JOURNAL OF MATERIALS SCIENCE 26 (1991) 3909–3913

Degassing of Al–Si–X powders assisted by flushing with argon or nitrogen

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The results reported in this paper showing the effect of different degassing modes on the Al–20Si–3Cu–1 Mg powder are a complement of our previous papers concerning the continuous and non-continuous degassing sequences of the same powder. This research was mainly directed at an improvement in the technique to remove volatile and gaseous contaminants from the porous compact made from the Al–20Si–3Cu–1 Mg powder. This improvement has been possible by modifying the conventional degassing process of the powder as reported previously, namely degassing of the powder assisted by flushing with depurative gases such as argon or nitrogen. It is apparent that flushing with argon or nitrogen increases the efficiency of moisture and hydrogen evolution in comparison with the conventional degassing mode.

1. Introduction

Because aluminium powders are covered with oxides which are very reactive with respect to moisture at room temperature, it is necessary to remove water and hydrogen, as well as other possible gaseous or volatile contaminants, from the surface oxide before complete densification. This prevents the development of high gas pressures during subsequent hot working or service at high temperatures, in the 100% dense powder metallurgy (P/M) product, which are sufficient to cause internal porosity, delamination or blistering [1, 2]. This can be accomplished by conventionally degassing the powder, under different heating sequences [3, 4].

The aim of the present work was to shorten the degassing process of the Al–20Si–3Cu–1Mg powder by modifying the conventional mode used previously [3, 4], namely degassing of the powder assisted by flushing with depurative gases such as argon or nitrogen.

In the modified degassing process, as used here, the cold compact is subjected to a treatment consisting of heating to different prescribed temperatures without degassing, followed by flushing with an innocuous depurative gas, and then a high-vacuum degassing treatment to remove the gaseous contaminants and the depurative gas as well.

The depurative gas chosen should be contaminant free and should not form reaction products which are deleterious to the final product. Suitable gases include nitrogen, argon and helium. The treatment, by which a depurative gas is infused, appears to minimize temperature gradients throughout the powdered mass which further facilitates decontamination.

2. Experimental procedure

The powder chosen for investigation consisted of a large amount of rapidly solidified P/M aluminium alloy, atomized in air, based on the hypereutectic Al–Si–X system containing 20 wt % Si, with an average particle size of 24 μm [5]. The chemical composition of this P/M alloy, as obtained by atomic absorption spectrophotometry, is Al–18.8 wt % Si–3.2 wt % Cu–1.1 wt % Mg–0.25 wt % Fe [5]. Experiments were performed recording moisture and hydrogen desorption to investigate different degassing modes at the same prescribed temperature.

The processing used before degassing consisted of 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, 3, 4]. Each can contained ~ 300 g Al powder after compaction.

Fig. 1 illustrates the arrangement used for degassing and flushing a canned powdered metal. A metallic can (1) is shown containing a P/M compact of ~ 65% theoretical density (2). Metallic pads (3) are double welded at the bottom and at the top of the can. The conduit (4) with a filter (5) is welded to the pad of the can and is connected with a vacuum source (turbomolecular pump with a quadrupole mass spectrometer) and with a gas source. Valves (6, 7) are provided so that the canned P/M compact can be alternately subjected to degassing treatment under high vacuum, and then flushed with the depurative gas. The

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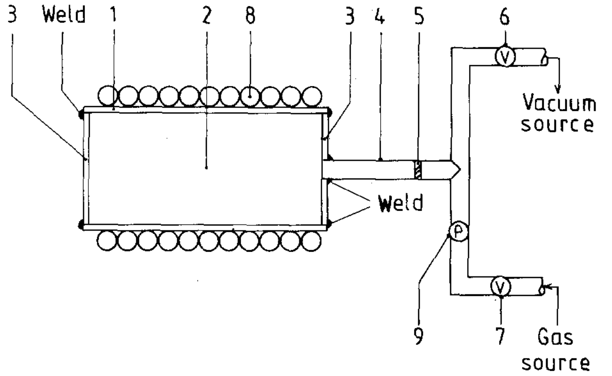

Figure 1 Arrangement used for degassing and flushing a canned powdered metal: (1) metallic can, (2) P/M compact, (3) metallic pads, (4) evacuation conduit, (5) filter, (6) vacuum valve, (7) gas valve, (8) induction furnace, (9) digital pressure gauge.

can is placed in an induction furnace 8. The degassing apparatus contains a set of thermocouples for temperature control and a digital pressure gauge (9) to control the flushing pressure. The cans, pads, and evacuation tubes were made of 6063 (Al–0.4Si–0.7Mg) aluminium alloy.

