JOURNAL OF MATERIALS SCIENCE 26 (1991) 1631 - 1634

Heating sequence and hydrogen evolution in alloyed aluminium powders

J. L. ESTRADA, J. DUSZCZYK, B. M. KOREVAAR
Laboratory for Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL, Delft, The Netherlands

The results reported here, showing the effect of a non-continuous degassing sequence on the Al–20Si–3Cu–1Mg powder, are a complement of previous work concerning the continuous degassing of the same powder. The degassing experiments were carried out, under high vacuum, in the temperature range 20 to 550 °C in a horizontal furnace heated at a uniform heating rate of 2.5 °C min^{-1}. The partial pressures of the released gases were monitored and analysed during the heating phase by a computerized Edwards EQ80F residual gas analyser (RGA). RGA measurements indicate that water and hydrogen are the main degassing products. A complete degassing can only be achieved if the sample is heated up to a temperature where the chemical reactions are finished in the applied time. Thermodynamical equations alone are not enough to explain the kinetics of degassing of aluminium powders. The diffusion of aluminium through its surface oxide layer (Al_2O_3), described by the self-diffusion of aluminium, can explain to a large extent the kinetics of degassing aluminium powders.

1. Introduction

It has been demonstrated that the processing of the Al–20Si–3Cu–1Mg P/M aluminium alloy must include a degassing step which improves room and elevated temperature properties of the final product [1] and that the fundamental aspects of moisture and gas evolution during degassing of a porous billet can be described in a semi-quantitative manner by means of a kinetic approach [2].

It is apparent, from our previous results [2], that the temperature is the principal parameter which influences the degassing behaviour and that the diffusion of aluminium through its surface oxide layer can explain, to a large extent, the kinetics of the degassing of aluminium powders. The aim of the work presented in this paper was to degas the Al–20Si–3Cu–1Mg powder, under high vacuum, in a non-continuous way with a different heating sequence to that used for continuous degassing [2].

2. Experimental procedure

The powder chosen for investigation consisted of a batch of rapidly solidified P/M aluminium alloy, atomized in air, based on the hypereutectic Al–Si–X system containing 20 wt % Si, produced by the Japanese firm Showa Denko K. K., with an average particle size of ~ 24 μm [3]. This alloy belongs to a heat-treatable group.

Experiments were performed recording mainly moisture and hydrogen desorption to investigate the degassing behaviour at different temperatures. The chemical composition of this P/M alloy, as obtained by atomic absorption spectrophotometry, is shown in Table I [3].

The processing used before degassing concerned the cold precompaction of the loose powdered aluminium alloy in a can. The precompaction was carried out on a uniaxial hydraulic press with a rigid die. A compaction pressure of 160 MPa was used in order to provide a material with about 65% theoretical density, leaving a proper level of interconnected porosity to allow subsequent degassing to occur efficiently [1].

Each can contained ~ 300 g aluminium powder after compaction. A cover plate with an evacuation tube was welded to the end of the can and the evacuation tube was connected to a vacuum source (turbomolecular pump connected with a quadrupole mass spectrometer). The cans and evacuation tubes were made of 6063 (Al–0.4Si–0.7 Mg) aluminium alloy.

The vacuum degassing experiments were carried out, in the temperature range 20 to 550 °C, in a horizontal furnace heated at a uniform heating rate of 2.5 °C min^{-1}. Released gases were monitored and analysed during the heating phase by a computerized Edwards EQ80F residual gas analyser (RGA). Temperatures in different locations of the can were simultaneously recorded. The unit measures total vacuum pressure and analyses the partial pressures over the mass range 1 to 80 atomic units (a.m.u.). Partial pressures are measured by the peak corresponding to m/e, where m is the atomic mass and e the electric

TABLE I Chemical composition of rapidly solidified powder (wt %) [3]

Powder	Si	Cu	Mg	Fe	Al
J1	18.8	3.2	1.1	0.25	bal.

0022–2461/91 $03.00 + .12 © *1991 Chapman and Hall Ltd.*

charge; the sensor being a quadrupole mass spectrometer.

3. Results and discussion

The powder particle surface mainly consists of an aluminium oxide/hydroxide layer which in the case of the air-atomized Al–20Si–3Cu–1Mg, has a thickness of ~ 40 nm [3]. Upon heating in vacuum the hydrous surface of cold precompacted powder is degassed. Fig. 1 shows the mass spectrum, generated by the residual gas analyser, with the relative amounts of water and hydrogen evolved, and the temperature ranges over which each gas is given off [2]. Oxygen and other components were also detected, although at much lower partial pressures. These results indicate that water and hydrogen are the main degassing products. They are evaporated from physically adsorbed moisture and decomposed hydroxides from the surface layer [4]. Fig. 1 shows a release of hydrogen up to 550 °C.

