

# Evolution of alloying elements during outgassing in an aluminium zinc magnesium alloy made by powder metallurgy

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To obtain high-quality products from aluminium alloys powders, degassing is usually carried out before consolidation. But, in the case of Al-Zn-Mg alloys an evaporation of alloying elements may occur during outgassing. The aim of this work was to determine the influence of degassing conditions (temperature, pressure, nature of the gaseous atmosphere) on the stability of the alloy composition. These studies were performed on X7091 alloy by means of thermogravimetry and temperature-programmed desorption technique. The results show that liberation of alloying elements is closely connected with the evolution of the surface oxide layer which itself depends on various thermodynamic and kinetic parameters. The role of water vapour in the gaseous environment was particularly emphasized.

## 1. Introduction

Rapid solidification of conventional aluminium alloys produces a finer grain structure and finer distribution of intermetallic phases. Therefore, products with improved mechanical properties are obtained (e.g. X7091 alloy). Furthermore, greater benefits from the development of new aluminium alloy compositions may be expected, especially with respect to high-temperature materials (e.g. Al-Fe8-X alloy).

However, during the production of powders by atomization, oxygen and/or water vapour contained in air or in an inert gas lead to the formation of an amorphous hydrated oxide layer. This layer evolves during consolidation and induces porosity phenomena and/or surface blistering. In order to extend applications of aluminium powder metallurgy to aerospace industry which requires high-quality products, hot vacuum degassing must be carried out before sintering.

Pickens [1] considered in 1981 that degassing was the key to successful applications of the aluminium powder metallurgy. The importance of degassing for good properties has also been emphasized by Meunier [2]. According to papers published by Kim *et al.* [3, 4] on X7091 alloy, the oxide layer is dried by degassing at 520°C which releases water from alumina hydrates. The water evacuated may react with metals (aluminium or magnesium) to form Al<sub>2</sub>O<sub>3</sub> amorphous film or MgO crystallites, and hydrogen is released. These results are in good agreement with the early works of Arbuzova and co-workers [5, 6] in the 1970s.

More recently, hydrogen evolution on X7091 alloy has been studied by Lalauze and co-workers [7, 8] by means of the temperature-programmed desorption technique. The authors showed that two kinds of hydrogen formation may occur. Hydrogen is generated either from water of aluminium hydroxides or

from adsorbed water. Therefore, the chemical reaction between the metal and the adsorbed water is conditioned by the break up of the oxide layer which enables zinc and magnesium to evaporate at 400°C. Such a partial sublimation which can annihilate the high mechanical properties of the sintered alloy was also observed by Morgan *et al.* [9] who worked on preforms of X7091 aluminium powder. Moreover, the authors pointed out the sublimation at 460°C and determined the optimal degassing temperature at 400°C by means of thermogravimetry. It should be observed that Morgan *et al.*'s paper did not specify the heating rate. Roberts [10] was also aware of the ill effects of a prolonged degassing time at high temperatures, and determined that a temperature set at 310°C under 10<sup>-2</sup> Pa was sufficient to produce a blister-free consolidated product.

These inconsistent results show the intricacy of the reactions that occur during outgassing. Therefore, a greater understanding of the degassing process is still necessary in order to determine the optimal conditions for obtaining a powder metallurgy product with very good properties.

The aim of this work was to attempt to determine the influence of the environmental gaseous atmosphere on the desorption of chemical species and on the liberation of volatile alloying elements. These investigations were achieved by means of thermogravimetry (TGA), temperature-programmed desorption (TPD) and completed by the results of X-ray photoelectron spectroscopy (XPS).

## 2. Experimental procedure

X7091 powder (Al; Zn = 6%; Mg = 2.2%; Cu = 1.6%) produced by Aluminium Pechiney, was atomized in cold air. The surface area determined by the

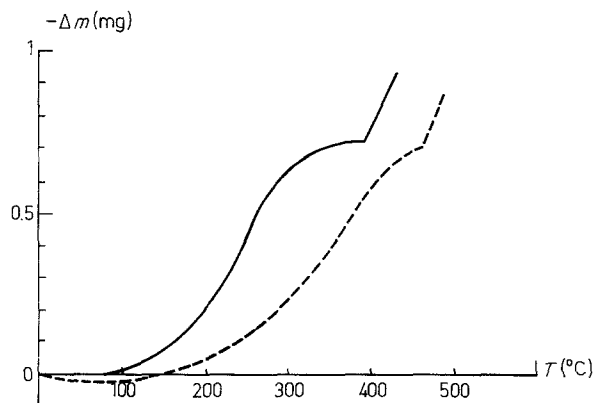


Figure 1 TGA curves at (—)  $2^{\circ}\text{C min}^{-1}$  and (---)  $20^{\circ}\text{C min}^{-1}$ , under a  $10^{-2}$  Pa dynamic vacuum.

