

Phase changes in sintering of Al/Mg/NaCl compacts for manufacturing Al foams by the sintering and dissolution process

D.X. Sun*, Y.Y. Zhao

Department of Engineering, University of Liverpool, Liverpool L69 3GH, UK

Received 11 November 2003; received in revised form 20 April 2004; accepted 6 May 2004

Available online 17 August 2004

Abstract

Addition of small amount of Mg in the Al/NaCl compacts has previously found to be an effective method for improving the sintering in manufacturing Al foams by SDP. However, the mechanism of the improvement is not fully understood. This paper investigates the phase changes in the Al/Mg/NaCl compacts during heating up and sintering by thermogravimetric analysis and electron microscopy. The results showed that the alumina hydrates formed on the surface of the Al particles gradually dissociate into hydrous alumina during heating up. Mg consumes the oxygen trapped in the compact and reduces some of the Al oxide to form MgAl_2O_4 . Consequently, more fresh metal contacts between the Al particles and less further oxidation during sintering lead to the improved sintering response.

© 2004 Published by Elsevier B.V.

Keywords: Al foam; Sintering and dissolution process; Mg reduction; MgAl_2O_4

1. Introduction

Al foams were first produced in 1950s and 1960s [1,2]. A wide range of liquid and solid state processing methods were developed in 1980s and 1990s [3–6] for manufacturing Al foams for commercial applications as light structures, noise dampeners and impact energy absorbers in the building and transport industries [7]. The sintering and dissolution process (SDP) is a novel method developed in the University of Liverpool for producing Al foams [8–12]. In SDP, an Al powder is mixed with a NaCl powder at a pre-specified proportion and compressed into a compact under a pressure of 200–300MP. The compact is sintered at a temperature of 610–680 °C for 2.5–50 h, depending on the composition and size of the compact. An Al foam is obtained when the NaCl in the sintered compact is dissolved in a hot water bath. SDP is one of the most cost-effective routes among the currently available processing methods for producing Al foams. The main advantages of SDP are uniform and accurately controlled cell sizes and porosities. The cell sizes of the foams can vary in a wide range of 100–5000 μm .

One of the challenges encountered in the development of SDP is overcoming the resistance of the Al oxide to

sintering to achieve a strong bonding between the Al particles. The mechanical rupture of the Al oxide layer by applying a high pressure during the compaction of the Al/NaCl mixtures can enhance the sintering process. However, the rupture mechanism alone is not sufficient to lead to a strong bonding between the Al particles because a significant proportion of the Al oxide layer is still intact [13]. Addition of Mg in the Al/NaCl compacts has found to be an effective method for reducing the Al oxide and improving the sintering of Al particles [10]. However, the reducing mechanism is not fully clear.

This paper investigates the phase changes in the Al/Mg/NaCl compacts during sintering by thermogravimetric analysis and electron microscopy, and discusses the mechanism by which the addition of a small amount of Mg enhances the sintering of Al.

2. Experimental procedure

The precursor materials used for fabricating the Al foam samples were a commercially pure, gas atomised Al powder, a commercially pure Mg powder and a culinary NaCl powder with particle sizes in the ranges of 50–400, 100–500 and 100–3000 μm , respectively. The NaCl powder was

* Corresponding author.

predried in an electrical furnace at 400 °C for 30 min. The Al, Mg and NaCl powders, 70, 0.15 and 29.85 wt.%, respectively, were then thoroughly mixed. The powder mixture was then divided into two portions, each of which was compacted under a pressure of 250 MPa using a hydraulic press. One of the compacts, a cubic with a side length of 2.5 mm, was used for thermogravimetric analysis. A differential scanning calorimeter (TG-DSC 111) was used to measure the heat flow and weight change of the compact when it was heated from room temperature to 650 °C at a rate of 10 °C min⁻¹ and then cooled down to room temperature at a rate of 5 °C min⁻¹. The heating and cooling process was carried out in an atmosphere of nitrogen with a purity of 99.99% at a pressure of 1 bar with a purging flow rate of 24 ml⁻¹. Another compact was sintered in an electrical furnace at 650° for 20 h. The sintered compact was placed into a hot flowing-water bath of ~ 95 °C for 2.5 h to dissolve the NaCl particles. The obtained foam was annealed at 550 °C for 0.5 h to relieve the residual stresses. The foam specimen was first filled with epoxy in vacuum and then cut into thin slices. A thin foam sample was ground to ~ 100 μm in thickness and further reduced to less than 50 μm by ion milling in argon. The sample, held in a 3-mm Cu ring, was analysed in a JEOL 2000 FX transmission electron microscope.

