

DESTRUCTION OF AMORPHOUS $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ ALLOY UNDER GASEOUS AND ELECTROCHEMICAL CHARGING WITH HYDROGEN

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Introduction

Processes of destruction under charging magnesium alloys with hydrogen have not been studied well enough yet. Authors [1,2] indicate that processes of direct and destructive hydrogenation are determined by thermodynamic characteristics of a system, temperature, and pressure. J.J.Reili and R.H.Wiswall have described processes of destructive charging with hydrogen of the intermetallic compound Mg_2Cu [3]. In paper [4] it has been shown that complete separation of the hydride and intermetallic compound formed as a result of decomposition does not take place. The material obtained consists of particles with developed surface between the constituents.

In this work our results for destructive charging with hydrogen of the amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ alloy are presented.

Experimental

Magnesium $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ alloys were prepared in the form of ribbons with a width of 5mm and a thickness of 30-60µm using single-roller melt spinning in an Ar atmosphere. Charging of the amorphous samples with hydrogen was performed either in a 0.1 N NaOH solution containing $5 \times 10^{-5} \text{ mol/l As}_2\text{O}_3$ at a cathodic current density of $i = -1 \text{ mA/cm}^2$ or in a gas phase under a hydrogen pressure of 30 bar and temperatures of 200 and 300°C. The samples were examined by an X-ray spectroscopy in Co-radiation. The amount of hydrogen was determined by means of a hydrogen analyser LECO 402.

Results and discussion

Electrochemical charging of the amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ alloy with atomic hydrogen has shown that at room temperature absorption of hydrogen leads to the decomposition of the initial compound. Our paper [5] has reported data of transmission electron microscopy, which confirm the formation of the following compounds: MgH_2 , YH_3 , and Cu_2Mg .

The reaction $2\text{Mg}_2\text{Cu} + 3\text{H}_2 = \text{Cu}_2\text{Mg} + 3\text{MgH}_2$ (1)

($\Delta G_{298} = -7,3 \pm 1,1 \text{ kkal/mol}$) proceeds above 200°C. At room temperature under pressure up to 880 atm it does not occur [3]. Ternary hydride Mg_2CuH_2 was not fixed either. The heat of formation at 298°C was found for Mg_2Cu and Cu_2Mg to be 4.0 ± 1.1 and $5.4 \pm 1.1 \text{ kkal/mol}$, respectively. The formation of Cu_2Mg is thermodynamically more preferable because in this case ΔH is more negative relative to that for Mg_2Cu , which stands for the absence of the ternary hydride Mg_2CuH_2 . On the other hand, the destruction of Mg_2Cu may yield pure copper according to the reaction $\text{Mg}_2\text{Cu} + 2\text{H}_2 = \text{Cu} + 2\text{MgH}_2$ (2) ($\Delta G_{298} = -6,9 \text{ kkal/mol}$). Reaction (2) is more preferable at room temperature ($\Delta G_{562} = +1.6 \text{ kkal/mol}$).

We think that under electrochemical saturation, free copper may be formed alongside with the formation of Cu_2Mg , which is indirectly confirmed by the high content of absorbed hydrogen, 4 mass %, and the data of scanning microscopy (Fig. 1), where areas with high copper content (light ones) are observed.

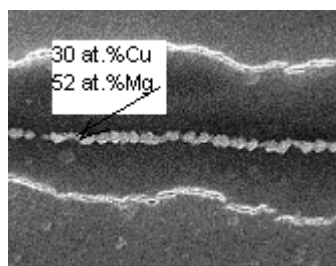


Fig.1 SEM photos for the alloy $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ saturated by hydrogen up to 4 mass%.

