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TEMPERATURE PROGRAMMED DESORPTION STUDIES OF OUTGASSING OF ALUMINIUM POWDER

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The mechanical properties of powder metallurgy (P.M.) aluminium alloys may be influenced considerably by the hydrogen content. To obtain high-quality alloys, it is necessary to optimize the degassing of the powder before sintering. Such a process involves an understanding of the mechanism of the desorption of H_2 from the surface of the powder.

By means of the temperature programmed desorption technique, hydrogen evolution has been studied on an X7xxx (Al, Zn, Mg, Cu) P.M. alloy. The results show a large influence of the atomization procedure (with air or with helium). Hydrogen formation results from water decomposition at the contact of the alloying metals, but two different mechanisms may occur.

— Water is chemisorbed on the sample and the decomposition process is conditioned by the break-up of the oxide layer, followed by the evaporation of zinc and magnesium.

— As a function of the temperature, water is liberated in the network of the oxide by a transformation of the aluminium hydroxides and may react with metal at the metal-oxide interface.

It is possible to improve the mechanical properties of aluminium alloys through powder metallurgy (P.M.). The rapid solidification of the atomized droplets allows an increase in the solubility of the alloying elements and refinement of the microstructure. However, the ductility of P.M. aluminium alloys mostly depends on the oxides or adsorbed gases present on the surface of the small particles [1–7], and can be very low if these surfaces are not correctly degassed before sintering. Generally, the surface of aluminium powder consists of Al-oxides or/and Al-hydroxides formed during atomization. Depending on the composition of the alloy and the thermodynamic conditions, various oxides originating from the oxidation of alloying elements may also appear.

An important contribution published by Kim et al. [6] concerns the identification of oxides present on the surface of P.M. alloy 7091 with 6.5 wt% of Zn and 2.4 wt% of Mg. The authors observed that the powder is initially coated with a wet $Al(OH)_3$

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surface layer. According to this paper, degassing at 520° induces two important phenomena:

1) Degassing dries the surface layer by liberating water from hydrates. It is well known that several Al-hydroxides exist and that an irreversible process may occur at different temperatures:

$$Al_2O_3 \cdot 3H_2O \rightarrow Al_2O_3 \cdot H_2O \rightarrow \gamma\text{-}Al_2O_3$$

2) The liberated water may react with metals (Al or Mg) to form Al_2O_3 amorphous film or MgO crystallites:

$$3\ H_2O + 2\ Al \rightarrow Al_2O_3 + 3\ H_2$$

and

$$H_2O + Mg \rightarrow MgO + H_2$$

During hot pressing, dry Al-oxide and MgO crystallites facilitate the break-up of the surface oxides and promote a better homogeneous distribution of the broken-up product in the alloy. The mechanical properties of the aluminium alloy seem to depend greatly on such a distribution.

In another way, several authors have studied the degassing conditions of a cold compacted sample. In order to analyse the chemisorbed gases or the dehydration process of the surface, Morgan et al. [5] used a mass spectrometer analyser and presented ion intensities versus temperature for H_2O, CO, CO_2 and H_2. The hydrogen spectrum was characterized by two peaks, located at 350 and 390°, respectively. As mentioned by Morgan et al., these results are in good agreement with those published by Arbuzova et al. [4]. Hydrogen formation can be attributed to a reaction between metal and water liberated by the dehydration of oxides. These authors also pointed out a partial evaporation of zinc and magnesium at 480°. The optimal degassing temperature of such a compacted sample was determined at 400° just after hydrogen liberation. A correlation between hydrogen content, oxygen content and the ductility of the material has recently been established by Meunier [7].

In fact, the published papers concerning the optimal degassing temperature are not always in good agreement and the mechanisms proposed for hydrogen formation are not always clearly determined. In order to obtain more details about the mechanisms, we have made some temperature programmed desorption (TPD) experiments in an activated atmosphere (D_2O). The aim of the present investigations was to attempt to determine the origin of the hydrogen, the influence of the environmental gaseous water on the chemisorbed species, and the nature of the gas included in the powder.

