Characterisation of mechanically milled and spark plasma sintered pure aluminium

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1. Introduction

During the last decade there has been an enormous effort to develop bulk nanostructured and ultra-fine grained materials as they offer significant potential for exhibiting enhanced mechanical properties compared to their microstructured equivalent [1-3]. Numerous process methods have been developed to produce the bulk material, which can broadly fall into two categories: 1) consolidation of nanoparticles or ultra-fine grained powders [2, 3] and 2) severe plastic deformation of a bulk microstructured material [4, 5]. This work focuses on the first method where ultra-fine grained powders have been formed using mechanical milling (MM) [2, 3]. MM is a type of solid state powder processing, typically using highly energetic ball milling, in which elemental powder particles are mechanically mixed in order to produce composite powder particles or to synthesise a variety of stable and metastable nanocrystalline materials with controlled microstructures [1-3]. However, the MM processing technique can also be used to obtain nanoparticles in aluminium alloys by milling in the presence of a process control agent (PCA) which enables a balance between fracture and welding to be established enabling refinement of the powder particle size. The role of the PCA, however, can be quite complex because in addition to preventing the occurrence of excessive welding of the aluminium powder particles it can also react with the aluminium during milling or subsequent heat treatments [6] leading to the formation of second phases such as γ-Al_2O_3 [7] and / or Al_4C_3 [8].

A number of consolidation processes have been applied to fabricate bulk nanostructured materials from MMed powders, e.g. a combination of cold pressing and hot extrusion, hot pressing (HP), hot isostatic pressing (HIP) and more recently spark plasma sintering or synthesis (SPS) [9, 10]. The SPS method is a novel technique developed for sintering advanced ceramics and composite materials. In this method, a pulsed DC current is used concurrently with a uniaxial pressure to in principal sinter the MMed powders. The major advantage of the SPS process is that it allows fabrication of bulk materials from MMed powders using relatively short sintering times at nominally low temperatures. Therefore, coarsening of both fine grains and nano-sized particles in the MMed powders can be avoided. In addition to this, it has also been suggested that another advantage of SPS is the plasma generated between particles to facilitate the sintering process also aids in the elimination of surface impurities leading to enhanced sintering and consolidation [10].

Some mechanical properties of nanostructured pure aluminium produced by mechanical grinding (MG) and SPS have been investigated in [11]. This work showed that the SPS materials fabricated from 8 h mechanically ground aluminium powders exhibited compressive 0.2% proof stresses of 440 MPa at room temperature. These results clearly implied that the combination of MM or MG and SPS processes can produce nanostructured materials with enhanced mechanical properties compared to those produced by conventional powder metallurgy routes, such as HP, HIP or a combination of cold pressing and hot extrusion processes. However, there is limited microstructural characterisation of SPS consolidated materials, particularly at the grain scale level, making it difficult to elucidate the underlying sources of the improved properties.

The aim of the present work thus was to characterise a nanostructured pure aluminium material produced by MM of pure aluminium powder followed by compaction via SPS. Characterisation of microstructure for the SPS material was primarily

conducted using the electron backscatter diffraction (EBSD) technique in the scanning electron microscope (SEM). Particular focus has been paid to analysis of the aluminium matrix grain structures, grain boundary misorientation distribution and crystallographic textures.

2. Experimental procedures

The starting material was air-atomised 99.9% pure aluminium powder with an average diameter of 100 μm. Stainless steel balls of 7 mm diameter together with 10 g of the pure aluminium powder and stearic acid ($C_{17}H_{35}COOH$) as a PCA were sealed in a hardened steel vial using a glove box filled with argon. The ball to powder mass ratio was approximately 7:1. MM was performed at room temperature using an SPEX8000 mixer/mill with processing time varied from 4 h to 8 h. The average Vickers microhardness of the MMed powders was determined from 15 particles per sample with a microhardness tester using an applied load of 10 g.

The MMed powders were consolidated by an SPS apparatus. This system consists of a uniaxial press with maximum force of 100 kN, and a power supply capable of producing a DC pulsed current with a maximum of 5 kA at 10 V. 7 g of the MMed powder was placed in a graphite die of 20 mm in diameter and 40 mm in height, and heated under vacuum with an applied pressure of 49 MPa at 873 K for 1 h. The Vickers hardness of the SPS materials was measured with a Vickers hardness tester using an applied load of 1 kg. Density of SPS materials was measured based on the Archimedes method.

Investigation of the aluminium matrix grain orientations was undertaken for the 8 h SPS specimen in its compression plane, using high-resolution EBSD. The specimen was mechanically ground, pre-polished using 3 and 1 μm diamond pastes and finally polished using a 0.5 μm colloidal silica suspension. To ensure there was no polishing residue on the surface to be analysed the specimen was ultrasonically cleaned in isopropanol just prior to EBSD analysis. Acquisition of EBSD data was done using an FEI Sirion field-emission gun scanning electron microscope equipped with a fully automatic HKL Technology EBSD attachment, and operated at 10 kV. Orientation mapping was performed on a rectangular grid with a step size of 0.04 μm covering an area of 22 × 13 μm^2. The corresponding data processing was then carried out using the HKL Channel 5 software.

