ELSEVIER

Journal of Alloys and Compounds 218 (1995) 259–262

Journal of
ALLOYS
AND COMPOUNDS

On products of InMg corrosion in wet air and their conversion during annealing in vacuum

I. Uszyński, R. Kubiak

W. Trzebiatowski Institute for Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 937, 50-950 Wrocław, Poland

Received 3 September 1994

Abstract

The corrosion process of InMg alloy and the conversion of corrosion products by annealing in vacuum have been investigated by X-ray powder diffraction and energy-dispersive spectroscopy methods. The crystalline indium phase and an amorphous phase with a composition corresponding to the formula of the mineral pokrovskite ($Mg(OH)_2MgCO_3 \cdot 0.5H_2O$) were found as corrosion products. Their further conversion during annealing in vacuum at various temperatures was examined. The experimental corrosion data for AuCu(I) and InMg were compared.

Keywords: Corrosion; Annealing; Indium; Magnesium

1. Introduction

It is well known that magnesium shows high chemical activity even in a normal atmosphere. In spite of this, magnesium is used for manufacturing many technically important alloys. Therefore the examination of magnesium alloy corrosion may still be of interest.

In the present paper we investigate InMg alloy for two reasons: it corrodes in wet air at room temperature in a reasonable time (days) and it has the AuCu(I)-type crystal structure [1]. We have already investigated the corrosion of AuCu alloys in air [2]. This gives us the additional possibility to compare observed corrosion effects in InMg and AuCu alloys.

2. Experimental details and results

2.1. Sample preparation

An ingot of InMg alloy was obtained by melting a stoichiometric mixture of indium (99.999% purity) and magnesium (99.99% purity) at 720 °C for 0.5 h in a corundum crucible enclosed in a quartz ampoule under vacuum. The obtained ingot was converted into filings. The X-ray powder diagram (see Fig. 1(a)) for the InMg filings confirms the homogeneous tetragonal structure.

2.2. InMg corrosion in wet air at 297 K

The changes caused by the corrosion of InMg samples were observed by sequential X-ray exposures in a D-5000 powder diffractometer with Cu $K\alpha$ radiation and measuring the variations in sample weight. The powder diagrams (Fig. 1) show a decreasing intensity of diffraction lines from the InMg crystalline phase and an increasing intensity of lines from the indium crystalline phase. After 20 days only the pure indium crystalline phase can be detected (see Fig. 1(d)). Fig. 2a reveals the layer microstructure of the homogeneous InMg alloy. After corrosion the layer microstructure is destroyed (Fig. 2b). The sample weight (Fig. 3) increases during corrosion. After 16 days the corrosion process accelerates and runs spontaneously. The variations in integrated intensities from indium (see the plot for the (222) diffraction peak in Fig. 3) also support such corrosion behaviour. The sample weight increase and the X-ray analysis indicate that the corrosion process of InMg alloy leads to pure crystalline indium and amorphous pokrovskite ($Mg(OH)_2MgCO_3 \cdot 0.5H_2O$) products.

2.3. Conversion of InMg corrosion products by annealing in vacuum

The corroded sample was pressed into a pellet and annealed in vacuum at various temperatures. The chem-