3. Results and discussion

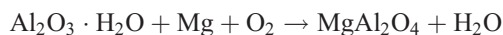
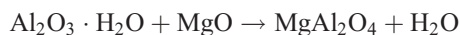
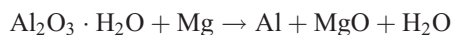
Fig. 1 shows the variations of the heat flow and the weight change of the Al/Mg/NaCl compact with temperature in the differential scanning calorimeter. The weight of the sample generally decreased when it was heated up from room temperature to 430 °C and then increased slightly when it was heated up further. However, there were two sharp changes, a weight increase at 300 °C and a weight decrease at 430 °C. The heat flow to the sample varied around 2.8 mW to maintain a constant heating rate of 10 °C⁻¹. The heat flow gradually decreased between 220 and

310 °C and increased between 310 and 405 °C. There was a sharp increase in heat flow at 450 °C.

The Al/Mg/NaCl compact may be subject to complex physical and chemical changes during the heating up. The NaCl particles are not expected to have any chemical changes except absorbing moisture at low temperatures and gradually releasing the absorbed water during heating up. The particles of the gas atomised Al powder are unavoidably covered with an oxide layer because of the high reactivity of Al. During the handling in air, the particles absorb water both physically and chemically and the oxide consequently becomes Al hydroxides with one or three water molecules [14,15]. The thickness of the surface layer of the Al hydroxides and physically absorbed water continues to grow at room temperature [16]. When the powder is heated up, the physically absorbed water is gradually released. Anderson et al [17] reported that alumina trihydrate (Al₂O₃·3H₂O) is decomposed into the alumina monohydrate (Al₂O₃·H₂O) at 150–310 °C. Al₂O₃·H₂O will finally dissociate into the anhydrous alumina (Al₂O₃) if the temperature rises to 500 °C and all the absorbed water will eventually be released [17].

Fig. 1 shows that between 220 and 310 °C there was a steady increase in the heat flow to the sample and a more rapid decrease in the sample weight. This is consistent with the decomposition of alumina trihydrate into alumina monohydrate in this temperature range [17]. Between 310 and 405 °C, the heat flow to the sample gradually decreased to the normal level and the weight decrease slowed down. This seems consistent with the decomposition of alumina monohydrate to anhydrous alumina.

The amount of Mg added to the compact only accounted for 0.15 wt.%. However, its high reactivity can result in significant chemical changes, leading to a different pattern of heat flow as well as minor changes in the sample weight. Mg has a high affinity to oxygen and is easily oxidised. The weight increase at 300 °C was very likely due to the oxidation of Mg. Fig. 1 also shows that there was a minor decrease in the heat flow corresponding to 300 °C. As the oxidation of Mg is an exothermic reaction, this seems to confirm that the Mg oxidation did take place at about 300 °C. Mg can also reduce the oxide or hydroxides of Al, because of its higher reactivity. The possible reduction reactions are:



These reduction reactions may have sped up the dehydration. Fig. 1 shows that there was a sharp decrease in weight at 430 °C and then the weight ceased decreasing

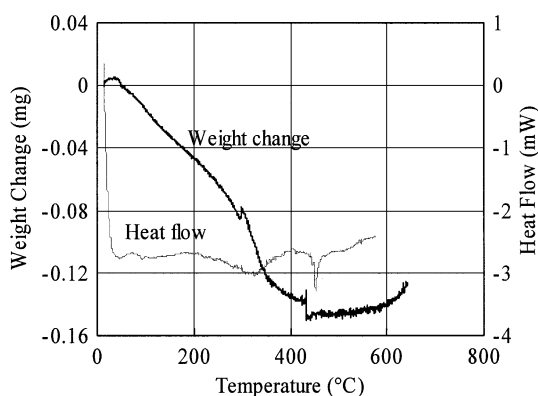


Fig. 1. Heat flow and weight change during heating up of an Al/Mg/NaCl compact with 0.15 wt.% Mg.