3. Experimantal results and discussion

Figure 1 compares the hardness between the MMed powders and the subsequently SPS processed materials for the different MM processing times together with the measured density of the SPS materials. The hardness of the pure aluminium powder before and after 4 h and 8 h of MM process was approximately 44 HV, 138 HV and 118HV, respectively. These hardness measurements for MMed powders contained an error of ± 10 %. The hardness values of the SPS materials produced from the 4 h and 8 h MMed powders were higher than that of the MMed powders. In particular, a significantly greater level of hardness was found for the SPS material fabricated from the 8 h MMed powder with its hardness being approximately 1.3 times higher than that of the MMed powder. These results indicate that the SPS process was beneficial for the consolidation of the MMed powders into the bulk materials, and the selected conditions for the SPS process in the current research

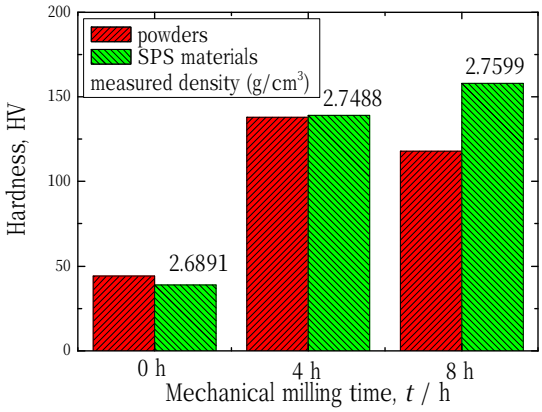

Fig. 1 Comparison of hardness between MMed powders and SPS materials together with measured density of the pure aluminium SPS materials.

were favourable for the MMed powders used. It should also be noted that the hardness values of the MMed pure aluminium powders in the present research are significantly higher than that of ultra-fine grained pure aluminium produced by either equal channel angular processing (ECAP) [4] or back pressure equal channel angular consolidation (BP-ECAP) of particles [12], suggesting that MM is much more effective at imparting large strains into particles than these other methods.

The relative density of the SPS materials produced from the 0 h, 4 h and 8 h MMed powders was 99.6 %, 101.8 % and 102.3 %, respectively. For these calculations the theoretical density of pure aluminium (2.699 g / cm^3) was used and any effect of solid-state reaction products and/or impurities were ignored. In terms of the relationship between the hardness and relative density it has been clearly shown that when the relative density has a value of over 100 %, the hardness of the SPS materials was greater than that of the parent MMed powder. This observation clearly implies that to produce enhanced bulk mechanical properties a full dense SPS material needs to be produced.

Figure 2 shows an EBSD orientation image map (OIM) obtained from the aluminium matrix of the 8 h MMed plus SPS processed material. The map clearly shows that the grain distribution has a bimodal character, being composed of relatively fine grains with diameters of approximately 300 nm and contiguous coarse grains having diameters between 2 and 5 μm.

Corresponding {001} pole figures of the coarse and fine grains are shown in Figs. 3 (a) and (b), respectively. As expected the texture of the coarse grain appears on first viewing to be very strong due to the limited number of grains analysed; however, it is of interest to note that whilst these grains are contiguous there does not appear to be any orientation relationship between them suggesting the texture of the coarse grains is random. For the fine grains the texture is random with a maximum intensity of 1.6 times random. Analysis of boundary misorientation in the OIM shows that the vast majority to be of high angle (> 15°) for both coarse and fine grains. This is statistically confirmed in Fig. 4 which shows

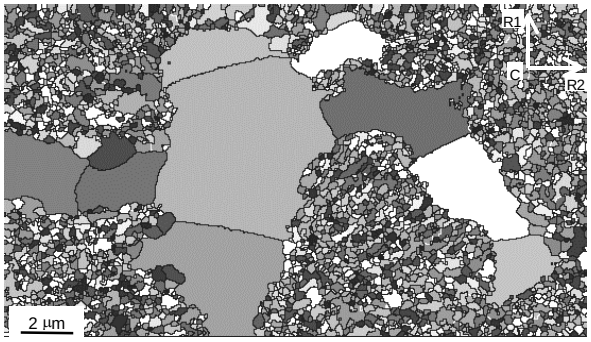

Fig. 2 Euler contrast orientation image map of 8 h MMed pure aluminium powder consolidated by SPS. White and black lines represent misorientations of > 2° and 15°, respectively. C represents the compression direction and R1 and R2 are two orthogonal directions arbitrarily defined in the compression plane.

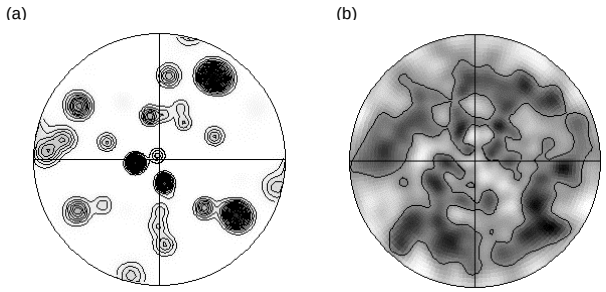

Fig. 3 {001} pole figures of (a) coarse grains and (b) fine grains for the orientation map shown in Fig. 2. Each contour line represents a multiple of 1 x random intensity.