Fig. 2 represents XRD patterns for the amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ alloy after gas saturation. As seen, at 200°C processes of crystallization take place; thus gas saturation is accompanied by crystallization. At 200°C saturation is slow, therefore for 10 h only 0.17 mass % hydrogen content could be achieved. The XRD patterns identify the YH_2 phase and oxides CuO , Cu_2O , and Y_2O_3 , which are also observed after the

crystallization of the initial alloy in an argon atmosphere. At 300 °C upon saturation for 1 h, copper is reduced from oxides, and processes of saturation become more intense. The oxides of Y and Mg remain. Fig. 2 (curve 3) points to the presence of the YH₂ phase and traces of MgH₂ at 300°C. The contents of these phases increases with increasing holding time. At a hydrogen content of 1.2 mass %, Mg is still observed. Therefore, the increase in MgH₂ content may be prescribed both to reaction (1) and to the reaction $Mg + H_2 = MgH_2$. As seen in the XRD patterns, with increasing hydrogen content, the amount of Cu₂Mg, noticeably increases and lines of Mg disappear.

Upon 20 h saturation, hydrogen content attains 3.3 mass%. The X-ray analysis data are shown in Fig. 3.

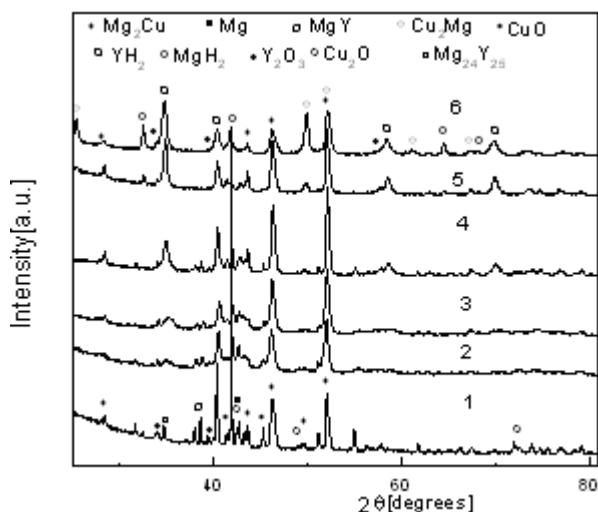


Fig. 2. XRD patterns of the Mg₆₅Cu₂₅Y₁₀H_x alloy. Saturation from a gaseous phase at : 200 °C: (2)-5h, 0.03mass%, (3)-10h, 0.17 mass% 300°C: (4) -1h, 0.26mass%; (5)-5h, 1.26 mass%, (6)-10h, 2.3 mass%. (1) the initial alloy heated in argon at 300°C.

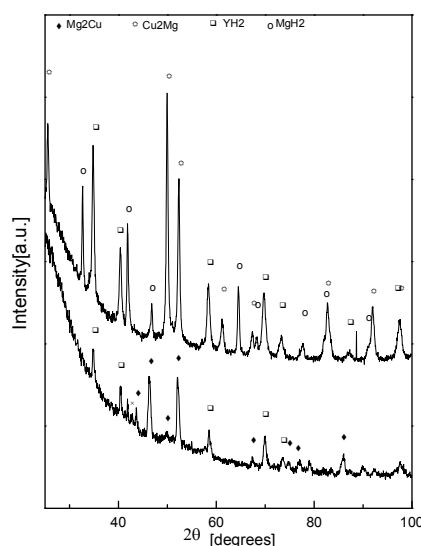


Fig.3. XRD patterns of Mg₆₅Cu₂₅Y₁₀H_x hydrogen-saturated from a gas phase at 300°C for 20 h up to 3.3 mass % hydrogen.

Conclusions

Charging of copper-containing magnesium based alloys involves alloy destruction with the formation of Cu₂Mg and MgH₂ phases under both electrochemical and gas charging, which is possible to explain high diffuse mobility of the restored copper. It should be noticed that charging of the amorphous alloy Mg₆₅Cu₂₅Y₁₀ with atomic hydrogen leads to the formation of the YH₃ phase whereas under saturation from a gas phase YH₂ forms.

References

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