BET method (krypton) was approximately  $0.24\text{ m}^2\text{ g}^{-1}$ . The particle size distribution was about 18 to  $54\text{ }\mu\text{m}$ .

For thermogravimetric studies, a "Setaram" MTB 10-8 microbalance was used. The chamber can be pumped down with rotary and turbomolecular pumps. Residual pressure in the quartz reactor containing the sample was then  $10^{-2}$  Pa. The chamber was connected with an inlet system for gas introduction. In some experiments, the water vapour pressure in the reactor was fixed by means of a water-containing cell maintained at the required temperature.

The TPD experiments were carried out in a quartz reactor connected to a "Balzers QMG111" quadrupole mass spectrometer used for analysing the species released by the alloy during heating under low residual pressure ( $10^{-3}$  Pa). For all experiments, the weight sample was equal to 0.7 g.

### 3. Results and discussion

#### 3.1. Thermogravimetric analysis

The thermogravimetric curves as a function of temperature were obtained under dynamic vacuum ( $10^{-2}$  Pa) and for two different heating rates (2 and  $20^{\circ}\text{C min}^{-1}$ ). The results are shown in Fig. 1. Two successive weight losses,  $\Delta m$ , are recorded: the first is explained by water and hydrogen liberation, the second may be ascribed to sublimation of volatile alloying elements. Chemical analysis of the sample before and after thermal treatment at  $450^{\circ}\text{C}$  (Table I) shows an important sublimation of zinc.

It should be noticed that sublimation only occurs when a specific quantity of water vapour (0.1%) has been degassed. Such a quantity may be attributed to the limit value for precipitation of a new hydroxide aluminium phase. It follows that sublimation occurs at a temperature which depends on the heating rate ( $390^{\circ}\text{C}$  at  $2^{\circ}\text{C min}^{-1}$  and  $470^{\circ}\text{C}$  at  $20^{\circ}\text{C min}^{-1}$ ) and therefore on the degassing kinetic process.

TABLE I Chemical composition of the alloy before and after a thermal treatment at  $450^{\circ}\text{C}$  under vacuum

	Initial alloy	After heating to $450^{\circ}\text{C}$ at $2^{\circ}\text{C min}^{-1}$
Zn (%)	6.30	3.05
Mg (%)	2.25	2.25
Cu (%)	1.58	1.55

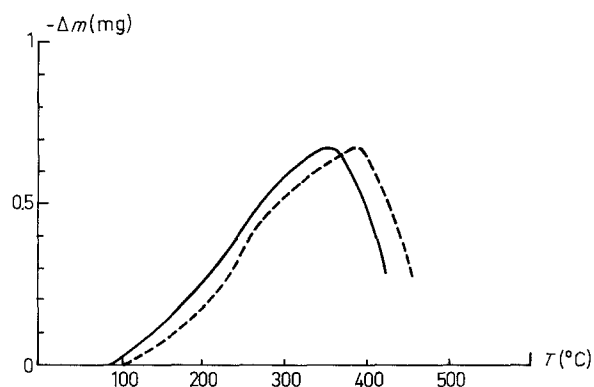


Figure 2 TGA curves at (—)  $2^{\circ}\text{C min}^{-1}$  and (---)  $20^{\circ}\text{C min}^{-1}$ , under atmospheric pressure.

Similar experiments were carried out under various gaseous atmospheres. Fig. 2 shows that under atmospheric pressure water desorption is followed by a weight gain which may be ascribed to an oxidation process. As previously mentioned for sublimation, this process occurs at a critical outgassing water vapour amount. The same corrosion phenomenon is observed under an oxygen pressure of 13 kPa (Fig. 3). From these interesting results it can be deduced that there is a competition between oxidation and sublimation of the alloy. This competition is well illustrated in Fig. 4 where the analysis has been performed under a 133 Pa vacuum.