SSDI 0925-8388(94)01390-X

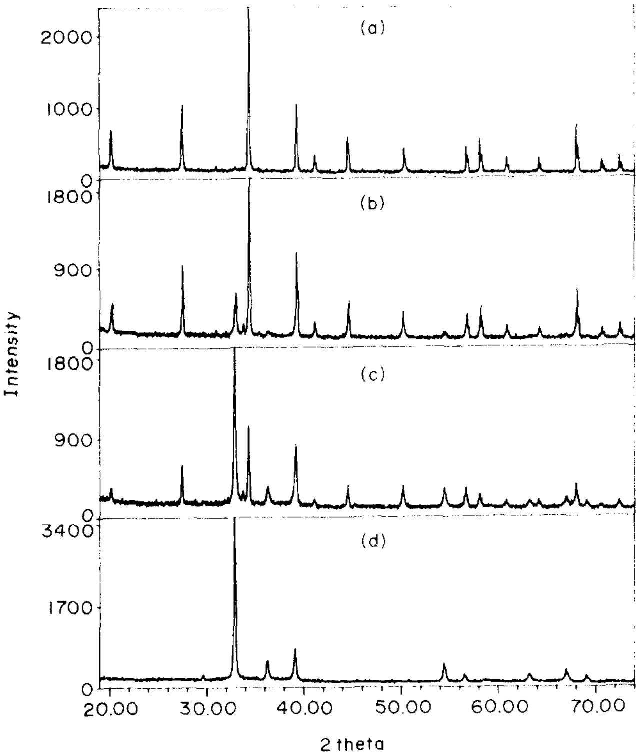

Fig. 1. X-Ray powder diffraction patterns of InMg alloy: (a) homogeneous alloy; (b)–(d) samples corroded for (b) 15, (c) 16 and (d) 20 days.

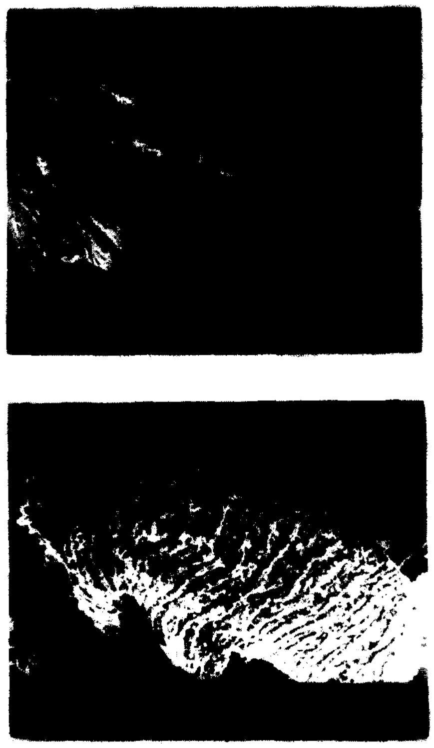

Fig. 2. Electron micrographs of a single InMg filing: a, homogeneous; b, corroded.

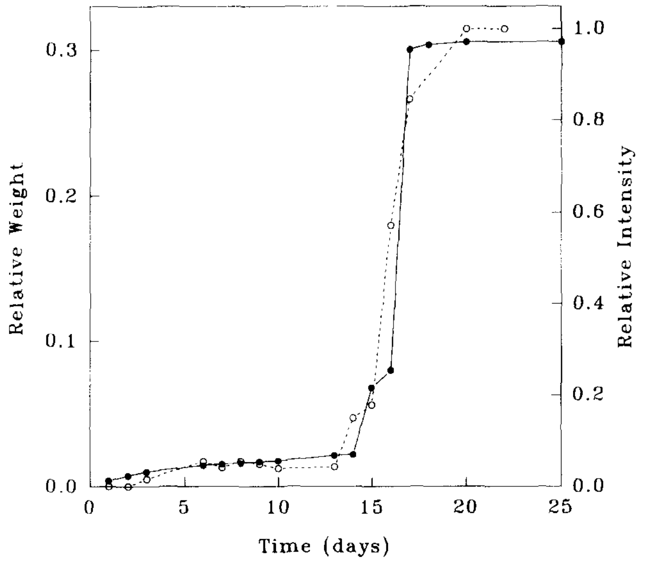

Fig. 3. Variations in sample weight (full curve) and indium (222) diffraction peak intensity (broken curve) during corrosion.

