

FABRICATION OF Al/Al₂O₃ COMPOSITE BY POWDER FORGING OF ALUMINUM POWDERS AND MANGANESE OXIDE POWDERS

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Abstract

Aluminum matrix composites having Al₂O₃ as reinforcement phase is fabricated by powder metallurgy method. Mixture of Al-1at.%MnO₂ is cold compacted and hot forged to produce high density billet. Annealing of forged billet is subsequently carried out to generate Al₂O₃ in-situ from chemical reaction between Al and MnO₂. Phase identification by X-ray diffraction technique verifies formation of Al₂O₃, as reinforcement phase, along with formation of MnO and Al₆Mn phases, after annealing. MnO is the product of incomplete reduction of MnO₂ by Al, while formation of Al₆Mn is due to the release of manganese to the aluminum matrix beyond the limit of solubility. Tensile strength and ductility of the obtained Al/Al₂O₃ composite reaches 120 MPa and 8%, respectively, for forged billet which are anneal at 600°C for 30 h. Annealing at higher temperature and for longer time results in decrease of tensile strength.

1 Introduction

Metal matrix composites (MMCs) having aluminum alloy as matrix materials are widely used in aerospace application. A strong interface between aluminum alloy matrix and reinforcement phase crucially determines failure behavior of the composite. One method to create strong bonding at interface is to generate the reinforcement phase via chemical reaction during fabrication, which is the so-called in-situ method.

Fabrication of Al/Al₂O₃ composite via powder metallurgy method from the mixture of Al and Al₂O₃ powders usually results in weak bonding at interface due to the poor wettability between the two phases [1]. In addition, Al₂O₃ is chemically inert; consequently, successful sintering between Al₂O₃

powder and Al₂O₃ film on Al powder requires temperature greater than 1600°C [2]. In-situ method, therefore, is an alternative which is able to generate Al₂O₃ phase in alloy matrix, by carefully selecting oxidizing agent to chemically react to aluminum and produce Al₂O₃ phase. In this research, MnO₂ powder is added to Al powder to create Al₂O₃ reinforcement phase in-situ via chemical reaction between Al and MnO₂ powders. Extensive study of decomposition of MnO₂ by M.I.Zaki et al. in non-oxidizing atmosphere shows that, starting at 550°-600°C, MnO₂ decomposes to Mn₅O₈, Mn₂O₃, and eventually resulting in Mn₃O₄ at 950°-1050°C. Under reducing atmosphere (H₂); however, MnO₂ decomposes at 400°-500°C to MnO, which is stable up to 1050°C [3]. In this experiment, MnO₂ powders are surrounded by Al powders, and are expected to be reduced by the aluminum matrix, with the formation of Al₂O₃, and Mn in solid solution or as Al₆Mn intermetallic.

A study by Hamid et al. used MnO₂ powder to successfully produce Al/Al₂O₃ composite in liquid state, by stirring MnO₂ powder into molten aluminum alloy [4]. In this study, MnO₂ powder is mixed with Al powder to generate Al₂O₃ phase in solid state, via powder metallurgy method.

2 Experimental Procedure

Aluminum powder (99.8 μm, mean particle size 148 μm), were mixed with MnO₂ powder (99% purity, mean particle size 14 μm), to make a powder mixture with compositions Al-1at.%MnO₂, equivalent to Al-3.1wt%MnO₂. Powder mixing was done by pouring the powders and Ø5-mm alumina balls, at 1:5 weight ratio, in a 500 ml polyethylene bottle. The bottle was shaken at 60 Hz for 3 h by a rocking mill (Seiwa Giken, model RM-05). The mixed powders were cold pressed in a Ø30-mm die under 142 MPa pressure to make a cold compact.

Cold compacts were consolidated by powder forging. The cold compact was heated to 600°C at heating rate of 5°C/min, and hold at the temperature for 15 min, under Ar atmosphere. Subsequently, the heated specimen was immediately taken out of the furnace and forged by a 200-ton servomotor screw press (Enomoto machine co.) using 660 MPa at initial strain rate of 17.5 s⁻¹. The forging die size is Ø35 mm, and kept at 300°C.

