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Properties of nano-structured pure Al produced by mechanical grinding and spark plasma sintering

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Abstract

Air-atomised pure aluminium powder was mechanically grinded (MG) using a vibrational ball mill, and mechanically grinded powder was sintered by spark plasma sintering (SPS). Solid-state reactions of MG powder after various heat treatments were studied by X-ray diffraction (XRD). The mechanical properties of the SPS materials were evaluated by hardness and compression testing. Characterisations of the solid-state reactions between the MG powder and process control agent (PCA) after heating at temperatures from 573 to 873 K for 24 h suggested the following products. No solid-state reaction was observed after heating up to 573 K for 24 h. Formation of γ-Al_2O_3 occurred in the 4 h MG powder after heating at 773 K for 24 h, whereas the mixture of γ-Al_2O_3 and Al_4C_3 was observed in the 8 h MG powder after heating at 773 K for 24 h. The full density of the SPS material was obtained with the condition of applied pressure at 49 MPa at 873 K for 1 h. The Vickers hardness of the SPS material produced from no MG process and 64 h MG powders exhibited HV39 and HV159, respectively, and the SPS material based on no MG process and 8 h MG powders showed room temperature compressive proof stresses of 173 and 440 MPa, respectively.

Keywords: Nano-structured materials; Metal matrix composites; Mechanical alloying; Phase transitions; X-ray diffraction

1. Introduction

Particle-reinforced aluminium matrix composites with lightweight are of considerable interests as a class of materials capable of advanced structural and thermal applications. Mechanical alloying (MA) and subsequent hot extrusion of aluminium-based composite materials has been shown to produce desirable mechanical properties at room and elevated temperatures [1]. Various particulate-strengthened aluminium composites produced via powder metallurgy routes have been experimentally developed for applications in structural components [2,3]. Furthermore, the technique of mechanochemical synthesis (i.e. reaction milling (RM) [4]) has attracted considerable interest due to the unique properties that can be developed.

Spark plasma sintering (SPS) is a novel technique developed for sintering advanced ceramics and composite materials. The advantage of the SPS process is that it allows fabrication of bulk materials from powders using relatively short sintering times at low temperatures compared to that of hot press (HP) and hot isostatic press (HIP) processes. Therefore, coarsening of fine grains and nano-sized dispersed particles in MA powders can be avoided.

The SPS techniques are due to pulse electric current flows directly in the sintered materials and mould. A very high heating efficiency is offered for the materials that are very difficult to be sintered by the other processes. It is well known that the Al powders are hardly sinterable materials because of the oxide layer on its surface. This layer should be broken up in order to achieve high packing density. It can be possible to obtain bulk materials of mechanically alloyed Al powders using SPS.

In the present work, effects of mechanical griding and heat treatments on solid-state reaction and mechanical properties of mechanically ground pure aluminium powder were investigated by X-ray diffraction and mechanical tests. Additionally, SPS process is applied to produce fully densification of bulk materials, and characteristics of the SPS materials, such as mechanical properties and solid-state reaction, were clarified.

2. Experimental procedures

Air-atomised pure Al powders with average diameters of 100 μm were mechanically ground (MG). Stainless steel balls of 7 mm in diameter together with 10 g of the pure Al powder and stearic acid ($C_{17}H_{35}COOH$) as a process

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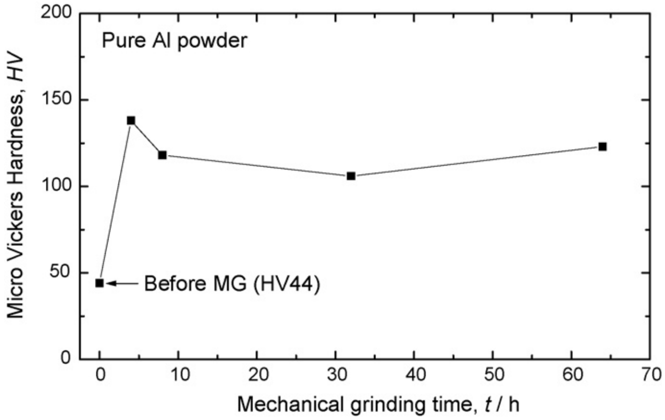

Fig. 1. Change in Vickers microhardness of pure Al powder with mechanical grinding time.

control agent were sealed in a hardened steel vial using a glove box filled with argon. The ball to powder mass ratio was approximately 7:1. The MG process was performed at room temperature using an SPEX8000 mixer/mill. The MG processing time was varied from 4 to 64 h. The MG powders were heat treated at temperatures from 573 to 873 K for 24 h. XRD analysis was performed on both the MG powders and SPS materials using a Cu Kα radiation source and operating at 40 mA and 60 kV. The average Vickers hardness of the MG powders was determined from 15 particles per sample with a microhardness tester using an applied load of 98 mN. The MG powders were consolidated by SPS. Seven grams of MG powder was placed into a graphite die of 20 mm in diameter 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 using an applied load of 9.8 N.

