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Thermal Stability of Nanostructured Pure Aluminium Produced by Mechanical Milling and Spark Plasma Sintering

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Thermal stability of the bulk materials fabricated from mechanically milled pure aluminium powder by spark plasma sintering (SPS) was investigated by hardness measurements and microstructural characterisations by the electron backscatter diffraction (EBSD) technique. No significant decrease in the Vickers hardness was observed after various SPS materials heating at 873 K for over 500 h due to formation of γ-Al_2O_3 and Al_4C_3. Those intermetallic compounds formed *via* mechano-chemical reactions between pure Al and stearic acid, added as a process control agent, during heat treatments. EBSD analysis clearly revealed that the SPS material possessed a mixture of fine grains approximately 300 nm in diameter and coarse grains 2-5 μm in size. This bimodal aluminium matrix grain structure exhibited the crystallographic random textures, and grain boundary misorientations are virtually all high angle (>15°). After heating at 873 K for over 500 h, those microstructures of the SPS materials still kept a similar size of the grains.

Keywords: *mechanical milling, electron backscattering diffraction (EBSD), aluminium, ultrafine-grained microstructure, spark plasma sintering.*

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 at room and elevated temperatures [1-6]. A combination of mechanical milling (MM) and spark plasma sintering or synthesis (SPS) can be one of potential processes for producing nanostructured bulk materials starting from nanoparticles or ultra-fine grained powders [7, 8]. MM is a type of solid state powder processing, in which elemental powder particles are mechanically mixed in order to produce nanoparticles or to synthesise a variety of stable and metastable nanocrystalline powders [1-3]. It has been reported that applying the MM process for pure aluminium powder with stearic acid, added as a process control agent (PCA), can be obtained refinement of the powder particle size. In addition, solid-state reaction between the aluminium powder and PCA occurred during milling or subsequent heat treatments [7] leading to the formation of second phases such as γ-Al_2O_3 [9] and / or Al_4C_3 [10]. The SPS method is a novel sintering process that allows the compacted powders to be sintered at relatively lower temperatures with relatively short heating and holding times compared to that used in conventional consolidation processes. In this method, a pulsed direct current-voltage is applied concurrently with a uniaxial pressure to in principal sinter the MMed powders. The process effectively prohibits the growth of the bulk materials resulting better mechanical properties. 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 and oxide layers leading to enhanced sintering and consolidation [11, 12].

Some mechanical properties of nanostructured pure aluminium produced by mechanical grinding (MG) and SPS have been investigated in [7]. The SPS materials fabricated from 8 h mechanically ground aluminium powders exhibited compressive 0.2% proof stresses of 440 MPa at room temperature [7]. 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

2.1 Material preparations

Air-atomised 99.9% pure aluminium powder with an average diameter of 100 μm was used. Stainless steel balls 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 MMed powders were consolidated by an SPS apparatus. Seven grams 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.

2.2 Material evaluations

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 after covering specimens by oil wax to prevent penetration of water into pores. 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 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. Results and Discussion

Figure 1 shows the hardness of SPS processed materials for the different MM processing times together with the measured density of the SPS materials. The hardness values of the SPS materials produced from the 0 h, 4 h and 8 h MMed powders were approximately 39 HV, 139 HV and 158HV, respectively. 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 4 times higher than that of the non-MMed powder. These results indicate that the combination of MM and SPS process was beneficial for the producing high hardness of the bulk materials, and the selected conditions for the

SPS process in the present research 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 [13].

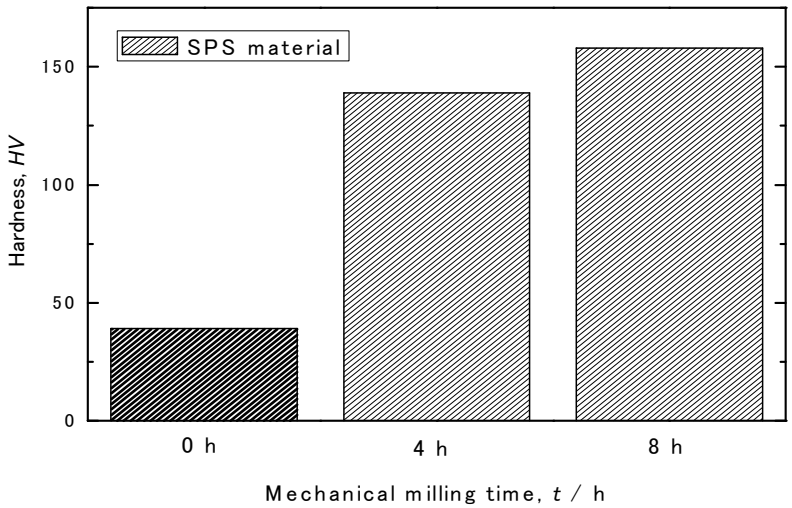

Fig. 1 The Vickers hardness of the SPS bulk materials fabricated from 0 h, 4 h and 8 h MMed powders.

Figure 2 presents changes in Vickers hardness of various SPS materials as function of different heating time at 873 K. The different hardness level of the as-SPSed state was corresponded to the hardness of the starting MMed powders. The hardness decreased slightly at the initial stages of heating up to 24 h, and no significant decrease was observed after the SPS materials heating at 873 K for 24 h due to formation of γ-Al_2O_3 and Al_4C_3 identified by X-ray diffraction analyses.