Forged billets were annealed to generate in-situ Al₂O₃ reinforcement phase. Annealing was done by heating the forged billet to sintering temperature using heating rate of 5°C/min, and furnace cooled. The sintering temperatures were 600 and 650°C. The holding time for sintering at 600°C was varied as 10, 20, 30, and 40 h, in air atmosphere. For comparison, additional set of experiments of forging and annealing using only pure aluminum powders was carried out.

Specimens were polished to mirror finished by SiC paper, followed by 1-µm diamond paste. The microstructure was investigated by optical microscope, and scanning electron microscope (SEM) with energy dispersive spectrometry (EDS), (JEOL, model JSM 6400). Phases present in the specimen were characterized by X-ray diffractometer (XRD), using CuK_α radiation, (Rigaku, model D/Max2000). For tensile test, the billet was machined according to Figure 1. The direction of applied tensile load was perpendicular to forging axis.

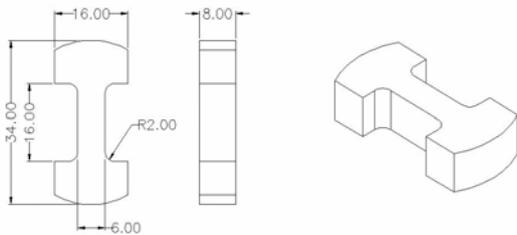


Fig. 1. Schematic drawing of tensile specimen.

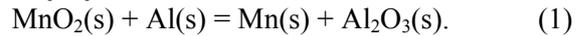
Thermal analysis of Al-1at.%MnO₂ powder mixture were characterized by differential thermal analyzer (DTA), (Netzsch, model STA 409). Heating rate is 5°C/min, from 30 to 800°C, under flow of nitrogen.

Identification of reinforcement phase in the billet was by dissolution in HCl solution. The billets were grinded to make small chips. The chips were then placed in 5 liters of 2 M HCl for 24 h to dissolve the aluminum matrix. The sediment after dissolution, which is the reinforcement phase, was

filtered by Whatman filter paper #42. The filter paper was placed in porcelain crucible, dried and completely burnt by heating at 800°C for 3 h. The residual particles left in the crucible were characterized by XRD.

3 Results and Discussion

In-situ formation of Al₂O₃ reinforcement phase is ideally by the reaction:



However MnO₂ is known to decompose to several intermediate oxides at elevated temperature [3]. Figure 2 shows the result of differential thermal analysis of the powder mixture of Al-1at.%MnO₂. Decomposition of MnO₂ and melting of aluminum are indicated by endothermic peaks at 520 and 660°C, respectively. There are two broad exothermic peaks in the 220 to 270°C and 560 to 660°C ranges, which may indicate formation of Al₂O₃ reinforcement phase. Annealing temperatures of forged specimen are therefore selected as 600 and 650°C.

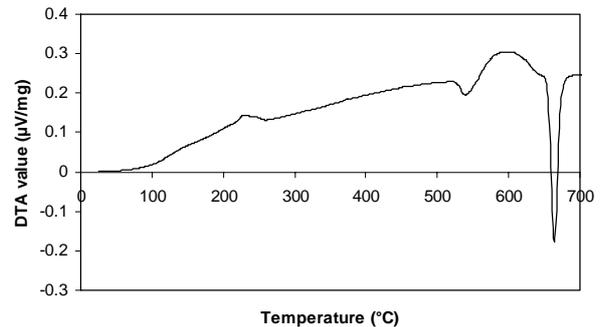


Fig. 2. Differential thermal analysis of Al-1at.%MnO₂ powder mixture.

The powder mixtures were cold compacted under 142 MPa pressure. Low compacting pressure was applied to limit to the relative density of the compact to about 90%. A too high relative density caused bursting of the specimen during heating prior to forging. The cause of bursting may be the rapid release of oxygen gas due to decomposition of MnO₂ during heating prior to forging. Relative density of the forged billets is in the range of 98 to 99%. Figure 3 shows the microstructure taken by SEM of the hot forged specimen annealed at 650°C for 30 h. There are three distinct areas: light grey area of the matrix (labeled A), dispersed regions of dark grey bands (labeled B), and disconnected white strings (labeled C). The dispersed black dots are the diamond powders of the polishing paste. EDS analysis of the

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three areas are summarized in Table 1. Alumina is formed in area A, without residual manganese oxide. Area A therefore represents complete reaction according to Eq. 1. In area B, aluminum and manganese elements are found with oxygen element. It may be included that area B represented the region where decomposition of manganese oxide does not go to completion. The white string phase is always surrounded by dark grey phase. This means that alumina is formed at the interface between the original manganese oxide phase and the aluminum matrix; although, close observation at higher magnification can not give clear outline of interfaces.