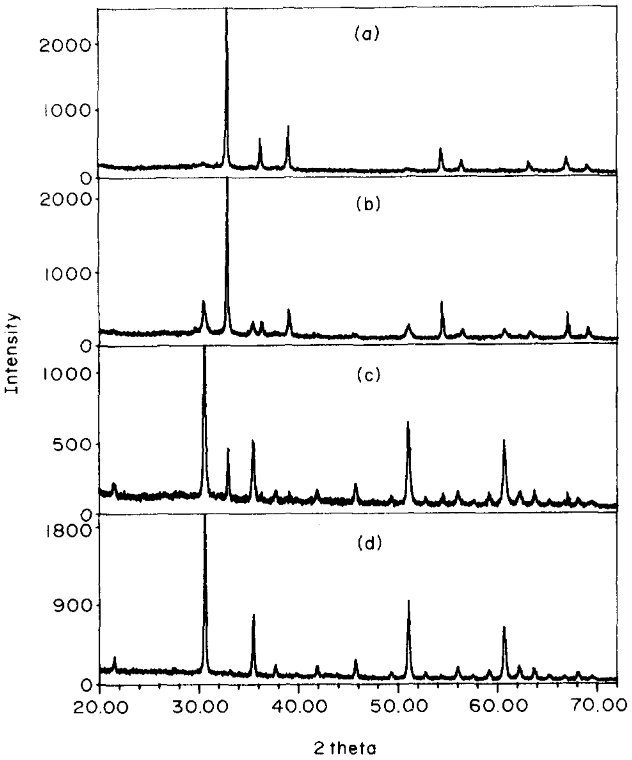

Fig. 4. X-Ray powder diffraction patterns of pellets (a) A, (b) B, (c) C and (d) D.

ical composition and microstructure of the pellet were monitored using an X-ray powder diffractometer and an energy-dispersive X-ray microanalyser. The annealing conditions and detected chemical elements are listed in Table 1.

The diffraction patterns in Fig. 4 show the formation of In_2O_3 crystalline phase during annealing of the pellet in vacuum. In pellet A annealed at 110 °C the indium phase dominates (Fig. 4(a)); however, an increase in