Very pure Ar and very pure N_2 were used for the experiments. Their respective purity data are given in Table I.

Three different sets of experiments were performed: conventional degassing, modified degassing, and continuous re-degassing from room temperature up to 550 °C.

2.1. Conventional degassing

The canned powder was heated, without degassing, from room temperature to 200 °C, from 200–300 °C, and from 300–400 °C. Once the established temperature was reached the evacuation system was opened and the sample degassed for 3 min to obtain a reference value for the level of gas evolution (stages a and b) and conventionally degassed for 1 h (stage c → d). After each stage the evacuation system was closed (Fig. 2).

TABLE I Purity data of Ar and N_2 used for flushing

	Guarantee	Typical analysis (v.p.m.)
Ar, N_2	$\geqslant 99.9990$	$\geqslant 99.9994$ vol %
N_2, Ar	< 2	1
H_2O	< 4	3
O_2	< 4	2
Carburetted hydrogen, C_xH_y	< 0.5	0.5

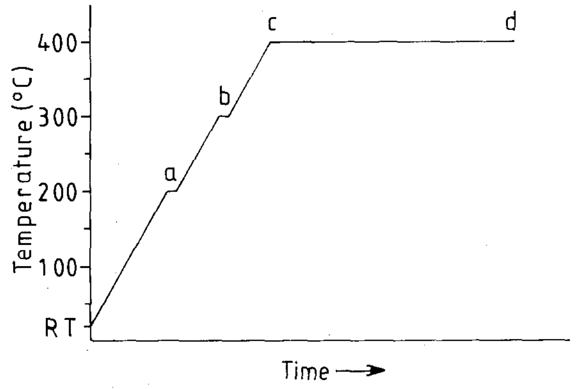

Figure 2 Time–temperature degassing profile (conventional degassing). See text for details.

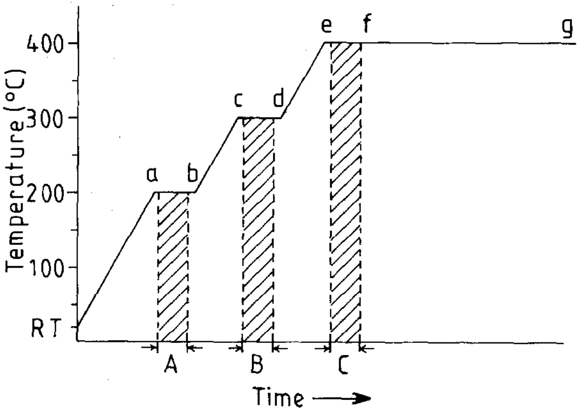

Figure 3 Time–temperature degassing and flushing profile (modified degassing). See text for details.

2.2. Modified degassing

The canned powder was heated, without degassing, from room temperature to 200 °C, from 200–300 °C and from 300–400 °C. Once the established temperature was reached the evacuation system was opened and the sample degassed for 3 min to obtain a reference value for the level of gas evolution (stages a, c and e). After each of these stages the evacuation system was closed, the gas source opened and the canned powder flushed (filled with the gas and pumped out) for 10 min with a depurative gas at a pressure of 2 atm (stages A, B and C). This cycle was carried out only once at each of these stages. Ar and N_2 were used to run two independent series of experiments. After each flushing the gas source was closed, the evacuation system opened and the sample degassed for 3 min to measure the level of gas evolution just after flushing (stages b and d) and conventionally degassed for 1 h (stage f → g). After each one of the degassing stages the evacuation system was closed (Fig. 3).

2.3. Continuous re-degassing from room temperature to 550 °C

Directly after degassing, as established in Figs 2 and 3, each sample in turn, still under vacuum, was cooled down to room temperature and heated again to 550 °C at a uniform heating rate of 2.5 °C min^{-1} and continuously re-degassed, under high vacuum.