Experimental

Apparatus

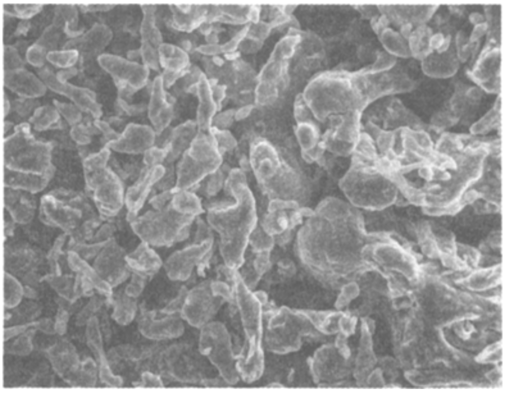
The TPD experiments were carried out in a horizontal furnace; the temperature was raised at a uniform rate (20 or 2 deg/min); 0.7 g of aluminium alloy was loaded in a quartz reactor; the chamber was connected with a turbo molecular pump, with an air inlet for D_2O introduction and with a quadrupole mass spectrometer (Balzers QMG 111A). The thermodesorption spectrum $\left(\frac{dN_A}{dt} = f(T)\right.$ with N_A the gas concentration of species A) of every species was represented by a peak and the temperature T_M of its maximum was generally characteristic of the species A.

Sample treatment

Experiments were performed with an X7xxx (Al, Zn, Mg, Cu) aluminium powder produced either by atomization in air (denoted XA) or by atomization in helium (denoted XHE). In the case of D_2O experiments, 0.7 g of powder was evacuated ($P < 10^{-5}$ mbar). Afterwards, the reactor chamber was connected for 5 minutes with the test-tube containing D_2O. The tube was maintained at 0° and the D_2O pressure vapour was about 5 mbar. This was repeated three times and it was established that the ratio D_2O/H_2O was about 3.3.

Powder characterization

The surface area determined by the B.E.T. method (krypton) was approximately 0.2 m^2/g for the two specimens. The particle size distribution was about 18–30 μm

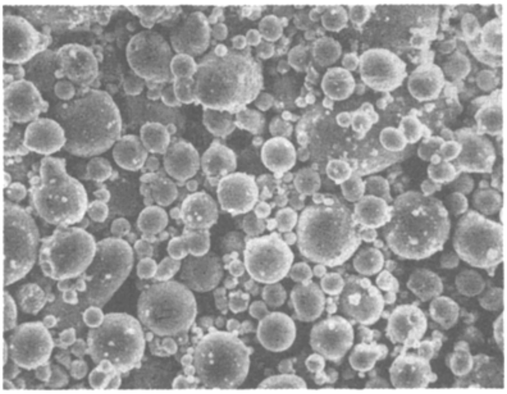


Picture 1 SEM micrograph of an helium atomized powder

for XHE and about 18–54 μm for XA. Such a difference may be interpreted by the shape of the grains: rounded for XHE, and elongated for XA (see Pictures 1 and 2).

The main alloying elements were analyzed by an atomic adsorption method: Zn = 6.3 wt%, Mg = 2.25 wt%, Cu = 1.6 wt%.

The most interesting results concerns oxygen contents determined by an activated method: 3210 ppm of O_2 for XA, 1350 ppm of O_2 for XHE. These results will be used later.



Picture 2 SEM micrograph of an air atomized powder

Results and discussion

TPD experiments on XHE alloy

These experiments deal with water and hydrogen desorption analysis as a function of the temperature. In order to obtain information about hydrogen, the following experimental procedure was adopted.