In order to ascertain the behaviour of the alloy during annealing under an inert atmosphere, the powder was initially evacuated ( $P = 10^{-2}$  Pa) and an argon pressure was introduced at  $20^{\circ}\text{C}$  into the chamber. Then, the sample was heated to  $500^{\circ}\text{C}$  ( $20^{\circ}\text{C min}^{-1}$ ). From Fig. 5, curve 1, it can be observed that around  $400^{\circ}\text{C}$  the alloy undergoes a rapid oxidation process. As the initial and residual oxygen pressures are too low to induce such a phenomenon, it is suggested that desorbed water may be dissociated at the contact of the alloy. In order to promote the water diffusion in the gaseous environment, experiments were performed under flowing argon ( $3\text{ l h}^{-1}$ ). Curve 2, Fig. 5, shows that no sublimation or oxidation occurs at a temperature greater than  $400^{\circ}\text{C}$ . Here, water molecules are removed from near the surface powder by the gas stream. It should be pointed out that the amount of water liberated is not affected by such conditions. Therefore, it is expected that a high-quality product will be obtained by utilization of

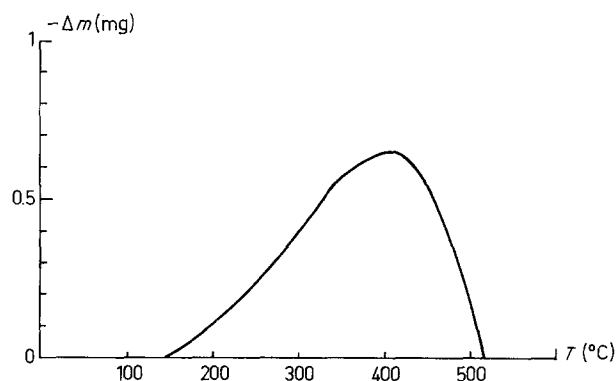


Figure 3 TGA curve at  $20^{\circ}\text{C min}^{-1}$  under a 13 kPa oxygen pressure.

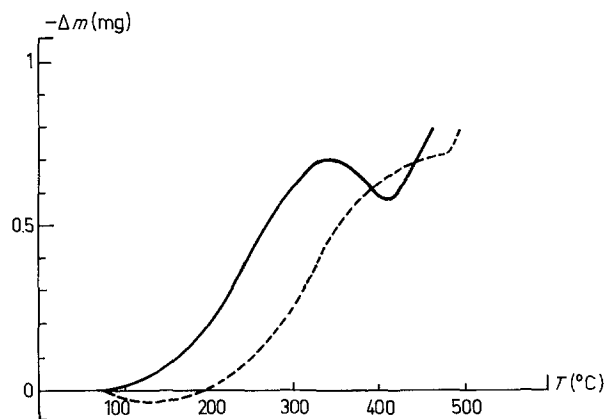


Figure 4 TGA curves at (—)  $2^{\circ}\text{C min}^{-1}$  and (---)  $20^{\circ}\text{C min}^{-1}$ , under a 133 Pa dynamic vacuum.

argon. This conclusion is not in agreement with Danilkin *et al.*'s work [11] that showed superior properties for material degassed under vacuum conditions in comparison with a material degassed under flowing argon.

### 3.2. Correlation with TPD experiments

The experiments investigated water and hydrogen desorption analysis as a function of temperature. They were performed at 2 and  $20^{\circ}\text{C min}^{-1}$  under a residual air pressure of  $10^{-3}$  Pa. The results are presented in Figs 6 and 7. In both cases, large water desorption occurs around  $250^{\circ}\text{C}$  at  $2^{\circ}\text{C min}^{-1}$  and around  $320^{\circ}\text{C}$  at  $20^{\circ}\text{C min}^{-1}$ . It should be noticed that an important increase in ionic intensities occurs for hydrogen and water in Fig. 7 in comparison with those indicated by Fig. 6. However, the total quantities of desorbed water which can be assessed by integration of the curves as a function of time are quite similar.