Released gases were monitored and analysed during the degassing stages by a computerized Edwards EQ80F Residual Gas Analyser (RGA). The unit measures total vacuum pressure and analyses the partial pressures over the mass range 1–80 atomic mass units (a.m.u.). Partial pressures are measured by the peak corresponding to the ratio *m*/*e*, where *m* is the atomic mass and *e* the electric charge; the sensor being a quadrupole mass spectrometer.

3. Experimental results

The powder particle surface mainly consists of an aluminium oxide or hydroxide layer which in the case of the air-atomized Al–20Si–3Cu–1Mg P/M powder has a thickness of ~ 40 nm [5]. Upon heating in vacuum the hydrous surface of the cold precompacted powder is degassed. The corresponding mass spectrum, generated by the residual gas analyser, shown in [1], indicates that H_2O and H_2 are the main degassing products although oxygen and other components (such as CO and CO_2) were also detected. Based on these results [3] and those obtained previously [4] and with the objective of improving the degassing mode, experiments were carried out to degass the powder in accordance with the heating sequences shown in Figs 2 and 3.

The results can be split into two parts: conventional and modified degassing as established in Figs 2 and 3, and continuous re-degassing from room temperature up to 550 °C.

3.1. Conventional and modified degassing

The changes of the partial pressures of H_2O and H_2 as a function of temperature and flushing are shown in Figs 4 and 5, respectively.

Big drops can be seen in the partial pressures of H_2O and H_2 as a direct result of flushing, with Ar or N_2, at 200, 300 and 400 °C. However, if the sample is subsequently heated to 300 °C, after flushing at 200 °C, the partial pressures of H_2O and H_2 and those corresponding to the non-flushed sample are practically the same. If the sample is heated to 400 °C, after flushing at 300 °C, the partial pressure of H_2O of the sample flushed with Ar and that of the non-flushed sample have about the same value but the value for the N_2-flushed sample is slightly lower. In the case of H_2 the partial pressures of the flushed samples are well below those of the non-flushed sample with the lowest value when N_2 is used. After flushing at 400 °C and degassing under high vacuum at this temperature for 1 h, the partial pressures of H_2O and H_2 for the non-flushed samples are about two orders of magnitude higher with respect to those treated by the modified process (degassing + flushing with a depurative gas). Even though the values of the partial pressures of H_2O do not appear on Fig. 4, after degassing the flushed samples at 400 °C, they were recorded by the printer.

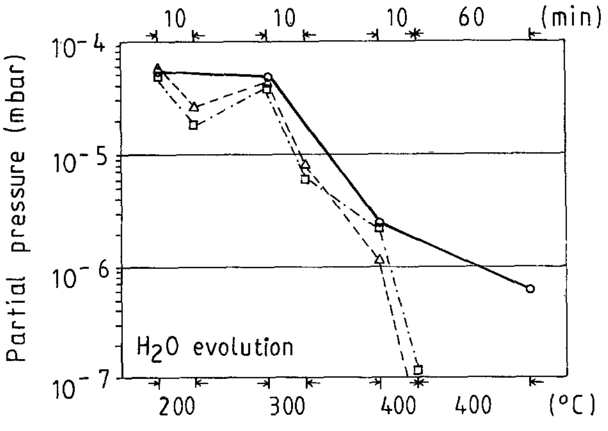

Figure 4 Effects of different degassing modes on H_2O evolution of the air-atomized Al–20Si–3Cu–1Mg powder. (—○—) Conventional degassing, (·—□·—) Ar flushing, (--△--) N_2 flushing.

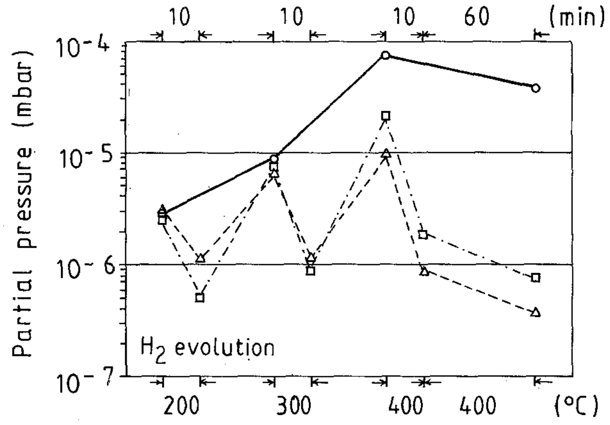

Figure 5 Effects of different degassing modes on H_2 evolution of the air-atomized Al–20Si–3Cu–1Mg powder. For key, see Fig. 4.

