PREPARATION AND PHASE FORMATION OF Al-Mn ALLOYS

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1. Introduction

Increasing need for new permanent magnets is a driving force for an investigation of new kind of magnetic materials and alloys in which the rare-earth elements are replaced by a more abundant and/or less strategically important ones. Al-Mn systems might be one of the possible candidates. These systems are interesting as perspective alternative to conventional high-strength RE based magnets applied in information storage systems including magnetic optic drives, hard disks [1-8,13]. Magnetic properties of Al-Mn systems are determined by existence (formation) of τ-MnAl phase, responsible for high coercivity and saturation magnetization [13], low density/light weight and corrosion resistance coupled with low cost of its constituent elements. The magnetic properties of Mn–Al system are sensitive to the microstructure and the presence of defects developed during the τ-phase formation. These attributes are strongly determined by the nature of production route employed [3,6,7,11]. Mn–Al magnets might posess many practical and commercial applications as they surpass the performance of conventional hard ferrites, like in hybrid automobiles, alternative energy sources and several other important applications [13,14]. Thus that the development of strategies for processing Al-Mn–based bulk magnets with required τ-phase and fine-grained morphology is a technological challenge, potentially to be solved by non-equilibrium processing techniques such as melt spinning, splat quenching, mechanical alloying, gas atomization and plasma arc discharge [3]. The required ferromagnetic phase is strongly influenced by the starting composition (Mn-to-Al ratio), and exists between 49-60 at. % Mn.[3,7-11], preparation methods and the subsequent annealing treatments. The metastable ferromagnetic τ-MnAl phase, first reported by Kono [6] and Koch et al. [7], exhibits tetragonal superstructure similar to the phases of other binary systems such as FePt and CoPt. Pure τ-phase formation is possible by rapid quenching only, when the parent high temperature hexagonal close packed (hcp) ε-phase is created followed by suitable isothermal annealing or by controlled cooling. This ε-phase is the parent or precursor phase for the ferromagnetic tetragonal τ phase [3,6,7,11,14]. The overall phase composition of the Al-Mn alloys containing between 49-60 at. % Mn has been broadly discussed elsewhere [3,6,7,11-15], not providing unambiguous description of the structure and the presence of the τ-phase yet.

The Mn-Al phase diagram on Fig 1.have shown that the transformation - two-step reaction process of ε into τ phase could take place by different mechanisms depending on the microstructure and purity of the ε phase. From the parent hexagonal ε-MnAl phase, which is A3 structure with lattice parameters a = 2.69Å and c = 4.38Å, through the intermediate *B*19-structured ε'-phase, with lattice constants of a≈ b≈ c≈ 3,006Å, the τ-MnAl can be obtained by isothermal annealing at temperatures in the range 623–923 K. Occurrence of this intermediate phase depends on thermal treatment. It has been reported that this transformation is accompanied by diffusional nucleation and growth processes [6,7,11-13]. The nucleation and growth of the τ-MnAl phase, characterized as a metastable tetragonal $L1_0$ superstructure (similar to CuAu type), also as a tetragonal phase (tP2), with lattice constants of a = 3.94Å and c = 3.58Å [6,7,11-15] and being the only ferromagnetic phase of AlMn, has been

elaborated by several groups. Process referred to as a "massive" transformation preferentially forming at the grain boundaries of the ε-phase. Nucleation of the τ-MnAl phase takes place almost exclusively and heterogeneously along the prior ε-phase grain boundaries [3,6-11,16-18], its formation has also been reported to be accompanied by micro-twinning, which is associated with stress relaxation at the growth front [14].

In this work we shall show preliminary results on formation of ferromagnetic MnAl compound from rapidly quenched precursors by thermal processing.
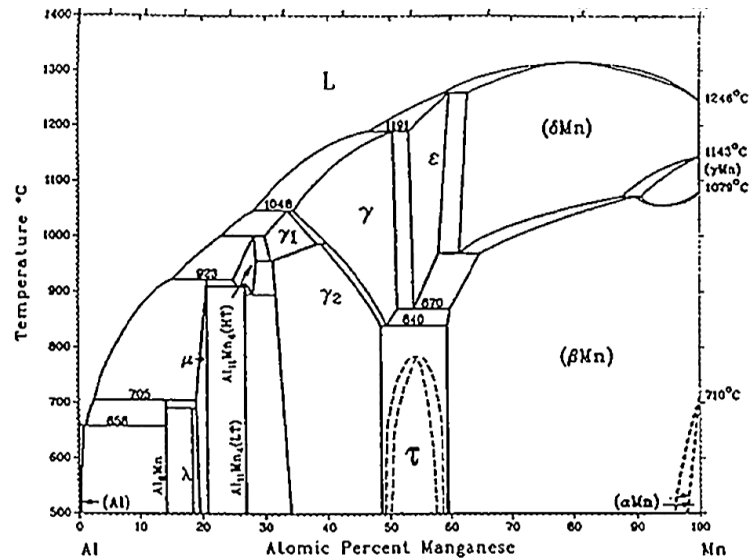

