walcher, W. Rajner, The effect of native Al_2O_3 skin disruption on properties of fine Al powder compacts, J Alloys Comp. 509 S (2011) S235–S238.
[18] B. Rufino, F. Boulc'h, M.-V. Coulet, G. Lacroix, R. Denoyel, Influence of particles size on thermal properties of aluminium powder, Acta Mater. 55 (2007) 2815–2827.