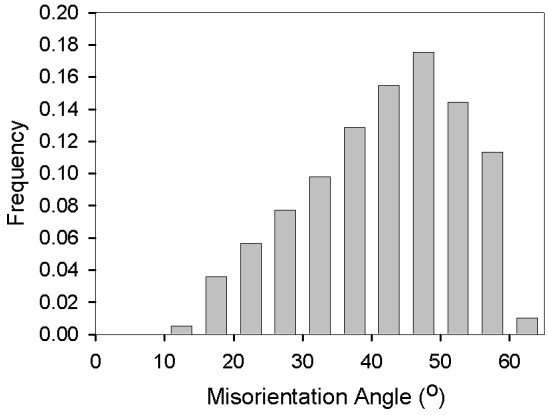

Fig. 4 Histogram showing the distribution of misorientation angles between the small grains.

the distribution of boundaries for the fine grain material. This data also corresponds closely to the Mackenzie distribution [13] for a random aggregate of cubic crystals confirming the lack of preferred orientation in the fine grains.

Comparison of the average grain size of the current material with that of ultra-fine grained pure aluminium produced by either equal channel angular processing (ECAP) [4], ~ 4 μm, or back pressure equal channel angular consolidation (BP-ECAP) of particles [12], 0.83-1.06 μm, suggests that MM in conjunction with SPS can produce bulk, fully dense finer grained material than severe plastic deformation processes. Moreover, virtually all grain boundaries in the SPS material are of high angle, e.g. misorientations are greater than 15º, whereas an average misorientation of only 9.2º has been reported for material produced by four passes BP-ECAP [12]. Thus, it appears that the combination of MM and SPS processing used in the present research is a very effective way of producing true high-angle grain boundaries, which in turn leads to higher strengths via Hall-Petch type strengthening mechanisms.

From this analysis we thus believe the enhanced strength generated in the MM plus SPS material results from refined grains with true high angle boundaries plus possible strengthening from intermetallic compounds produced by the solid-state reactions. At this stage, however, we are unsure if all the particles are located at grain boundaries or if some reside within grains to increase strength via dislocation particle interaction. This is the subject of a current TEM analysis of the material. Finally, it should be noted that bimodal microstructures produced through cryomilling and heat treatment of copper have produced high strength plus enhanced ductility [14] suggesting that the current material may also exhibit a large strain to fracture.

4. Conclusions

The combination of MM and SPS processes has been used successfully to fabricate bulk, fully dense nanostructured pure aluminium. The mechanical properties of the SPS material have been shown to be very sensitive to MM time. The microstructure of the SPS materials fabricated from the MMed powders possessed a mixture of fine, typically ~ 300 nm grains and contiguous coarse 2-5 μm grains. This bimodal structure possessed virtually all high angle grain boundaries together with no preferred grain orientation which leads to higher strengths via Hall-Petch type strengthening mechanisms.

Acknowledgements

The authors gratefully acknowledge the Toyo Aluminium Co. for providing pure aluminium powders. One of the authors (M. K.) would like to express his gratitude to Nihon University for the financial support to his sabbatical leave at The University of Sheffield during which a major part of the present study was conducted.

References

[1] L. Lu and M. O. Lai, Mechanical Alloying, Kluwer Academic Publishers, 1998.

[2]B. S. Murty and S. Ranganathan, International Material Reviews, 43 (1998) 101 - 141.

[3] C. Suryanarayana, Progress in Materials Science, 46 (2001) 1 - 184.

[4] Y. Iwahashi, Z. Horita, M. Nemoto, T. G. Langdon,Acta mater., 45 (1997) 4733 - 4741.

[5]I.V. Alexandrov, K. Zhang, A.R. Kilmametov, K. Lu and R.Z. Valiev, Materials Science and Engineering A, 234 - 236 (1997) 331 - 334.

[6] R. F. Singer, W. C. Oliver, W. D. Nix, Metall. Trans. A11 (1980) 1895 - 1901.

[7] Joint Committee of Powder Diffraction Standards (JCPDS) : 10-0425, International Centre for Diffraction Data, 1999.

[8] Joint Committee of Powder Diffraction Standards (JCPDS) : 34-0799, International Centre for Diffraction Data, 1999.

[9] M. Tokita, Mater. Sci. Forum 308 - 311 (1999) 83-88.

[10] M. Omori, Mater. Sci. Eng. A 287 (2000) 183 - 188.

[11] M. Kubota, J. Alloys and Compounds, Journal of Alloys and Compounds, 434 - 435 (2006) 294 - 297.

[12] K. Xia, X. Wu, T. Honma, S. P. Ringer, J. Materials Science, 42 (2007) 1551 - 1560.

[13] J. K. Mackenzie, Acta Metall., 12 (1964) 223 - 225

[14] Y. M. Wang, M. W. Chen, F. H. Zhou, E. Ma, Nature, 419 (2002) 912.