An anelastic spectroscopy, differential scanning calorimetry and X-ray diffraction study of the crystallization process of Mg–Ni–Fe alloys

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Abstract

The effects of heating-induced crystallization on the structural and mechanical properties of Mg–Ni–Fe amorphous ribbons were studied by anelastic spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction. DSC results show that the crystallization occurs through several non-reversible steps, which correspond to significant changes in the Young's modulus and concomitant irreversible elastic energy loss peaks. Moreover, an anelastic peak is found at 215 K, which for the first time indicates the presence of some dynamical process related to the simultaneous presence of different phases. The formation of a metastable Mg_6Ni phase is detected, which transforms into Mg and Mg_2Ni stable phases. A quantitative analysis of the different phases present at the different steps was also carried out.

1. Introduction

Magnesium–nickel alloys have attracted great interest [1] as hydrogen storage materials due to their hydrogen storage capacity (Mg_2Ni forms a ternary complex hydride Mg_2NiH_4, with 3.6 mass% of hydrogen [2]) and low cost. However, these materials are not yet ready for application in a functional hydrogen reservoir due to their unfavourable thermodynamic properties and slow kinetics of hydrogen absorption and desorption. In recent years, alloying and production of nanocrystalline and/or amorphous microstrucures by ball-milling and melt-spinning [1,3,4] have been found to improve the reaction kinetics. In fact the high surface to volume ratio and the great number of grain boundaries in nanocrystalline or disordered alloys enhance the gas–solid reactivity providing easy pathway for hydrogen diffusion [5]. Melt spin Mg–Ni–RE (RE = Y, Nd, . . .) [1] and Mn–Ni–Fe [4] ribbons have shown attractive hydrogen storage properties. Moreover, heat treatments of starting amorphous alloys up to the crystallization introduce a controlled microstructure which improves the mechanical properties and the hydrogen kinetics [5].

The knowledge of the crystallization mechanism of an amorphous alloy is useful in order to optimize the microstructure. In the present work, we report the effects of crystallization on the structural and mechanical properties in Mg–Ni–Fe alloys, by using anelastic spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction. To our knowledge, this is the first

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study of the intermediate nanostructured phases which form in the Mg–Ni–Fe alloy during crystallization.

2. Experimental

Three Mg–Ni–Fe ribbons were prepared by the melt-spinning technique [4]. Starting materials used for the preparation of the ribbons were: Mg pellets (99.9% purity), Ni and Fe powders (99.9% purity) weighted at the desired proportions. A small excess of Mg with respect to the desired composition was used due to inherent losses during melting. A graphite crucible containing these starting materials was heated in an induction furnace above 1773 K and, in order to ensure homogeneity, maintained at 1473 K for 60 min under 3 MPa of protective argon atmosphere. After cooling down to room temperature, the compounds were melted once again in a second graphite crucible applying an overpressure of argon (0.04–0.06 MPa) and pushed under protective argon atmosphere through a nozzle (0.6 mm diameter) onto a rapidly rotating cooled Cu wheel (40 cm diameter). The thickness of the ribbons obtained by this procedure was between 25 and 35 μm. The composition of the three samples used for the present work (called as ribbon 1, 2 and 3) is $Mg_{88}Ni_{11}Fe_1$, as resulting from EDS analysis.

Anelastic spectroscopy measurements are conducted suspending the samples on thin wires located at the nodal lines of flexural vibration modes and electrostatically exciting the corresponding mechanical resonances of the samples or by clamping the samples on one side. The sample vibration produces an alternate stress which interacts with the local lattice distortions introduced by the mobile entities and perturbs their site energies in such a way that the sites that are energetically favoured in the first half period become unfavoured in the second half. The system then looks for the equilibrium redistribution among the perturbed levels. At the temperature at which the relaxation rate τ^{-1} of the species is equal to the angular vibration frequency ω ($\omega\tau = 1$) the stimulated atomic migration is able to follow, by thermal activation, the sample vibration, and the coefficient of elastic energy dissipation Q^{-1} reaches its maximum value. The energy dissipation (or reciprocal of the mechanical quality factor Q) is measured from the decay of the free oscillations or from the width of the resonance peak. The measurement of the dynamic Young modulus E' is simultaneously obtained from the angular vibration frequency $\omega^2 = kE'/\rho$, where ρ is the mass density and k a numerical factor depending on the sample geometry [6]. The independent and concomitant measurements of Q^{-1} and E' allow the complex modulus $E = E' + iE''$ to be derived, being $Q^{-1} = E''/E'$. For a single relaxation time, τ, Q^{-1} is given by:

$$Q^{-1} = gv_0(\lambda_1 - \lambda_2)^2 \frac{cn_1n_2}{kT} E' \frac{(\omega\tau)^{\alpha}}{1 + (\omega\tau)^{2\alpha}} \qquad (1)$$

where c is the molar concentration of the jumping atoms and n_1 and n_2 their equilibrium fractions in sites 1 and 2; λ_1 and λ_2 the elastic dipoles [6] of the defects in their two configurations; g a factor of the order of 1/2 depending on the geometry of the jump and the type of sample vibration, v_0 the unit cell volume, τ a parameter equal to 1 for a single-time Debye process, and k is the Boltzmann constant. For classical processes is $\tau = \tau_0\, e^{W/kT}$, being W the activation energy. As τ is temperature dependent for thermally activated processes, the relaxation condition ($\omega\tau = 1$) is satisfied at low temperatures for fast processes and at high temperatures for slow processes.

Differential scanning calorimetry analyses of 10–15 mg samples were performed between 300 and 570 K by means of a Mettler-Toledo DSC822 system.

Power X-ray diffraction (XPD) measurements were performed with a Rigaku diffractometer equipped with a rotating anode source, a Ge(1 1 1) single crystal monochromator and a curved position sensitive INEL detector collecting 120° at once. The samples were inserted into Lindemann capillaries (0.5 mm diameters) and measured in Debye Scherrer transmission geometry.

3. Results and discussion

The heating-induced crystallization process was studied by the DSC measurement. Fig. 1 shows the DSC curve measured for the $Mg_{88}Ni_{11}Fe_1$ sample (small pieces from ribbon 3) between 300 and 675 K, on heating with a rate of 20 K/min followed

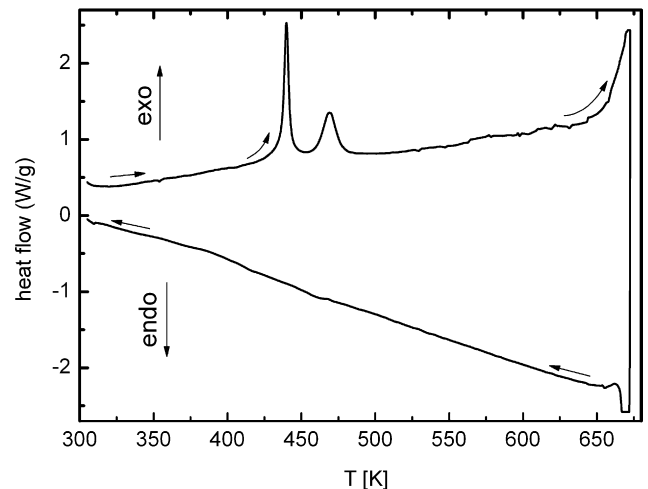Fig. 1. DSC curve of an amorphous $Mg_{88}Ni_{11}Fe_1$ sample measured during a heating and subsequent cooling run at a constant temperature rate of ± 20 K/min.

by a cooling at the same rate. On heating, two well-defined exothermic peaks are present at 440 and 468 K. Moreover, starting from 650 K a rapid increase in the heat flow is observed up to 675 K, which is the maximum heating temperature allowed by the experimental setup. This increase resembles to the low temperature side of a third peak with the maximum at a temperature above the highest measured temperature. On cooling down none of these features are displayed, suggesting that the observed peaks are due to non-reversible processes. This indicates that the crystallization process proceeds through several non-reversible steps, in agreement with similar DSC results obtained in Mg–Ni–Y systems [5,7], where after the first crystallization stage the formation of a metastable Mg_xNi_y phase has been observed, which however disappears after the process completion.

The anelastic spectroscopy is very sensitive to atomic rearrangements in solids and the measurement of the modulus is a powerful tool for studying phase transformations, since the formation of different phases is detected also at extremely low concentrations. For the above reasons this technique has been successfully employed to study phase transitions in combination with the DSC analysis [8]. In order to obtain more information about the structural relaxation, a systematic study of the anelastic spectrum during the heat-induced crystallization process has been conducted.

Fig. 2 shows the energy loss Q^{-1} and the vibration frequency (which is related to the dynamic Young modulus) of ribbon 1 during thermal cycling from room temperature up to progressively increasing heating temperatures and back to room temperature, in the range between 350 and 820 K. During the first two cycles to 350 and 400 K (curves a and b, respectively, in Fig. 2), Q^{-1} monotonically increases with the increase of temperature, and the same values are retraced on cooling. The frequency curve, instead, forms hysteresys loops which remain open on cooling down to room temperature. This irreversibility of the elastic modulus indicates that the material after the cycle is not exactly in the same starting state, and might be explained by a glassy-state behaviour of the amorphous phase. On increas-