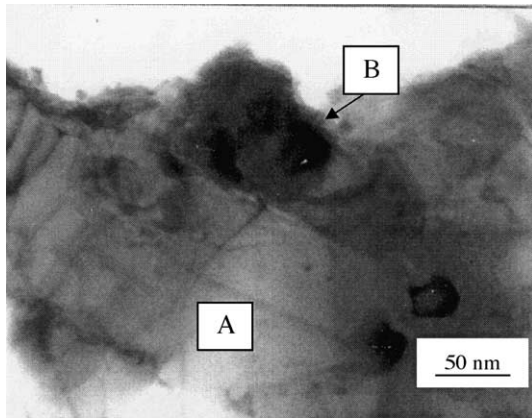


Fig. 2. Bright field TEM image of the Al foam with Mg addition.

with increasing temperature further, indicating that dehydration was complete well below the normal temperature of 500 °C [17]. The sharp increase in the heat flow to the sample at around 450 °C was probably due to the final evaporation of the released water molecules. At above 430 °C, the Al and Mg in the sample may be subject to

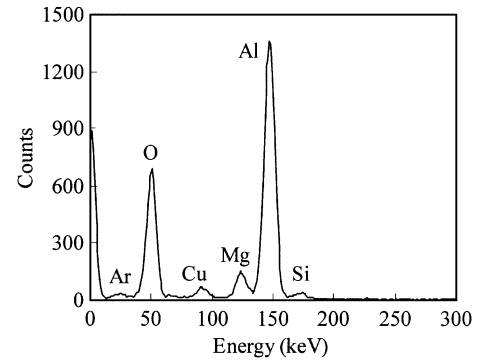


Fig. 4. EDX spectrum of the dark region B in Fig. 2.

oxidation by the residual oxygen in the chamber of the calorimeter. Accordingly, there was minor increase in sample weight and reduced heat flow to the sample.

Fig. 2 shows a bright field TEM image of the Al foam sample, with a dark particle (region B) in the matrix (region A). Fig. 3 shows the selected-area diffraction patterns taken from the dark region B and its neighbouring region A. Fig. 4 shows the EDX spectra taken from the dark region