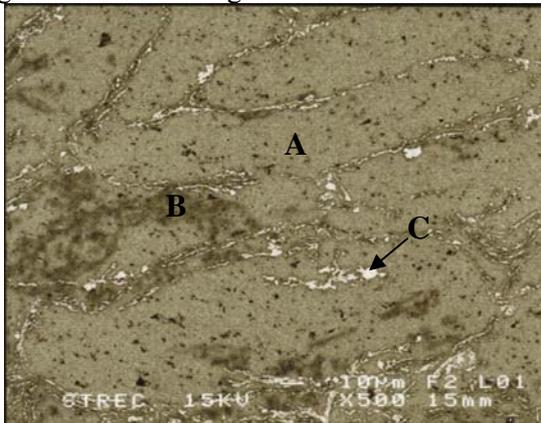


Fig. 3. Scanning electron microscope image of hot forged Al-1at.%MnO₂ forged and annealed at 650°C for 30 h.

Table 1. Chemical composition of the area A, B, and C in Figure 3.

Area	Oxygen (atom%)	Aluminum (atom%)	Manganese (atom%)
A	6	94	0
B	32	68	0
C	56	42	2

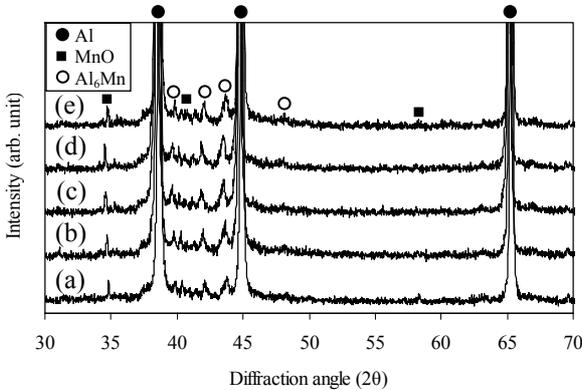


Fig. 4. X-ray diffraction patterns of Al-1at.%MnO₂ billets forged and annealed at 600°C for (a) 10, (b)

20, (c) 30, (d) 40 h, and (e) annealed at 650°C for 40 h.

Phase transformation of specimen is investigated by XRD. Figure 4 is XRD result of the specimen annealed at 600°C for 10, 20, 30, and 40 h, and annealed at 650°C for 40 h. From XRD patterns, Al₂O₃ phase is not found. However, there are peaks corresponds to Al, MnO, and Al₆Mn phases. This confirms the decomposition of MnO₂, and the dissolution of Mn into Al, with subsequent formation of Al₆Mn. Decomposition of MnO₂ is not complete; leaving MnO as a final product. Other kinds of manganese oxide compounds with higher O:Mn ratio such as Mn₂O₃ and Mn₃O₄ are not detected.

Amount of alumina formed in the specimen may be too little to be detected directly from the bulk specimen by XRD. Therefore, the specimen is dissolved in HCl solution, and residual particles are filtered off, and characterized by XRD. The result is shown in Figure 5. Alumina is the only phase identified. This confirms the EDS result, and the chemical reaction in Eq. 1. For comparison, additional forging and annealing experiment of pure aluminum powders was carried out. It is found that weight of residual particles from Al-1at.%MnO₂ specimens is greater than that of pure aluminum specimens at all annealing temperatures. In addition, weight of residual particles increases with the annealing time.