Fig. 1 *The binary Al-Mn system phase diagram [15].*

2. Experimental details

The samples in form of ribbons 3mm wide and ~ 17μm thick were prepared by planar flow casting method. The structures of the as–cast and isothermally annealed samples were investigated by X-ray diffraction (XRD) method using Bruker D8 Advance diffractometers (CuKα radiation) and also by transmission electron microscopy (TEM) using JEOL 2000FX at 200kV. The structure changes in this system were also observed by in-situ XRD analysis during isothermal annealing (440K for 12 hours). Using differential scanning calorimetry (DSC 7 Perkin Elmer) the transformation kinetic was investigated, this was used to define the temperature of transformation beginning (T_x) and their activation energy (E_{akt}) by the Kissinger method. The Curie temperature (T_c) for the evaluated magnetic phase was determined by the magnetic thermogravimetry (TGA7 Perkin Elmer) with small external magnet.

3. Results and discussion

The microstructure of $Al_{45}Mn_{55}$ sample in as-cast state was observed using TEM, the sample after quenching is not amorphous. The μm-sized grains contain micro twinning well visible in Fig. 2. Grains with different orientations exhibited numerous parallel slabs. The measurements of heat flow changes determined by DSC (Fig. 3a) show only one transformation from this crystalline state. The temperature of the transformation onset T_x is close to 700 K. With help of DSC measurements with different linear heating rates and Kissinger method the activation energy of this structure change was determined; E_{akt} is 186+/-4 kJ/mol (insert in Fig. 3a). The parameters of heat treatment to achieve the content of magnetic phase in the sample are chosen with respect to the DSC curves. The sample was isothermally annealed at 673 K for 12 hour and at 71 K for 1 and 12 hours. The annealed

samples exhibit a change in magnetic properties evidenced by TGA measurement (Fig. 3b). The Curie temperature $T_c = 635$ K was estimated from the decrease of magnetic weight of the sample annealed at 713 K for 1 hour during its subsequent heating after cooling to room temperature.
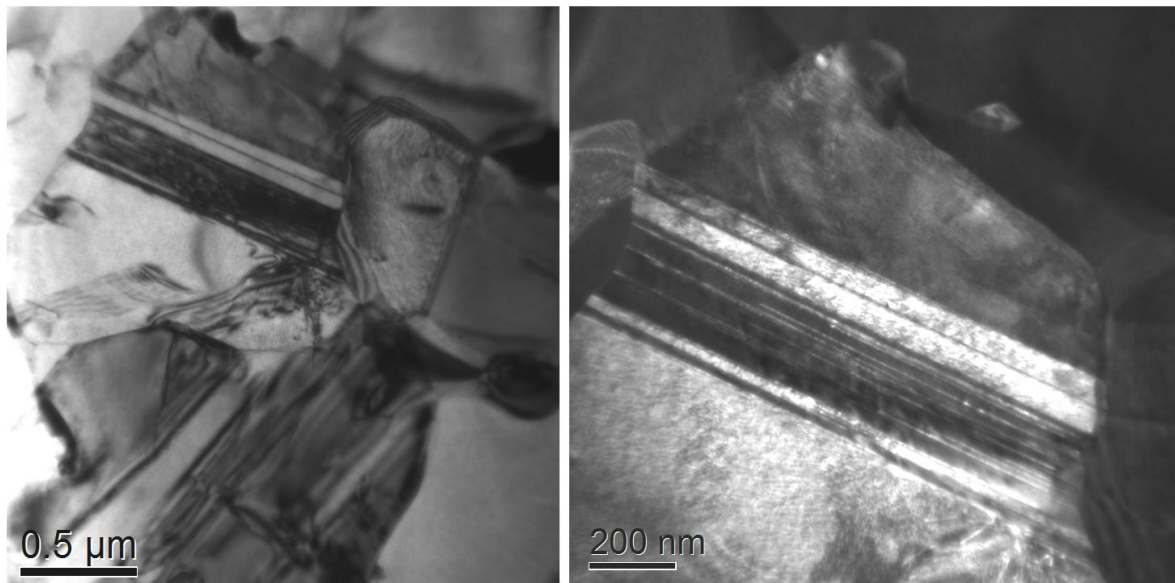