First the degassed sample ($P < 10^{-5}$ mbar) was heated up at 500° (20 deg/min); the TPD results are illustrated by curves 1 in Fig. 1. Large water and hydrogen desorptions appear, with a maximum at 200° and 400°, respectively. These results are in good agreement with those published by Morgan et al. [5]. Secondly, the degassed sample heated at 500° was cooled back to ambient temperature for one hour and then heated up again to 500° (20 deg/min). The results are illustrated by curves 2 in Fig. 1. It is interesting to note a small hydrogen regeneration in the surface of the sample. Thirdly, the sample was cooled back a second time with air for one hour, degassed and heated up to 500° (20 deg/min). The results illustrated by curves 1 in Fig. 1 are similar to those relating to the first thermal treatment; a large hydrogen and water liberation is observed again. The atmospheric pressure,

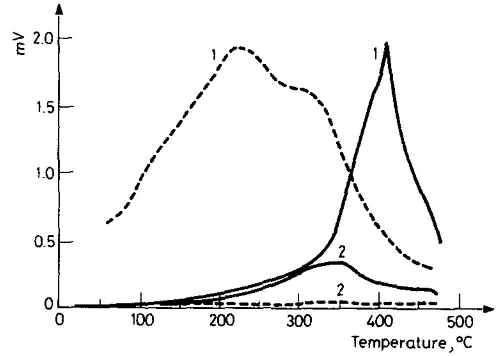


Fig. 1 XHE alloy TPD curves of hydrogen (—) and water (- - -)

and hence the water vapour pressure, appear to be very important parameters for the hydrogen regeneration process. In order to confirm such a hypothesis, TPD experiments were carried out under an activated water pressure. Figure 2 shows that a large part of D_2O has reacted with the Al after a D_2O treatment. Figure 3 shows D_2, HD and H_2 spectra; we can observe that the hydrogen is in large part substituted by HD or by D_2. It can be concluded that the presence of D_2 or HD may

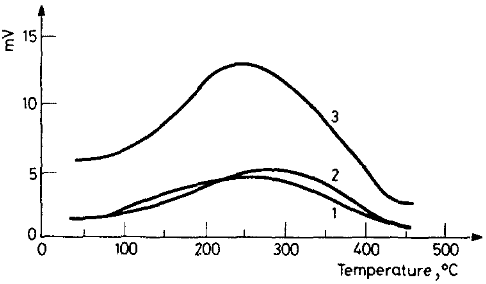


Fig. 2 XHE alloy TPD curves of H_2O (1), HDO (2) and D_2O (3)

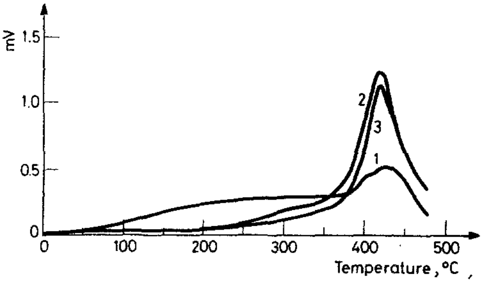


Fig. 3 XHE alloy TPD curves of H_2 (1), HD (2) and D_2 (3)

be ascribed to D_2O or HDO decomposition only and these results imply the following reaction process:

$$[\mathrm{D_2O}]+s\rightarrow \mathrm{D_2O}-s$$

and

$$\mathrm{D_2O}-s+\text{metal}\rightarrow \overset{\uparrow}{\mathrm{D}}_2+\text{oxide}$$

where s denotes an adsorption site.

Such conclusions exclude a process of alumina dehydration or a process of hydrogen diffusion from the bulk of the powder.

On the other hand, we have observed that hydrogen liberation at 400° is systematically followed by a metallic condensation product on the walls of the reactor chamber at the outlet of the furnace. Chemical analysis of the sample before and after hydrogen liberation shows a considerable loss of zinc and magnesium in the alloy (Table 1).

Table 1 Alloy composition before and after thermal treatment at 460° (XHE alloy)

Before partial sublimation	After partial sublimation	Weight loss
Zn 6.3 %	Zn 0.56%	91 %
Mg 2.25%	Mg 1.25%	44.5%
Cu 1.6 %	Cu 1.6 %	0 %

These results imply a partial sublimation of the material with a necessary break-up of the oxide at the surface of the powder. Thus it is very likely that water decomposition at the contact of the metal is widely promoted by the break-up of the oxide, and a correlation between hydrogen liberation and partial sublimation is probable.

It should be noted that experiments performed at 2 deg/min induce no important modifications in the hydrogen spectrum.