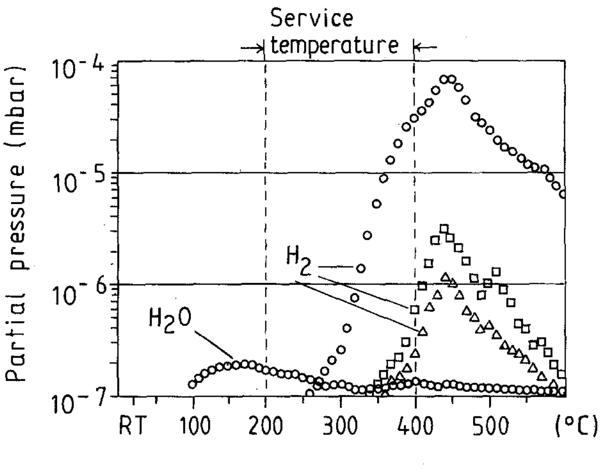

Figure 6 Re-degassing curves of the air-atomized Al–20Si–3Cu–1Mg powder after being degassed by different modes. (○) Conventionally degassed, (□) Ar flushed, (△) N_2 flushed.

3.2. Continuous re-degassing from room temperature to 550 °C

Fig. 6 and Table II show the changes of the partial pressures of H_2O, H_2 and O_2, as a function of temperature, recorded during the re-degassing process from room temperature to 550 °C. No traces of Ar or N_2 were detected. These results show that modified degassing assisted by flushing with Ar or N_2 is a more efficient process than conventional degassing. The difference, in partial pressures of H_2 evolution, between conventional degassing and modified degassing is up to approximately two orders of magnitude, in favour of the modified process, due to the lower levels of H_2O and O_2 left in the system after the original

TABLE II Experimental partial pressures of H_2O, H_2 and O_2 as a function of temperature during re-degassing from room temperature (RT) to 550 °C

T_D (°C)	Order of magnitude of experimental partial pressures (mbar)								
	Conventional[a]			Ar-flushed[a]			N_2-flushed[a]		
	p_{H_2O}	p_{H_2}	p_{O_2}	p_{H_2O}	p_{H_2}	p_{O_2}	p_{H_2O}	p_{H_2}	p_{O_2}
RT	10^{-8}	10^{-8}	10^{-8}	10^{-9}	10^{-10}	10^{-9}	10^{-9}	10^{-10}	10^{-9}
250	10^{-7}	10^{-7}	10^{-9}	10^{-8}	10^{-8}	10^{-11}	10^{-8}	10^{-9}	b
350	10^{-7}	10^{-6}	10^{-9}	10^{-8}	10^{-7}	b	10^{-8}	10^{-8}	b
450	10^{-7}	10^{-5}	10^{-9}	10^{-8}	10^{-6}	b	10^{-8}	10^{-6}	b
550	10^{-7}	10^{-5}	10^{-9}	10^{-9}	10^{-7}	b	10^{-9}	10^{-7}	b

[a] Original degassing mode.

[b] No trace.

degassing. The best results are obtained when N_2 is used.

It is apparent that after the Ar- or N_2-flushed samples have been re-degassed up to 550 °C, some residual H_2O and H_2 are still detected (Table II). The partial pressures of O_2, at 250 °C and above, and at 350 °C and above, for N_2- and Ar-flushed samples, respectively, do not appear because their values were lower than the minimum detectable partial pressure, namely 10^{-11} mbar.

4. Discussion

It can be concluded from these results that even after degassing at 550 °C the degassing reactions are not completed, and that temperature appears as the critical parameter governing the degassing reactions which is in agreement with the results obtained previously [3, 4]. However, it is very important to point out that the service temperature for products made of this alloy (Al–20Si–3Cu–1Mg) is in the range 200 to ~ 400 °C which in conjunction with the maximum levels of released gases recommended, 10^{-6} mbar for H_2 and 10^{-7} mbar for H_2O, allows these products to be used up to the threshold service temperature, without any risk of further H_2 or H_2O evolution (Fig. 6). As reported by Zhou and Duszczyk [6], the alloy involved in this research provides products with the best strength and elongation at the service temperature above 200 °C when heat treatment is not included in the processing.