Based on these results and with the objective of reaching a complete degassing, experiments were carried out to degas the powder with a different heating sequence to that used for continuous degassing [2]. A sample was degassed at different experimental temperatures, T_D: room temperature (RT), 250, 350, 450 and 550 °C (twice), as indicated in the time–temperature profile of Fig. 2 by the stages a, b, c, d, e and f, respectively. Table II shows the experimental partial pressures of the products water, hydrogen and oxygen accordingly obtained.

For convenience, the degassing results were split into three regions: room temperature; high temperatures; and continuous reheating from room temperature up to 550 °C.

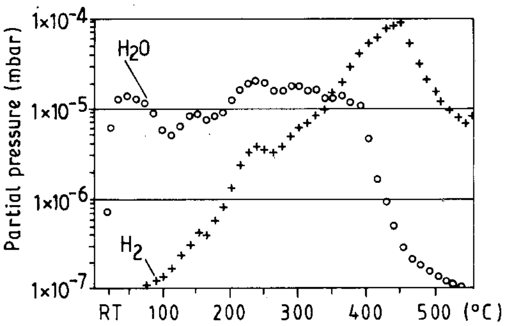

Figure 1 Degassing curves of air-atomized Al–20Si–3Cu–1Mg powder [2].

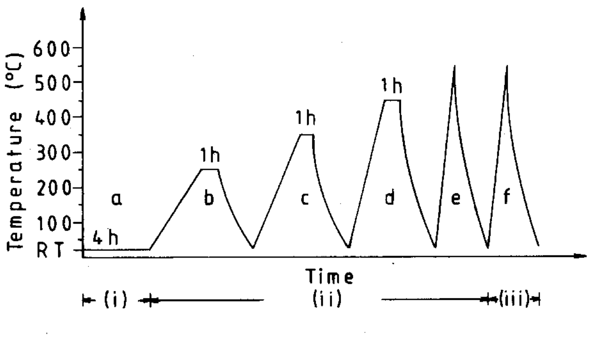

Figure 2 Time–temperature degassing profile.

TABLE II Experimental partial pressures of water, hydrogen and oxygen as a function of time and temperature

Degassing temp., T_D (°C)	Experimental partial pressures (mbar)		
	p_{H_2O}	p_{H_2}	p_{O_2}
RT	10^{-6}	10^{-9}	10^{-9}
RT, after 4 h	10^{-8}	10^{-10}	10^{-11}
250, after 1 h	10^{-5}	10^{-6}	10^{-8}
350, after 1 h	10^{-6}	10^{-6}	10^{-9}
450, after 1 h	10^{-8}	10^{-6}	10^{-10}
550	10^{-8}	10^{-6}	10^{-10}

3.1. Degassing at room temperature (stage a)

The change of the partial pressures as a function of time is shown in Fig. 3 and Table II. It can be seen that evacuation at room temperature lowers the gas pressure but strongly adsorbed water is not fully released regardless of the evacuation time (as appears from Fig. 4), whilst the evolution of hydrogen practically does not take place. The sample must therefore be heated in order to desorb these gases.

These results are consistent with the kinetic data, presented in [2], which indicate that the chemical reactions resulting in hydrogen evolution do not proceed.

3.2. Degassing at high temperatures (stages b to e)

Directly after evacuating at room temperature for 4 h, the sample was heated up to each degassing temper-

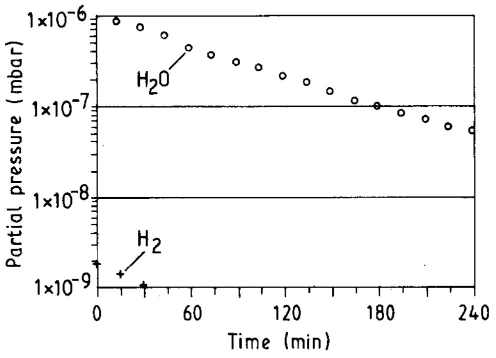

Figure 3 Al–20Si–3Cu–1Mg powder degassed at room temperature for 4 h.