TPD experiments on XA alloy

TPD mxperiments were performed at 2 deg/min, and results concerning water and hydrogen are reported in Fig. 4. It is interesting to note that the hydrogen spectrum is very different from the preceding one. Four peaks, located at 230, 300, 365 and 390°, are present, but liberation of hydrogen at 390° is always followed by a partial sublimation of the alloy. In an attempt to determine the origin of this difference in hydrogen evolution, several experimental procedures were adopted:

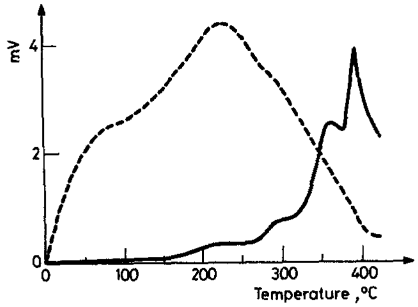


Fig. 4 XA alloy TPD curves of hydrogen (—) and water (- - -)

a) Influence of the temperature of degassing

On the basis of the previous hydrogen spectrum, different experimental temperatures of degassing T_G were selected: 150, 260, 320 and 380°. Initially, the sample was heated up to T_G and evacuated for 15 hours at this temperature, and the TPD spectra were recorded up to 400–410°. Results are presented in Figs 5 and 6. For $T_G = 150°$ (Fig. 5), no significant modifications are observed; the hydrogen spectrum is slightly shifted to a higher temperature. If $T_G = 260°$ (Fig. 5), the second peak, initially located at 300°, disappears completely and the shape of the third peak is modified. If $T_G = 320°$ or 380°, the hydrogen spectrum is always characterized by a large single peak at around 400° and the metal condensation appears simultaneously. It is also interesting to note that the time of degassing

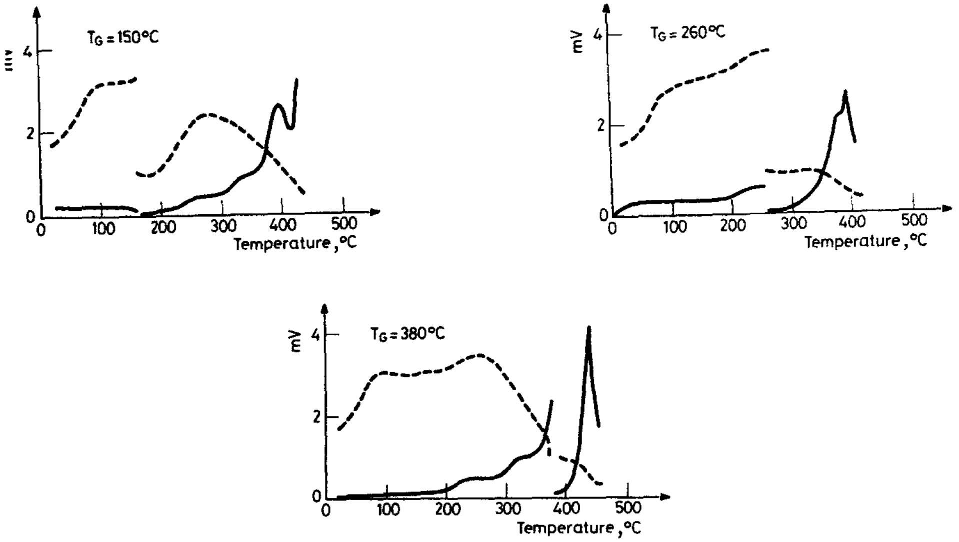


Fig. 5 XA alloy TPD curves of H_2 (—) and water (- - -) after degassing at T_G° during 15 hours