3. Results and discussion

Fig. 1 presents the change in Vickers microhardness of the pure Al powders as a function of different MG processing times. The hardness of the pure Al powder before MG was approximately HV44. The hardness of the pure Al powder increased dramatically to over HV130 after 4 h of MG, but a slight decrease was observed down to a value of HV120 after 8 and 32 h of MG. It is interesting to note that the pure Al powder exhibits a broad hardness plateau at HV125 after 64 h of MG, suggesting saturation of strain introduced by MG. Significant broadening and reduction in the X-ray diffraction peaks occurred after 4 h of MG, suggesting the formation of fine crystalline grains and/or a high density of defects in the matrix [5].

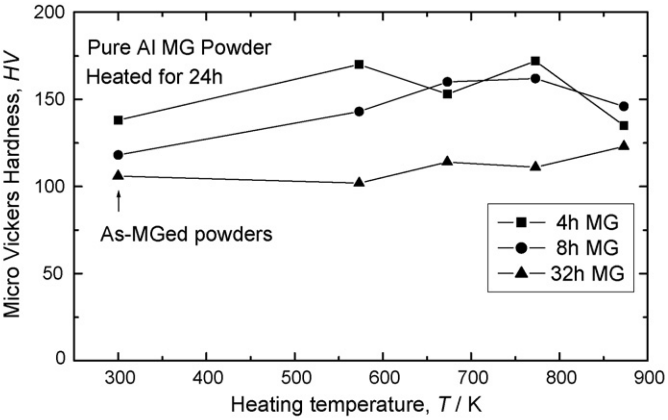

Fig. 2. Change in Vickers microhardness of pure Al MG powders on heating at various temperatures for 24 h.

Fig. 2 shows the change in the Vickers microhardness of the MG powders after 4, 8 and 32 h of MG and heating at temperatures from 573 to 873 K for 24 h, respectively. The Vickers microhardness of the pure Al powder after 4, 8 and 32 h of MG increased gradually between the heat treatment temperatures of RT and 573 K. Although heating temperatures at 873 K is approaching to the melting point of the pure Al, no significant

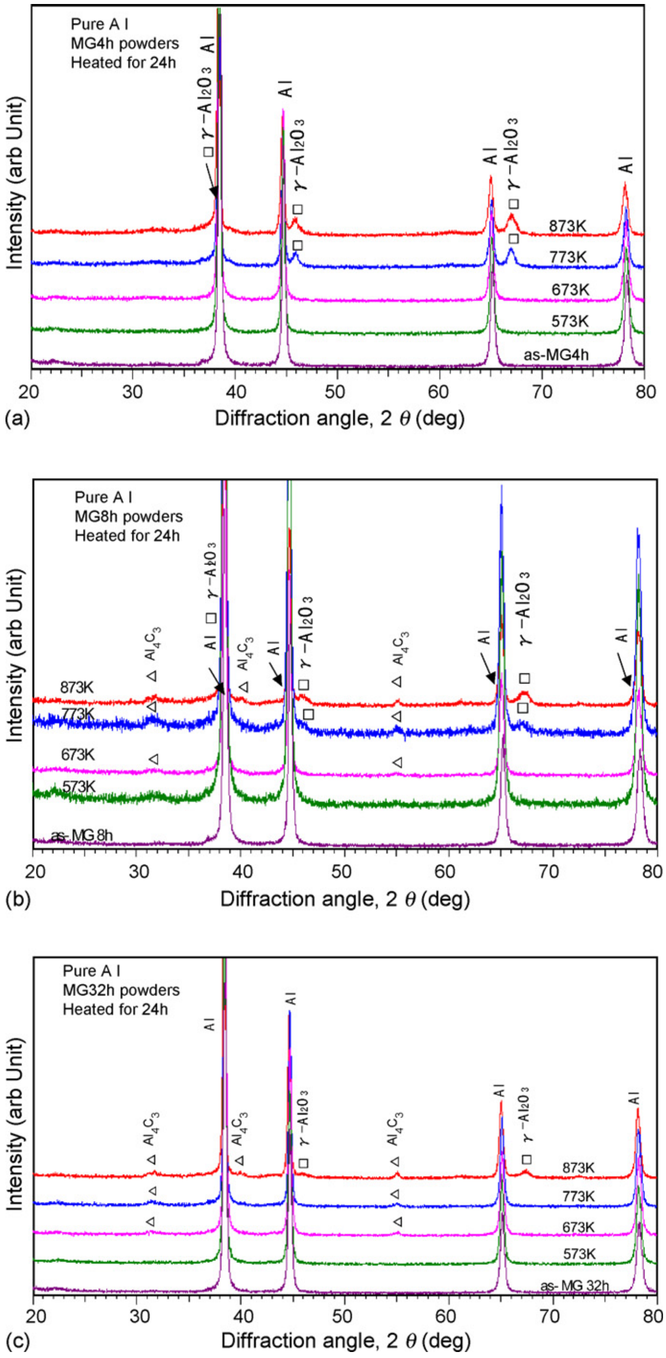

Fig. 3. X-ray diffraction patterns of various pure Al MG powders after isochronal heating at various temperatures for 24 h: (a) MG 4 h, (b) MG 8 h and (c) MG 32 h.