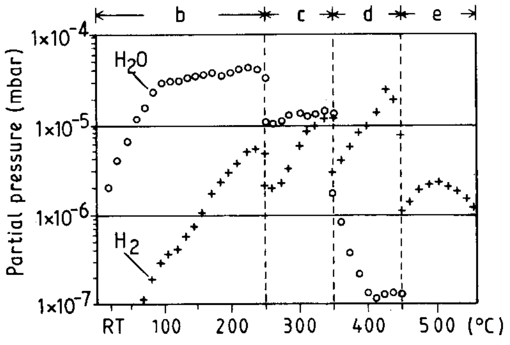

Figure 4 Al–20Si–3Cu–1Mg powder degassed as established in Fig. 2 (stages b to e).

ature, T_D, (see Fig. 2) at a uniform heating rate of 2.5 °C min^{-1}, under high vacuum, and evacuated for 1 h at this temperature (excepting $T_D = 550$ °C) while the partial pressures of moisture and hydrogen as a function of temperature were recorded. For simplicity, the degassing curves obtained (Fig. 4) are not wholly drawn, only selected portions of stages b to e are shown as if the process had been conducted in a continuous way.

If, for example, the sample is degassed at 250 °C for 1 h repeated degassings show lower and lower release of products, up to this temperature, until they become negligible; but, if the sample is degassed above $T_D =$ 250 °C, the desorption of both hydrogen and water follows approximately the same pattern as that followed for a sample which was degassed continuously from room temperature up to 550 °C (Fig. 1), although the relative amount of released products is lower.

The results from Fig. 4, for hydrogen as well as for water, are consistent with those obtained in [2] from which temperature appeared as the critical parameter governing the degassing reactions. This means that a complete degassing can only be achieved if the sample is heated up to the threshold temperature, where the reaction finishes, regardless of previous degassing stages at lower temperatures. Time of degassing is a secondary factor, which is, however, technologically important, due to its relationship with mass and porosity of the billet to be degassed.

It is apparent that after the sample was degassed up to 550 °C, hydrogen, some residual water and oxygen were still detected (Fig. 4, Table II).

It can be concluded from these results that even after degassing at 550 °C the degassing reactions are not completed.

3.3. Continuous reheating from room temperature up to 550 °C (Stage f)

The sample, still under vacuum, was then cooled down to room temperature and heated again, at a uniform heating rate of 2.5 °C min^{-1}, up to 550 °C. Only a negligible release of hydrogen was detected during this run below 550 °C.

Based on the thermodynamical and kinetic study of the surface reactions of this powder made in [2], it is apparent that the principal chemical reactions governing the degassing process are

$$Al(OH)_3 \rightarrow AlOOH + H_2O \quad (1)$$

$$2\,AlOOH \rightarrow Al_2O_3 + H_2O \quad (2)$$

$$\tfrac{2}{3}Al + H_2O \rightarrow \tfrac{1}{3}Al_2O_3 + H_2 \quad (3)$$

$$\tfrac{4}{3}Al + O_2 \rightarrow \tfrac{2}{3}Al_2O_3 \quad (4)$$

whose corresponding free energies at different degassing temperatures are presented in Table III [5].

From these calculations it can be concluded that Reactions 1 and 2 are not feasible at low temperatures, but proceed well at higher temperatures, whilst Reactions 3 and 4 proceed over the whole range of degassing temperature, and that the formation of hydrogen is thermodynamically favoured over the formation of water (Reactions 1, 2 and 3).

TABLE III Free energies of surface reactions for Al–20Si–3Cu–1Mg powder at different degassing temperatures

Temperature (°C)	ΔG° (cal mol^{-1})			
	Reaction 1	Reaction 2	Reaction 3	Reaction 4
RT	+ 1 502	+ 3 051	− 71 107	− 251 781
250	− 7 341	− 4 441	− 68 020	− 240 499
350	− 11 047	− 7 813	− 66 736	− 235 506
450	− 14 545	− 11 224	− 65 498	− 230 536
550	− 17 806	− 14 667	− 64 296	− 225 585

However, it is not possible to explain the kinetics of degassing of aluminium powders only by means of the thermodynamical equations; the diffusion of aluminium through its surface oxide layer (Al_2O_3) must also be considered.

Owing to the fact that a complete discussion has been made previously [2], we will restrict ourselves here to making some additional comments with respect to the approach used.

The low activity of aluminium at the surface of the oxide layer can be explained by the slow diffusion of aluminium atoms (ions) from the metal/oxide boundary to the outer surface of the oxide through the oxide layer with a thickness of about 40 nm [2]. For the diffusion coefficient of aluminium in an amorphous aluminium oxide layer accurate values could not be found in the literature. For the growth kinetics of oxide layers on aluminium by cation diffusion, very different activation energies are mentioned ranging from 95 to 226 kJ mol^{-1} [6–9]. Because of this uncertainty it has been assumed that the diffusion of aluminium through Al_2O_3 can be described by the self-diffusion of aluminium which is given as a function of temperature by [2, 10]

$$D_{Al} = 171 \exp(-142\,000/RT)\ \mathrm{cm^2\,sec^{-1}} \quad (5)$$

Following the same procedure established in [2], the number of aluminium atoms coming to the powder surface at different degassing temperatures and the corresponding number of molecules of water and oxygen are summarized in Table IV.