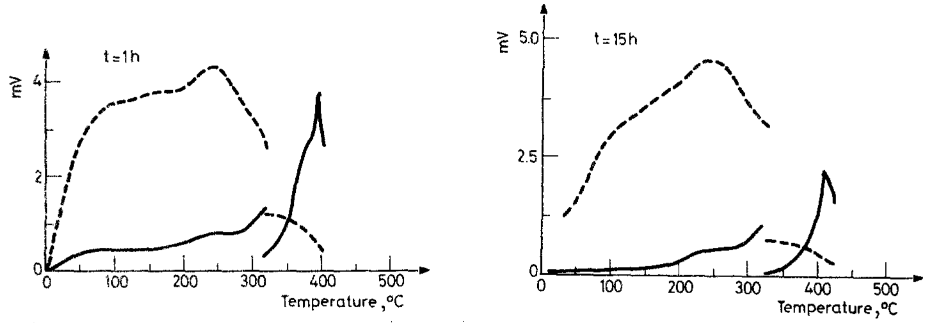


Fig. 6 XA alloy TPD curves of H_2 (—) and water (- - -) after degassing at 320° during *t* hours

affects the TPD curves (Fig. 6). If these results are considered, it appears that the first three hydrogen liberations are controlled by a kinetic process which is a function of the temperature. In contrast, the last hydrogen liberation is not determined by the nature of the previous degassing and no previous thermal treatment seems to have any influence on such a phenomenon.

In order to obtain information about the origin of the hydrogen, we again studied hydrogen regeneration at the surface of the XA alloy by means of activated water.

b) Hydrogen regeneration

In order to prevent a possible change in the surface states of the sample after the partial sublimation of the alloy, our experiments were initially limited to a temperature just before that of the last desorption peak. Figures 7 and 8 illustrate two successive TPD experiments carried out with the same sample. Figure 7 shows the first thermal treatment of the alloy initially evacuated at 20°, treated with D_2O, evacuated and heated up to 410°. Figure 8 shows results concerning the second thermal treatment of the previous sample treated with D_2O at 20°, evacuated and heated up to 410° again. We can observe that H_2 liberation during the first thermal treatment prevails before HD or D_2 liberation and that the H_2 liberation process cannot be reproduced after H_2O or D_2O treatment at 20°.

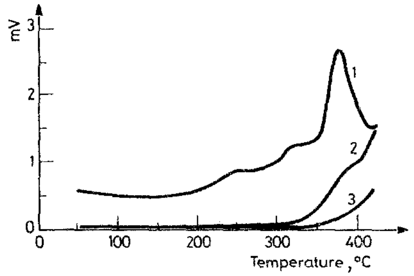


Fig. 7 XA alloy TPD curves of H_2 (1), HD(2) and D_2 (3) during the first thermal treatment

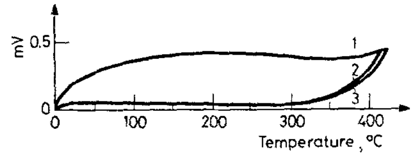


Fig. 8 XA alloy TPD curves of H_2 (1) HD (2) and D_2 (3) during the second thermal treatment

The first three hydrogen evolutions concern an irreversible phenomenon without any correlation with the ambient water vapour. On the other hand, the fourth peak is always present (Fig. 9) and may be regenerated by H_2O or D_2O treatment. From these results, it is possible to distinguish two kinds of hydrogen liberation for XA alloy:

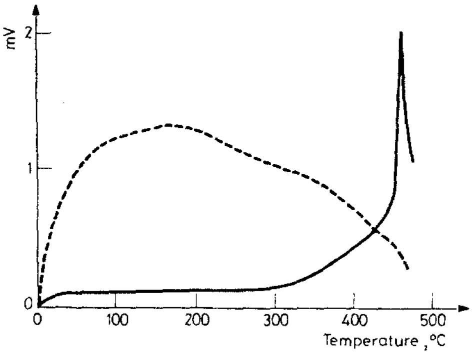


Fig. 9 XA alloy TPD curves of hydrogen (—) and water (– – –) during the second thermal treatment

First, the first three irreversible evolutions, which are controlled by a kinetic process. Such results may be correlated to the dehydration of aluminium hydroxide, in agreement with the conclusion published by Arbuzova et al. [3]. According to the experimental temperature, alumina may generate free water in the network of the oxide, and hydrogen formation occurs at the metal-oxide interface through the reaction of water with the metal.