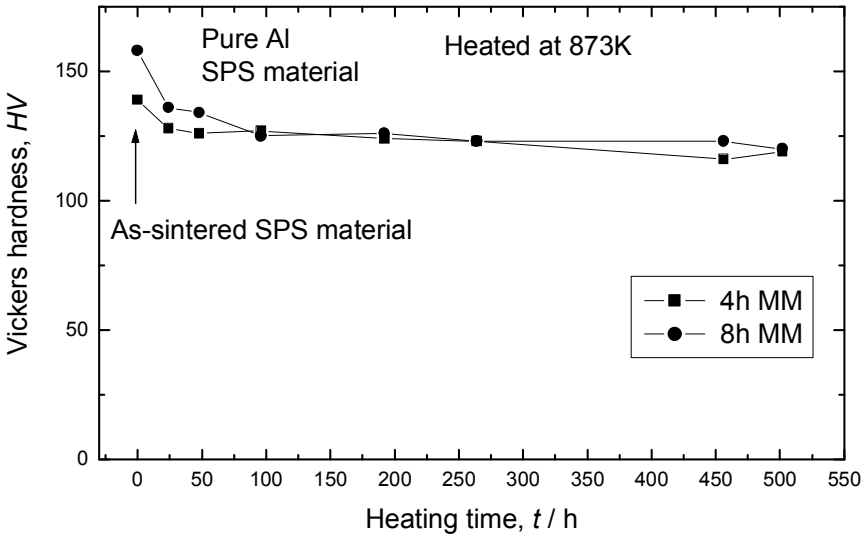

Fig. 2 The changes in the Vickers hardness of the SPS bulk materials fabricated from 4 h and 8 h MMed powders after heating at 873 K for various holding times.

Before heating at 873 K, the EBSD map of the bulk materials fabricated from 8 h MMed powders exhibited a bimodal pattern with approximately 300 nm and 2-5 m grain size for fine and coarse grains, respectively [14]. After heating at 873 K, it can be seen in Fig. 3 that there is no change in grain size and shapes of the grains. Both results show a bimodal pattern with approximately 300 nm and 2-5 m grain sizes for fine and coarse grains, respectively.

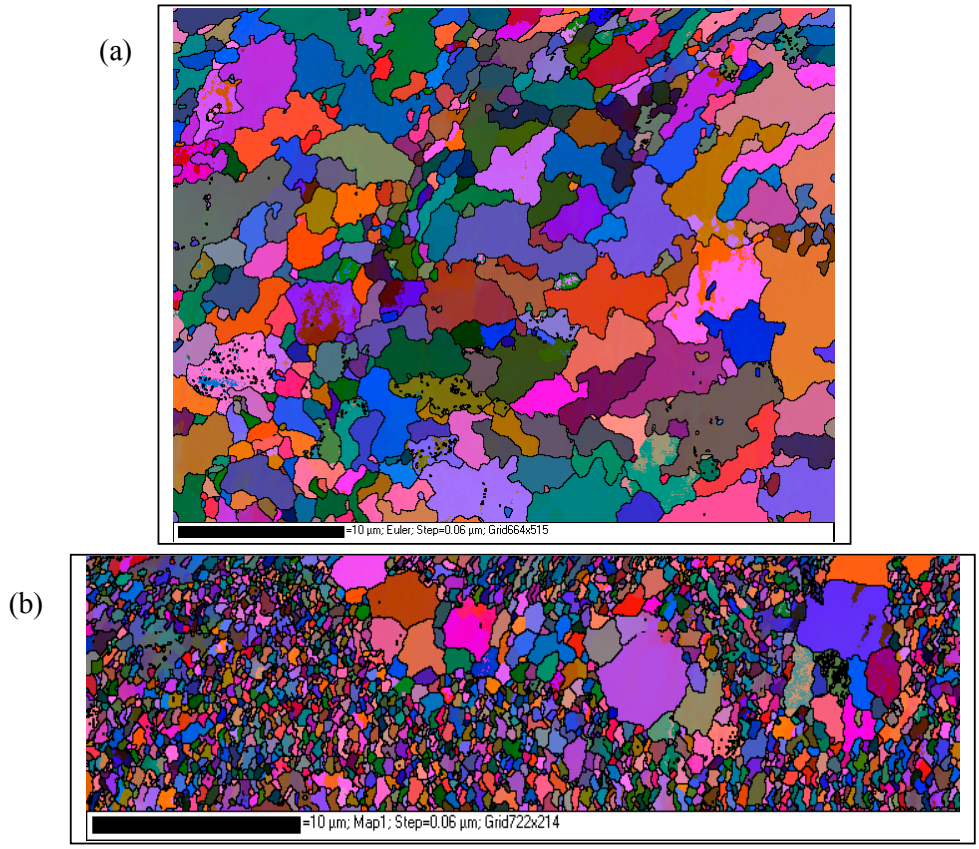

Fig. 3 Euler contrast image of the (a) 4 h and (b) 8h MMed pure Al powder fabricated by SPS after heat treatment for 24 hours under 873 K. White and black lines in the figure show misorientations of >2° and 15°, respectively.

4. Conclusions

The bulk materials produced by a combination of MM and SPS processes exhibited high thermal stability not only their hardness, but also microstructures. The mechanical properties of the finished product 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 that leads to higher strengths via Hall-Petch type strengthening mechanisms.

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