In 4 h degassing at room temperature (Fig. 2) the number of atoms of aluminium arriving at the powder surface is 2.3×10^6.

The results presented in Table IV, together with the total amount of molecules of water originally present in the gas system, calculated to be 3.6×10^{22} [2], lead

TABLE IV Number of aluminium atoms coming to the surface and number of molecules of water and oxygen

Degassing temp., T_D (°C)	Aluminium atoms per hour	Number of molecules	
		n_{H_2O}	n_{O_2}
RT	5.7×10^5	2.5×10^{11}	2.5×10^8
250	2.9×10^{16}	1.4×10^{14}	1.4×10^{11}
350	5.5×10^{18}	1.2×10^{13}	1.2×10^{10}
450	2.4×10^{20}	1.0×10^{11}	1.0×10^9
550	4.2×10^{21}	8.9×10^{10}	8.9×10^8

to the conclusion that Reaction 3 can go to completion in approximately 8.6 h at 550 °C. In the same way, the time necessary to complete this reaction at other temperatures can be calculated. However, it is necessary to point out that the values so obtained must be considered only as a general approximation.

On the other hand, as established previously [2], Reactions 1, 2 and 4 compete with Reaction 3. If sufficient free aluminium is available, hydrogen will be formed instead of water. However, at low temperatures, part of the water is removed as such, which means that not all water has to be converted into hydrogen. The experimental fact that above ~ 350 °C hydrogen is the most evolving gas means that above this temperature sufficient aluminium is available for Reactions 3 and 4 to proceed. This also means that Reactions 1 and 2 are still working at those high temperatures, which is in contradiction with the available thermodynamic data [2] and Table III, but may be caused by a stronger binding due to slow diffusion (or release) of water through the surface oxide layer.

4. Conclusions

1. A complete degassing can only be achieved if the sample is heated up to a temperature where the chemical reactions are finished in the applied time.
2. Thermodynamical equations alone are not enough to explain the kinetics of degassing of aluminium powders.
3. The diffusion of aluminium through its surface oxide layer (Al_2O_3), described by the self-diffusion of aluminium, can explain to a large extent the kinetics of degassing of aluminium powders.

Acknowledgements

The authors thank T. L. J. de Haan and W. Weerheijm for skillful assistance with the experiments, and Mr W. A. J. Brabander for welding the cans. The financial support of the National Polytechnic Institute in Mexico (IPN), the Royal Academy of Science in The Netherlands (KNAW), the Foundation for Technological Research (STW) and the Foundation for Fundamental Research of Matter is gratefully acknowledged.

References

1. J. DUSZCZYK, J. L. ESTRADA, B. M. KOREVAAR, Z. FANG, T. L. J. DE HAAN and P. COLIJN, Technical Report for Showa Denko K. K. (Tokyo, Japan), Delft University of Technology, The Netherlands, October 1987.
2. J. L. ESTRADA, J. DUSZCZYK and B. M. KOREVAAR, *J. Mater. Sci.* **26** (1991) 1431.
3. J. L. ESTRADA and J. DUSZCZYK, *ibid.* **25** (1990) 886.
4. A. I. LITVINTSEV and L. A. ARBUZOVA, *Poroshkovaya Metallurgiya* **49**(1) (1967) 1 (translation).
5. I. BARIN and O. KNACKE, "Thermochemical properties of inorganic substances" (Springer-Verlag, Berlin, 1987) pp. 11, 32, 34, 316, 323, 584.
6. E. A. GULBRANSEN and W. S. WYSONG, *J. Phys. Colloid. Chem.* **57** (1947) 1087.
7. W. W. SMELTZER, *J. Electrochem. Soc.* **103** (1956) 209.
8. A. F. BECK, M. A. HEINE, E. J. CAULE and M. J. PRYOR, *Corr. Sci.* **7** (1967) 1.
9. B. E. HAYDEN, W. WYROBISCH, W. OPPERMANN, S. HACHICHA, P. HOFMANN and A. M. BRADSHAW, *Surf. Sci.* **109** (1981) 207.
10. T. S. LUNDY and J. F. MURDOCK, *J. Appl. Phys.* **33** (1962) 1671.

Received 19 February
and accepted 9 March 1990