Secondly, the fourth hydrogen evolution, which is identical to that observed with XHE alloy, may be interpreted in terms of the break-up of the oxide at high temperature.

Such a reaction is catastrophic for metallurgical alloy properties and the thermal treatment responsible must be avoided in a degassing procedure.

As concerns the activated water treatment, in the first case it appears experimentally difficult to obtain H_2O substitution by HD or by D_2. This point may be explained by taking into account that constitutional water in Al-hydroxides is certainly more strongly bonded than chemisorbed water at the surface of the powder. Under such conditions, it appears difficult to substitute H_2O or D_2O, and consequently H_2 by D_2.

The difference between the XHE and XA hydrogen spectra implies a large modification in the nature of the oxides, and dry oxide formation is certainly promoted by atomization in helium. The difference in the nature of the oxide layer is confirmed by the oxygen contents analysed in the XHE and XA alloys: 1350 ppm and 3210 ppm, respectively.

Conclusions

It has been established that hydrogen liberation at the surface of the X7xxx aluminium alloy depends on the atomization procedure. In all cases investigated, hydrogen is certainly generated by water decomposition at the surface of the metal. However, depending on the nature of the oxide, two different kinds of hydrogen formation may occur. Firstly, hydrogen is generated from water of Al-hydroxides; its degassing induces the formation of a dry oxide layer at the surface of the alloy, and the mechanical properties will be preserved after sintering. Secondly, hydrogen is generated from adsorbed water. The chemical reaction between the metal and the water is conditioned by the break-up of the oxide at high temperature and such a procedure will annihilate the high mechanical properties of the sintered alloy.

It is evident that powder metallurgy will be a successful new way to obtain very high-strength aluminium alloy only if the degassing process is carried out under the first conditions.

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Zusammenfassung — Die mechanischen Eigenschaften von pulvermetallurgischen (P/M) Aluminiumlegierungen können wesentlich durch ihren Wasserstoffgehalt beeinflußt werden. Um hochwertige Legierungen zu erhalten muß die vor dem Sintern erfolgende Entgasung optimiert werden. Solch ein Prozeß erfordert die Kenntnis des Mechanismus der H_2-Desorption von der Oberfläche des Pulvers. Mittels der Temperaturdesorptionstechnik wurde die Wasserstoffabgabe von einer X7xxx-P/M-Legierung (Al, Zn, Mg, Cu) untersucht. Die Ergebnisse zeigen, daß die Atomisierungsprozedur (mit Luft oder Helium) einen wesentlichen Einfluß ausübt. Wasserstoff wird durch Zersetzung von Wasser an den Kontaktstellen der sich legierenden Metalle nach zwei unterschiedlichen Mechanismen gebildet. Einmal kann Wasser auf der Probe chemisorbiert und der Zersetzungsprozeß durch den Aufbruch der Oxidschicht, dem eine Verdampfung von Zink und Magnesium folgt, bedingt sein. Zum anderen wird im Gitter des Oxids Wasser durch Dehydroxylierung von Aluminiumhydroxid in Freiheit gesetzt, das mit dem Metall an der Metall-Oxid-Grenzfläche reagieren kann.

Резюме — Механические свойства порошковых металлургических алюминиевых сплавов в значительной степени затрагиваются наличием в них водорода. Для ролучения высококачественных сплавов, необходимо оптимизировать дегазацию порошка перед его спеканием. Такой процесс требует знания механизма десорбции водорода из поверхности порошка. С помощью метода температурной десорбции изучен процесс удаления водорода из сплава X7xxx (Al, Zn, Mg, Cu). Результаты показали значительное влияние метода атомизации (воздухом или гелием). Возможны два различные механизмы образования водорода, вследствии разложения воды, находящейся в контакте со сплавляющимися металлами. Первый состоит в том, что влага химически сорбирована на образце и процесс разложения обусловлен разрушением окисного слоя, за которым следует испарение цинка и магния. Второй является зависимым от температуры; вода выделяется в сетчатой структуре окисного слоя путем превращения гидроокисей алюминия и может реагировать с металлом на поверхности раздела металл — окись металла.