With respect to hydrogen liberation, four peaks located at 230, 300, 370 and  $390^{\circ}\text{C}$  (Fig. 7) are present but hydrogen desorption at  $390^{\circ}\text{C}$  is followed by the partial sublimation of the alloy. At  $20^{\circ}\text{C min}^{-1}$ , the hydrogen spectrum was shifted under high temperatures and the shape of the four peaks was not clearly defined. It should be noted that here, the last liberation of hydrogen and the metallic condensation on the reactor walls also appear at  $440^{\circ}\text{C}$ . Thus, these results are in good agreement with previous thermogravimetric studies which showed a relation between

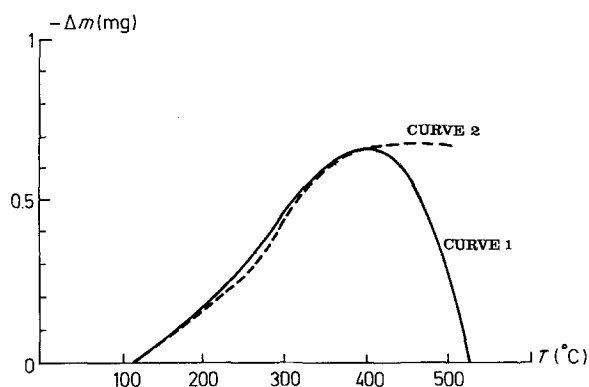


Figure 5 TGA curves at  $20^{\circ}\text{C min}^{-1}$  under a 13 kPa argon pressure (curve 1) and under flowing argon (curve 2).

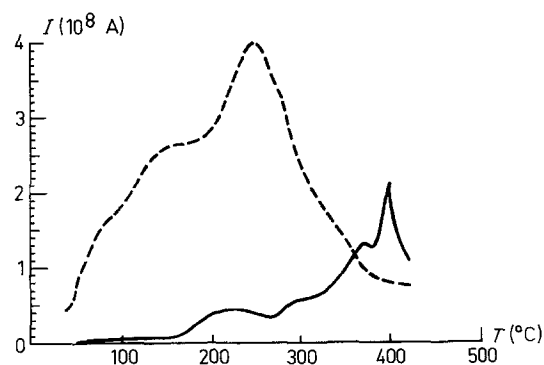


Figure 6 TPD curves of (—) hydrogen and (---) water at  $2^{\circ}\text{C min}^{-1}$ .

the water desorption kinetic process and the sublimation of volatile alloying elements.

### 3.3. Kinetic curves of sublimation and corrosion

The sublimation process was studied in isothermal and isobaric conditions fitting the heating rate up to the critical loss of water (0.1%). Therefore, the sublimation kinetic curves were recorded at  $390^{\circ}\text{C}$  (after heating of the alloy at  $2^{\circ}\text{C min}^{-1}$ ) and at  $440^{\circ}\text{C}$  (after heating at  $16^{\circ}\text{C min}^{-1}$ ) and for two values of residual air pressure. The results are reported in Fig. 8. At  $440^{\circ}\text{C}$ , the curves suggest a diffusion process of alloying elements and exclude the hypothesis of a sudden break-up of the oxide layer [8]. The parabolic shape implies diffusion through an oxide layer the thickness of which increases as a function of time. Such an evolution may be explained by a decomposition of water vapour at the outer oxide interface with alloying elements.

In order to determine corrosion kinetics of the alloy, samples were heated up to  $400^{\circ}\text{C}$  ( $2^{\circ}\text{C min}^{-1}$ ) under  $10^{-1}$  Pa. At  $400^{\circ}\text{C}$ , an oxidizing gas (air, oxygen or water vapour) was introduced into the chamber and weight gain was recorded. The influence of the nature of the oxidizing atmosphere is illustrated by Fig. 9. It should be noticed that the kinetic curves do not show a parabolic shape as expected. Therefore, the kinetic corrosion process must be more complex than a simple diffusion. Furthermore, it is important to confirm that water vapour plays a preponderant role in the oxidation process. Kinetic curves obtained for various values of water vapour pressure are presented