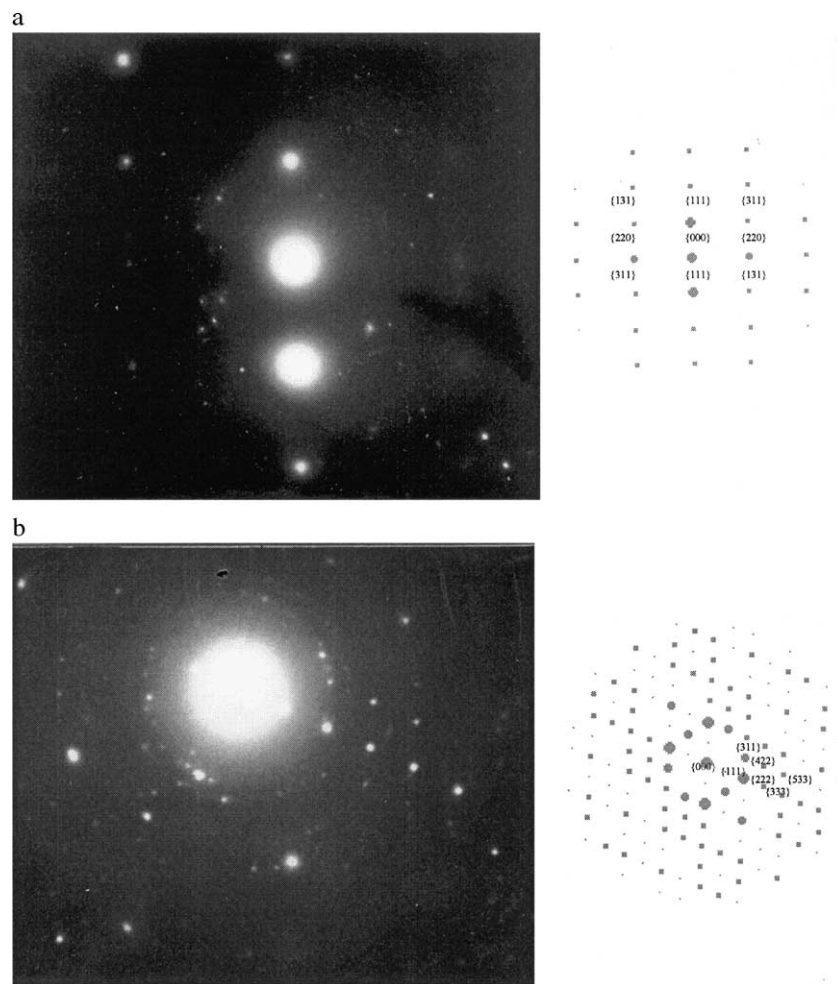


Fig. 3. Selected-area diffraction patterns taken from (a) the dark region B in Fig. 2 at the zone axis of [112] and (b) its neighbouring region A at the zone axis of [011].

Table 1
Composition of the dark region B in Fig. 2 determined by quantitative EDX analysis

| Element | <i>k</i> factor | Weight percentage (%) |
|---------|-----------------|-----------------------|
| O | 1.810 | 40.89 |
| Mg | 1.085 | 5.36 |
| Al | 1.044 | 52.31 |
| Si | 1.000 | 1.31 |
| Total | | 100.00 |

B. Table 1 shows the quantitative analysis results of the EDX spectrum taken from the region B. Apparently, the dark region consists of at least one phase containing Mg. The oxide layers developed during the oxidation of Al–Mg alloys are reported to be invariably composed of the spinel phase MgAl_2O_4 and MgO [13,18,19] and MgAl_2O_4 is thermodynamically favoured and often predominates in the oxide layers [20]. MgAl_2O_4 crystallites can also form by the reduction of the amorphous Al_2O_3 layer existing before the oxidation [20]. The selected-area diffraction pattern of the dark region in Fig. 2 is indexed as that of the cubic MgAl_2O_4 at a zone axis of [011] related to the diffraction pattern of the matrix Al at a zone axis of [112]. $\gamma\text{-Al}_2\text{O}_3$ and MgO also have a cubic structure and a similar lattice parameter as MgAl_2O_4 . However, MgO is unlikely to be the dominant phase in the dark region because MgO has an extremely low diffraction relative intensity at a plane of (111) [21]. The particle is therefore likely to be a mixture of MgAl_2O_4 and Al_2O_3 . From the composition of the particle determined by the quantitative analysis, the MgAl_2O_4 and Al_2O_3 phases are estimated to account for about 20 and 80 mol%, respectively.

The mechanism of the improvement of sintering in SDP by the addition of small amount of Mg has been speculated in a previous study [10]. The above results confirm that Mg absorbs the oxygen trapped in the compact and reduces the Al oxide films. As a consequence, more fresh metal contacts between the Al particles are formed and the Al particles are subject to less further oxidation during sintering. Both factors lead to improved sintering response.

The amount of Mg needed for consuming the air trapped in the Al/NaCl compacts is very small. The porosity of an Al/NaCl compact compressed under 250–300 MPa is estimated to be about 5 vol.% [12], which is equivalent to 1 vol.% of free oxygen in the compact. To consume all the free oxygen by forming the Mg oxide, less than 0.0004 wt.% of Mg is needed. Therefore, the majority of Mg in the Al/NaCl/Mg compact is available for the reduction of the Al oxide and hydroxides. The previous work showed that adding 0.15 wt.% Mg to the Al/NaCl compact improved the bonding between the Al particles markedly and consequently the static and impact energy absorbing capacities of the as-produced foams were increased significantly compared with those without Mg additions [10]. An addition of 0.5 wt.% Mg was found to be sufficient for achieving a good quality foam [10].