A discussion of the problem of gas evolution during (vacuum) degassing has been given previously [3, 4]. It was concluded that thermodynamic equilibrium cannot provide an explanation for the gas evolution as it is experimentally measured. A semi-quantitative description of the degassing processes was given based on the diffusion of aluminium atoms through the oxygen layer to the outer surface of the powder particles.

The main chemical reactions governing the degassing process are

$$Al_2O_3 \cdot xH_2O \rightarrow Al_2O_3 + xH_2O\,(\text{ads}) \qquad (1)$$

$$H_2O\,(\text{ads}) \rightarrow H_2O\,(\text{gas}) \qquad (2)$$

$$\tfrac{2}{3}Al + H_2O \rightarrow \tfrac{1}{3}Al_2O_3 + 2H\,(\text{ads}) \qquad (3)$$

$$2H\,(\text{ads}) \rightarrow H_2\,(\text{gas}) \qquad (4)$$

$$O_2\,(\text{gas}) \rightarrow 2O\,(\text{ads}) \qquad (5)$$

$$\tfrac{4}{3}Al + 2O \rightarrow \tfrac{2}{3}Al_2O_3 \qquad (6)$$

where ads stands for adsorbed.

Reaction 3 can only take place if a sufficient number of free Al atoms is available at the surface, which is determined by the diffusion of Al through the O_2 layer and by the amount of O_2 in the system, giving rise to the thermodynamically predominant Reaction 6.

It was found that above ~ 250 °C the diffusion of Al through the oxygen layer is sufficiently fast to transform the H_2O molecules created by Reaction 1 into H_2 molecules, according to Reaction 3.

In fact all important reactions in vacuum metallurgy occur at the interface between the solid phase and the gas environment and it is obvious that the conditions prevailing at that interface determine the rate of the reactions. The flushing of the degassing system with a neutral gas (Ar or N_2) at 2 atm of better than 99.999% purity will change these conditions. Most of the residual H_2O, H_2 and O_2 in the system will be driven out, thus at the start of the degassing the partial pressures in the gas atmosphere will be lower, promoting Reactions 2 and 4 and impeding Reaction 5.

Although the surface bonding energy of N_2 or Ar molecules is generally lower than for H_2O molecules, if there is N_2 (or Ar) present in excess then it is very likely that a thermally desorbed H_2O molecule can be replaced by a N_2 (or Ar) molecule due to this excess. An H_2O molecule which collides against the surface has a higher likelihood to be bonded than an N_2 (or Ar) molecule because its bonding energy is higher. But the number of collisions of the N_2 (or Ar) molecules (which, at a given volume and temperature, is proportional to the pressure applied, 2 atm $\approx 2 \times 10^3$ mbar in this case) is ~ 10^9 times higher than the number of collisions of the H_2O molecules at a partial pressure of 10^{-6} mbar. Thus, if somewhere in the surface a free place appears, an N_2 (or Ar) molecule will have more opportunity to occupy that place.

Once a layer of N_2 (or Ar) molecules is formed on the surface, any other molecule becomes weaker bonded to this layer, which promotes the degassing process (Figs 4 and 5). This is also proved by the re-degassing run (Fig. 6) where the gas evolution is very small below 400 °C. Above this temperature some H_2 formation still takes place although much less than with conventional degassing.

5. Conclusions

Thermodynamics of the degassing process is not essentially influenced by flushing with depurative gases. It is apparent that degassing the powder assisted by flushing with argon or nitrogen increases the efficiency of moisture (H_2O) and hydrogen (H_2) evolution, at the prescribed degassing temperature, in comparison with the conventional degassing mode.

Acknowledgements

The authors thank Professor B. M. Korevaar for support and stimulating discussion and to Mr W. A. J. Brabander for welding the cans. The financial support of the National Polytechnic Institute in Mexico (IPN), and the Programme for Innovative Research (IOP – Metals) in the Netherlands is gratefully acknowledged. Powders were supplied by Showa Denko K. K., Japan.

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Received 1 June
and accepted 19 June 1990