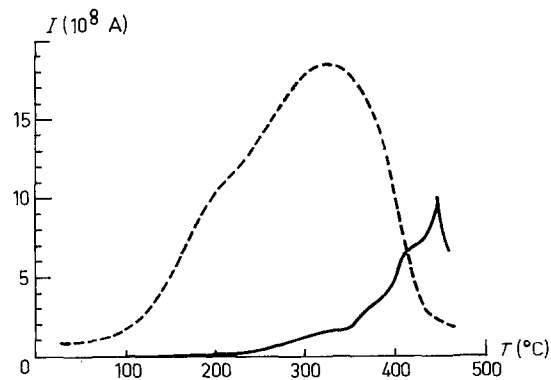


Figure 7 TPD curves of (—) hydrogen and (---) water at  $20^{\circ}\text{C min}^{-1}$ .

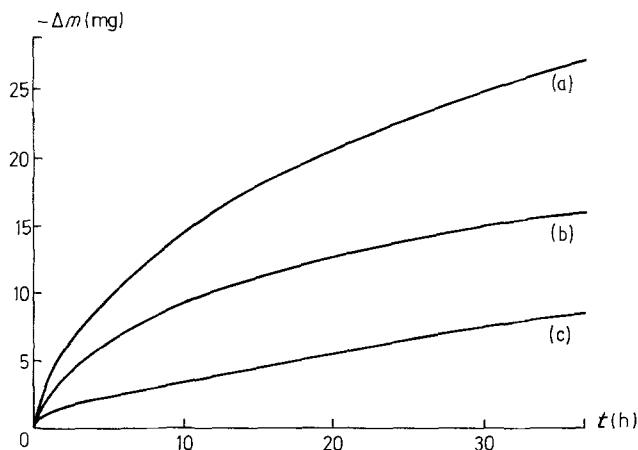


Figure 8 Influence of temperature and residual air pressure on the sublimation kinetics. (a)  $T = 440^{\circ}\text{C}$ ,  $P = 10^{-2}\text{ Pa}$ ; (b)  $T = 440^{\circ}\text{C}$ ,  $P = 10^{-1}\text{ Pa}$ ; (c)  $T = 390^{\circ}\text{C}$ ,  $P = 10^{-2}\text{ Pa}$ .

in Fig. 10. Chemical analysis of samples treated at  $440^{\circ}\text{C}$  for various times revealed that the alloying element concentration remained stable (Table II). Such analysis proves that sublimation did not occur. It is therefore interesting to determine the nature of the metallic elements responsible for this corrosion.

### 3.4. Characterization of an oxidized sample

The published data are in agreement concerning the nature of the oxidized element, in indicating that magnesium is the less-resistant element to corrosion. On the other hand, Csanady *et al.* [12] observed a segregation of alloying elements through SIMS investigations of aluminium magnesium alloy foils, particularly of magnesium, near the surface of the sheets, after annealing at  $400^{\circ}\text{C}$ . Kim *et al.* [3, 4] showed that magnesium oxide crystallites were initially present at the surface of untreated 7091 alloys.

In order to confirm magnesium oxidation during outgassing, XPS characterization of the surface powders was performed on different treated samples. The results obtained for oxidized powders revealed that a magnesium oxide layer is formed after annealing for 1 h 40 min in air at  $400^{\circ}\text{C}$  [13]. Taking into account the weight, the thickness of the magnesia layer can be determined as about 30 nm after oxidation for 24 h, whereas the oxide layer was only about 3 nm thick in the initial alloy as determined from XPS [13].

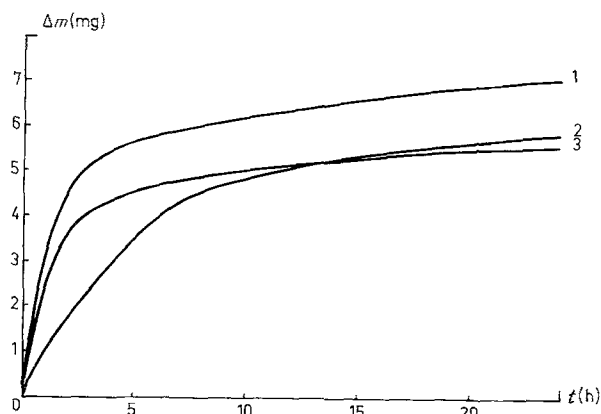


Figure 9 Corrosion kinetics for various oxidizing atmospheres: (1) air (100 kPa); (2) oxygen (1.3 kPa); (3) water vapour (1.3 kPa).