4. Conclusions

The thermogravimetric analysis of the Al/Mg/NaCl compact showed that the weight of the sample generally decreased and the heat flow to the sample varied around 2.8 mW when it was heated up from room temperature to 430 °C. The weight decrease and the main variations in the heat flow were due to the dissociation of the alumina hydrates formed on the surface of the Al particles into the hydrous alumina. A sharp weight increase and a corresponding minor decrease in the heat flow at 300 °C indicated that the oxidation of Mg took place by absorbing the oxygen in the compact and the chamber. The TEM and EDX analysis showed that MgAl_2O_4 was formed in the foam sample produced by SDP, providing evidence that Mg reduced the oxide and the hydroxides of Al during sintering. The results confirm that the improvement of sintering in SDP by the addition of small amount of Mg is due to the consumption of the free oxygen in the compact and the reduction of the Al oxide films.

Acknowledgements

The authors would like to thank Dr. R. Murray of the Department of Engineering and Dr. H. Lachas of the Department of Chemistry, the University of Liverpool, for assistance in conducting the TEM and TG-DSC work, respectively.

References

- [1] A. Sosnik, US Patent 4099 961 (1948).
- [2] H. Seliger, U. Deuther, *Freiburger Forschungshefte* 103 (1965) 129.
- [3] G.J. Davies, S. Zhen, *Journal of Materials Science* 18 (1983) 1891.
- [4] V. Shapovalov, U.S. Patent 581549 (1993).
- [5] J. Banhart, *Manufacture, Progress in Materials Science* 46 (2001) 559.
- [6] F. Baumgärtner, I. Duarte, J. Banhart, *Advanced Engineering Materials* 2 (2000) 168.
- [7] L.J. Gibson, M.F. Ashby, *Cellular Solids: Structure and Properties*, 2nd ed., Cambridge University Press, Cambridge, UK, 1997.
- [8] Y.Y. Zhao, D.X. Sun, *Scripta Materialia* 44 (2001) 105.
- [9] D.X. Sun, T. Fung, Y.Y. Zhao, in: J. Banhart, et al. (Eds.), *Cellular Metals and Foaming Technology*, Verlag MIT Publishing, Bremen, 2001, p. 227.
- [10] D.X. Sun, Y.Y. Zhao, *Metallurgical and Materials Transactions, B* 34 (2003) 69.
- [11] Y.Y. Zhao, *Journal of Porous Materials* 10 (2003) 105.
- [12] Y. Zhao, F. Han, T. Fung, *Optimisation of compaction and liquid-state sintering in sintering and dissolution process for manufacturing Al foams*, *Materials Science and Engineering A*, in press.
- [13] R.N. Lumley, T.B. Sercombe, G.B. Schaffer, *Metallurgical and Materials Transaction. A* 30A (1999) 457.
- [14] E.A. Bloch, *Metallurgical Reviews* 6 (1961) 193.
- [15] L. Ackermann, et al., in: G.J. Hildeman, et al. (Eds.), *High Strength Powder Metallurgy Aluminium Alloys II*, TMS, Warrendale, PA, 1985, p. 175.
- [16] J.E. William Jr., *ASM Metals Handbook*, ASM, Metals Park, OH, 1984, p. 125.

- [17] I.E. Anderson, et al., in: A. Russell, et al. (Eds.), *Powder Metallurgy Aluminum and Light Alloys for Automotive Applications*, 2000, p. 75, Michigan.
- [18] H.P. Leighly Jr., A. Alam, *Journal of Physics F. Metal Physics* 4 (1984) 1573.
- [19] M.H. Zayan, et al., *Oxidation of Metals* 34 (1990) 323.
- [20] G.M. Scamans, E.P. Butler, *Metallurgical Transactions. A* 6A (1975) 2055.
- [21] *Powder Diffraction File (Inorganic phase)*, International Center for Diffraction Data, (JCPDS, USA, 1980).