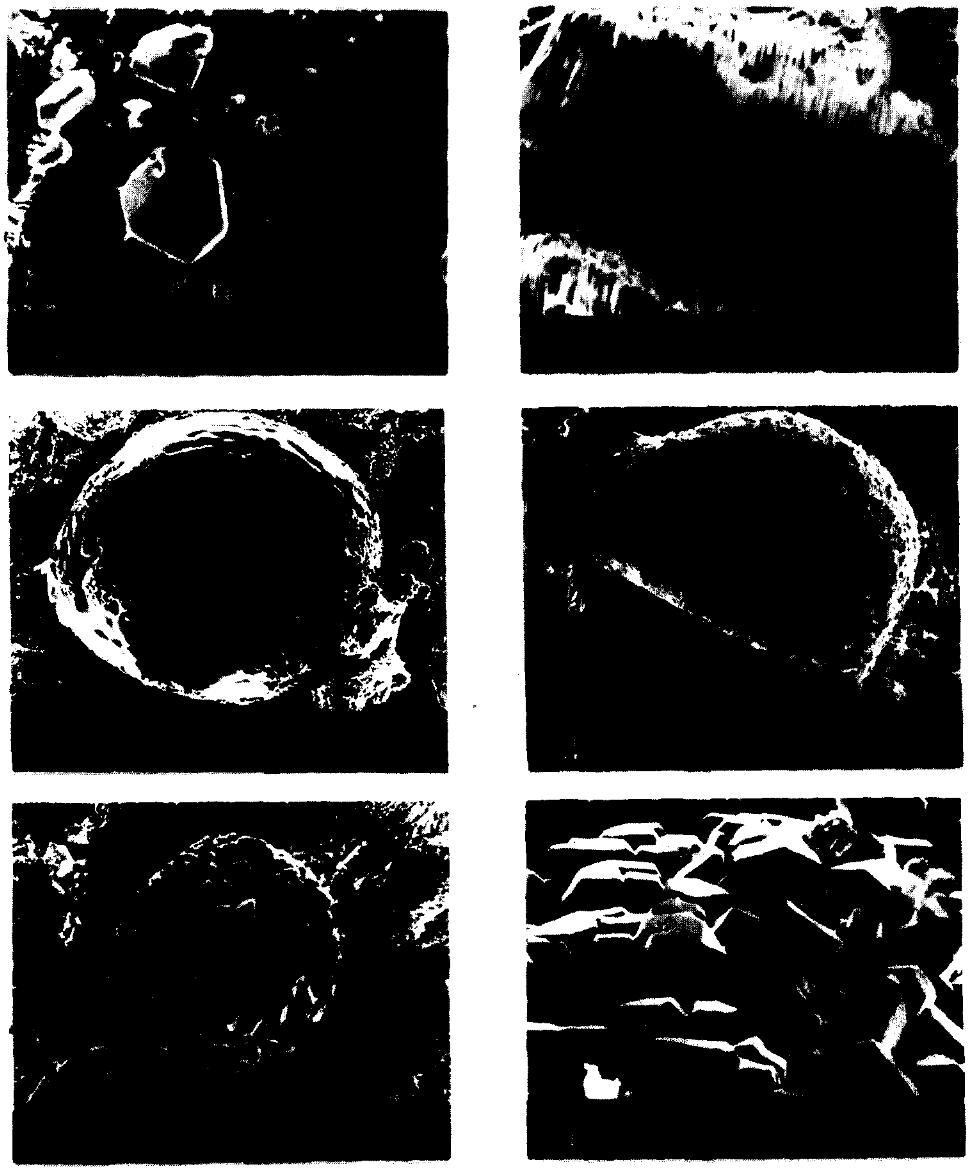

Fig. 5. Surface electron micrographs of pellets (a, b) A, (c, d) B and (e, f) C.

Table 1
Annealing conditions and chemical compositions of pellets

Pellet	Annealing conditions		Chemical elements
	Temperature (°C)	Time (days)	
A	110	7	In, Mg, O, C
B	210	7	In, Mg, O, C
C	350	14	In, Mg, O, C
D	550	14	In, Mg, O

background intensities at angular positions corresponding to In_2O_3 diffraction lines can be observed. Indium whiskers (Fig. 5b) and polyhedral indium crystals (Fig. 5a) are observed on the pellet surface. Annealing at 210 °C (above the indium melting temperature) leads to the growth of In_2O_3 (Fig. 4(b)). In fact, indium flows out of the specimen abundantly, forming drops on the pellet surface. An excess of indium spheres was removed before further investigations. By electron microscopy we observe on the pellet surface the remaining indium drops (Fig. 5c) covered with In_2O_3 and regions with visible craters (Fig. 5d) caused by gasification processes occurring in the sample. Subsequent extensive annealing at higher temperature (350 °C) yields the further formation of In_2O_3 phase (Figs. 4(c) and 4(d)) and its transformation to polyhedral crystals (Figs. 5e and 5f). Heat treatment of the pellet at 550 °C removes carbon from the specimen.

3. Discussion

InMg alloy corrodes easily in wet air and transforms to crystalline indium and amorphous pokrovskite. It is interesting to note that the indium separates in the form of well-developed polyhedral crystals far below its melting temperature.

It is useful to compare the experimental data for AuCu(I) and InMg corrosion processes. In tetragonal AuCu(I) and InMg crystals the Au or In atom layers and Cu or Mg atom layers are alternately stacked along the *c* axis of the crystal lattice. In both cases only one constituent atom is chemically active under the conditions used, e.g. Cu from AuCu transforms into Cu_2O and CuO and Mg from InMg transforms into pokrovskite. However, the corrosion paths are quite different. The corrosion in AuCu alloy is connected with the diffusion of Cu atoms to the grain surface and the redistribution of remaining Cu and Au atoms in the matrix crystalline net. In Ref. [2] we observed discrete steps upon changing the AuCu alloy composition to the next-nearest Au-richer phases. The Au_3Cu crystals or at least the Au-phase-forming polycrystalline samples are still closely attached along grain boundaries. The copper oxides are in the outer sheaths of individual alloy pieces (filings). Only the early stage of InMg corrosion is controlled by the diffusion of Mg atoms to the outer grain surfaces. Although magnesium must join with O_2, H_2O and CO_2 molecules to form the pokrovskite, we could not observe any discrete corrosion steps. After some time (strongly dependent on the air wetness) the corrosion process becomes spontaneous and the alloy structure is destroyed completely. Finally, indium layers are no longer chemically bound to remaining components and the sample converts into individual whiskers, passing into polyhedral crystals and amorphous pokrovskite.

The formation of In_2O_3 occurs owing to nascent oxygen liberation during the pokrovskite decomposition. Presumably, during annealing of the pellet at 110, 210 and 350 °C the pokrovskite decomposes to MgO, $MgCO_3$ and O_2, H_2 and H_2O products. At 550 °C a further decay process occurs: $MgCO_3$ decomposes into MgO and CO_2. Therefore elemental analysis does not reveal a carbon content in pellet D.

References

[1] N. Ino, M. Hirabayashi and S. Ogawa, *Trans. Jpn. Inst. Met., 6* (1965) 172.

[2] J. Janczak and R. Kubiak, *J. Alloys Comp., 182* (1992) 289.