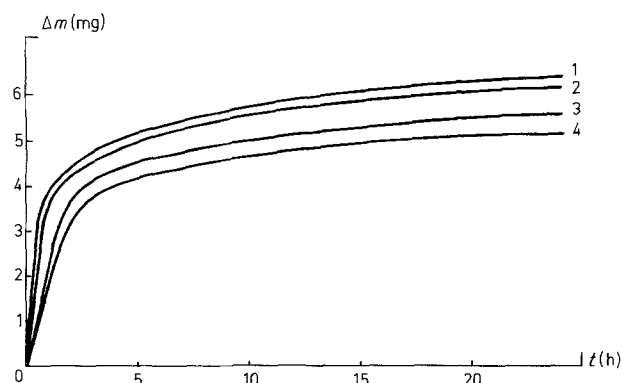


Figure 10 Corrosion kinetics for various values of the water vapour pressure: (1)  $P = 4\text{ kPa}$ ; (2)  $P = 2.7\text{ kPa}$ ; (3)  $P = 1.3\text{ kPa}$ ; (4)  $P = 330\text{ Pa}$ .

It should be kept in mind that the results obtained by means of the temperature-programmed desorption technique (TPD) are in agreement with the oxidation process. In previous papers [7, 8] the last peak of hydrogen was attributed to adsorbed water decomposition. Therefore, two oxidized samples, the first oxidized for 5 min after dehydration, the second for 24 h at  $400^{\circ}\text{C}$ , were analysed by TPD. It can be observed from Fig. 11 that the last peak at about  $440^{\circ}\text{C}$  has disappeared for the strongly oxidized powder. This very important result shows the "protective" role of the magnesium oxide layer in the oxidation phenomenon. This "protective" effect also occurs in favour of zinc as metallic condensation was not observed for the very oxidized sample. This alloying element can no longer pass through the thick oxide layer.

## 4. Conclusion

From our results, the following conclusions can be drawn concerning the surface evolution of X7091 aluminium alloy during outgassing.

Initially the alloy particles exhibit a hydrous aluminium oxide layer which protects the alloy against oxidation or sublimation. The stability of this layer is essentially a function of the amount of water which is itself dependent on temperature and pressure. For a critical degree of dehydration, structural changes occur and either oxidation or sublimation is then possible according to the nature and pressure of the gaseous atmosphere.

Unwanted liberation of zinc occurs under vacuum conditions and on the other hand, important oxidation of magnesium is promoted by annealing the powder in air. Zinc sublimation is prevented by the thick magnesia layer.

These investigations which showed the behaviour of

TABLE II Chemical composition of the alloy after various air thermal treatments

	Initial alloy	After heating to $400^{\circ}\text{C}$ at $2^{\circ}\text{C min}^{-1}$ under atmospheric pressure and holding at $400^{\circ}\text{C}$ for $t$				
		$t = 0$	$t = 0.5$	$t = 5$	$t = 16$	$t = 22.3$
Zn (%)	6.32	6.40	6.44	6.40	6.21	6.23
Mg (%)	2.24	2.29	2.32	2.25	2.23	2.21
Cu (%)	1.53	1.56	1.56	1.57	1.51	1.53

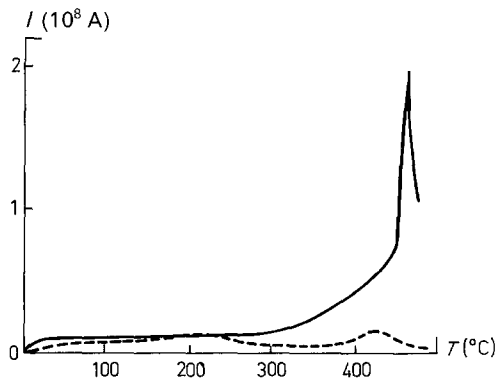


Figure 11 TPD of hydrogen for two samples treated in air at 400°C for (—) 5 min or (---) 24 h.

aluminium powder through outgassing under various atmospheres, help to determine optimal degassing conditions, and therefore to produce compact products with high mechanical properties.

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