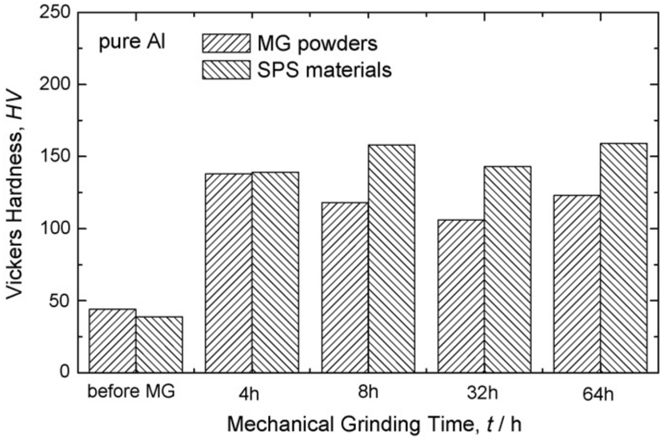

Fig. 4. Comparison of hardness between various MG powders and SPS materials.

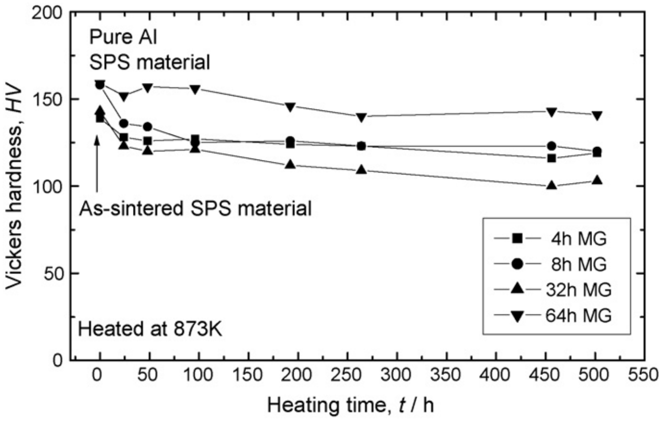

Fig. 6. Change in Vickers hardness of various SPS materials with different heating time at 873 K.

decrease in the Vickers microhardness was observed after 8 and 32 h of MG after heating at 873 K for 24 h.

X-ray diffraction patterns of the MG powders after (a) 4 h, (b) 8 h and (c) 32 h of MG and heating at temperatures from 573 to 873 K for 24 h are presented in Fig. 3. In the 4 h of MG powder, no solid-state reaction occurred after heating up to 673 K. However, partial reactions between pure Al and stearic acid ($C_{17}H_{35}COOH$) occurred after heating at 773 K. New diffraction peaks were observed near $2\theta = 46^\circ$ and 67°, which were identified as γ-Al_2O_3 [6]. The intensity of the γ-Al_2O_3 peaks increased after heating at 873 K, suggesting the promotion of a solid-state reaction during heating. As for the 8 h of MG powder, no solid-state reaction occurred after heating up to 573 K. However, partial reactions between pure Al and stearic acid occurred after heating at 673 K. New diffraction peaks were observed near $2\theta = 32^\circ$ and 55°, which were identified as Al_4C_3 [7], and γ-Al_2O_3 [6] was observed after heating at 673 and 773 K, respectively. The intensity of the γ-Al_2O_3 peaks decreased after heating at 773 and 873 K compared to that of in 4 h of MG powder, suggesting the suppression of a solid-state reaction during heating. When the MG time increased up to 32 h, solid-state reaction occurred after heating up to 673 K, and the formation of Al_4C_3 [7] occurred after heating at 673 K. However, the formation of γ-Al_2O_3 [6] occurred after heating at 873 K. These results suggest that solid-state reaction in MG powders is promoted by lower heat treatment temperatures as the MG processing time increases. In addition, solid-state reaction products of Al_4C_3 [7] is promoted by increasing MG processing time, but solid-state reaction products of the γ-Al_2O_3 is suppressed by increasing MG processing time. The hardness of the MGed pure Al after heating maintained the almost same hardness level as the MG stage due to the formation of γ-Al_2O_3 and Al_4C_3.