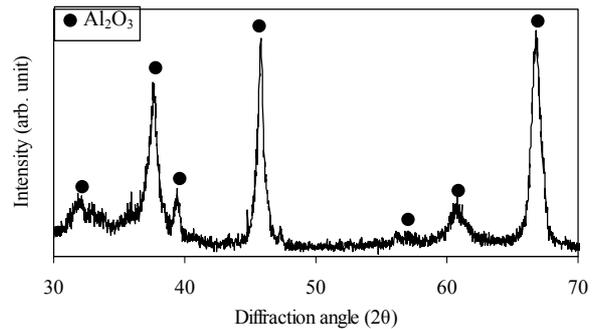


Fig. 5. X-ray diffraction pattern of residual particles after dissolution of Al-1at.%MnO₂ billet in HCl solution.

The results of tensile test of Al-1at.%MnO₂ billets are summarized in Figure 6. The ultimate tensile strength reaches that highest at 120 MPa for billet annealed at 600°C for 30 h. The tensile strength increases with the increase of annealing time. Together with the result of dissolution of billets in HCl solution, it may be stipulated that

strengthening of the specimen is due to the increase of alumina phase formed in-situ in the matrix during annealing. Annealing the specimen at 650°C for 40 h causes slight decrease of tensile strength to 115 MPa. It may be due to the softening of the aluminum matrix since the annealing temperature is very close to its melting point. Micro hardness measurement of matrix is difficult due to the presence fine distribution of reinforcement phase. For comparison, tensile strength of pure aluminum billets forged and annealed at 600°C is only in the 23 to 31 MPa range.

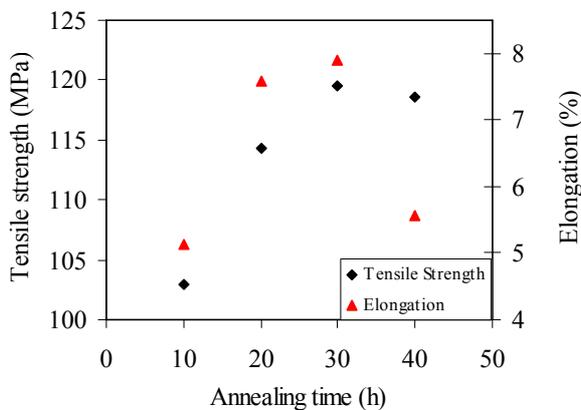


Fig. 6. Tensile strength and percent elongation of Al-1at.%MnO₂ billets annealed at 600°C for different times.

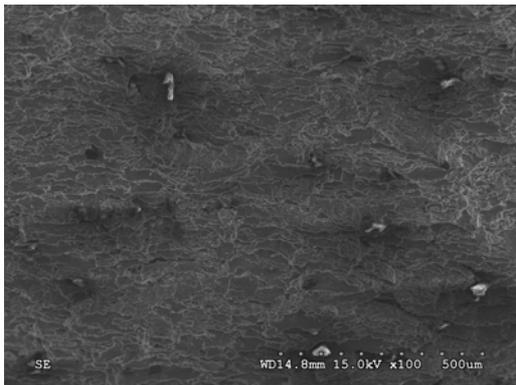


Fig. 7. Fracture surface of tensile specimen of Al-1at.%MnO₂ billet, forged and annealed at 650°C for 30 h.

Ductility of specimen varies with annealing time in the same way as the tensile strength does. At long annealing time, sintering is more complete, and results in an increase of ductility. Highest ductility is obtained as 8% for the specimen annealed for 30 h. Examination of fracture surface of tensile specimen shows uniform distribution of reinforcement phase,

shown as white protruding particles in Figure 7. In many areas, the reinforcement phase appears to be at the bottom of shallow cavity. This means that the reinforcement phase restrains deformation of the adjacent matrix, which is a strengthening mechanism of this composite.

4 Conclusion

Powder metallurgy method by hot forging and annealing can produce Al/Al₂O₃ composite from Al-1at.%MnO₂ powder mixture. The reinforcement phase, Al₂O₃, is generated in-situ via chemical reaction between Al and MnO₂ during annealing of forged specimen. Annealing temperature is 600°C, which is sufficiently high for chemical reaction to occur, but does not too severely soften the aluminum matrix. Tensile strength and ductility reaches 120 MPa and 8%, respectively, for specimen forged and annealed at 600°C for 30 h. Phases found in the specimen are Al, Al₂O₃, MnO, and Al₆Mn.

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