Fig. 4 compares the Vickers microhardness of the MG powders and bulk materials produced by the SPS process. The hardness values of the SPS materials produced from 8, 32 and 64 h MG powders were higher than that of the MG powders. These results indicate that the SPS process was beneficial for the consolidation of the bulk materials, and the selected conditions for the SPS process in the current research were optimal for the MG powders used.

X-ray diffraction patterns of the SPS materials are presented in Fig. 5. The formation of γ-Al_2O_3 [6] and Al_4C_3 [7] occurred after heating at 873 K for 3.6 ks as the SPS consolidation process. These results suggest that solid-state reaction in MG powders is promoted by consolidation process that exhibit good mechanical properties.

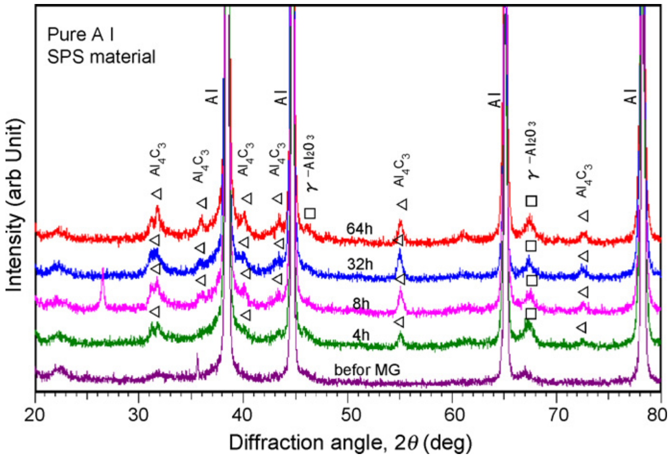

Fig. 5. X-ray diffraction patterns of SPS materials in pure Al powders with different MG time.

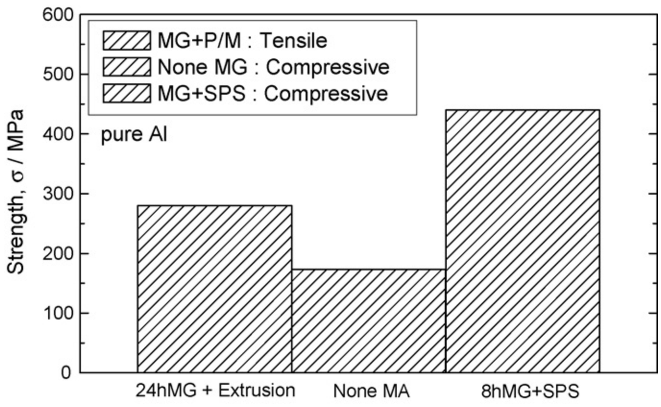

Fig. 7. Compressive proof strength at room temperature of MG 0 h and MG 8 h SPS materials compared with tensile strength of as-extruded MG 24 h P/M.

Fig. 6 shows changes in Vickers hardness of the various SPS materials as function of different heating time at 873 K. No significant decrease in the Vickers hardness was observed after the various SPS materials heating at 873 K for over 500 h due to formation of γ-Al_2O_3 and Al_4C_3.

The value of the 0.2% compressive proof stress for the SPS materials is shown in Fig. 7. The compressive proof stress of the 8 h MG SPS material (440 MPa) was approximately 2.5 times higher than that of no-MG SPS material (173 MPa). Furthermore, the values were only 20% lower than that of conventional high strength 7075-T6 alloy (505 MPa).

4. Summary

The formation of γ-Al_2O_3 and/or Al_4C_3 occurred by solid-state reaction between the pure Al and stearic acid in the heat heated MG powders. When MG time is relatively shorter, γ-Al_2O_3 is formed. On the other hand, when MG time is relatively longer, γ-Al_2O_3 is suppressed, and Al_4C_3 is formed. A higher heat treatment temperature was needed to promote solid-state reaction for the MG powders when MG time was shorter. In contrast, for a given composition, solid-state reaction occurred at relatively lower heating temperatures when the MG time was increased. The SPS material based on 8 h MG Al powder exhibited room temperature compressive proof stresses of 440 MPa.

References

[1] L. Lu, M.O. Lai, Mechanical Alloying, Kluwer Academic Publishers, 1998.
[2] D.G. Kim, J. Kaneko, M. Sugamata, Mater. Transact. JIM 36 (1995) 305–311.
[3] L. Blaz, J. Kaneko, M. Sugamata, R. Kamei, Mater. Sci. Eng. A 349 (2003) 111–119.
[4] P.G. McCormick, Mater. Transact. JIM 36 (1995) 161–169.
[5] B.D. Cullity, Elements of X-ray Diffraction, 2nd ed., Addison-Wesley, Reading, 1978.
[6] PDF:10-0425, International Centre for Diffraction Data, 1999.
[7] PDF:34-0799, International Centre for Diffraction Data, 1999.