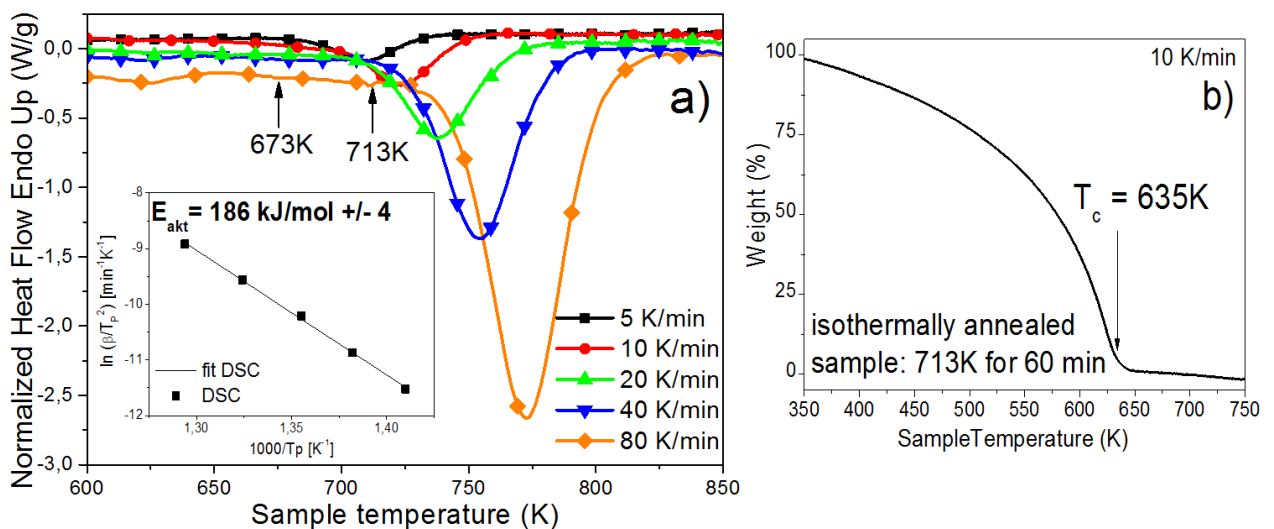Fig.2 *TEM images of as-cast $Al_{45}Mn_{55}$ sample.*

Fig. 3 *(a) DSC curves for $Al_{45}Mn_{55}$ measured with different heating rates Φ; inset shows the values of exotherm maxima, T_{max} used for calculation of E_{akt} by Kissinger method. (b) TGA curves for $Al_{45}Mn_{55}$ measured after heat treatment.*

Phase analysis of various heat-treated $Al_{45}Mn_{55}$ samples is shown on XRD patterns in Fig. 4. The comparison of these XRD patterns allows to follow the structure changes from nonmagnetic as cast state (nearly monophase hexagonal $Al_{45}Mn_{55}$ with a=2.703Å and c=4.374Å) to the transformation – (rearrangement) of Mn-rich phases. Annealed samples exhibit the presence of several Mn-rich phases. The master alloy contained also a certain content of tetragonal magnetic phase with small grain sizes. From this analysis it can be seen that the sample annealed by 713 K exhibits increased content of this magnetic phase at the expense of hexagonal $Al_{45}Mn_{55}$ phase, which is dominant in the as-cast structure. The phase

$Al_{11}Mn_{14}$ and the Al_8Mn_{11} are very similar and exhibit XRD peaks very closely together, differing by a shift in the lattice parameter *a* from 3,94 to 2,77Å of the same tetragonal structure. This measurement proved the transformation of hexagonal $Al_{45}Mn_{55}$ after annealing at higher temperature and sufficient time to tetragonal$Al_{11}Mn_{14}$. The comparison of two different annealing regimes shows that the temperatures of isothermal annealing should lie above 400K. X-ray diffraction pattern of investigated sample obtained during in-situ isothermal heating 713K for 12 hours is shown in Fig. 5 in form of intensity map. This isotherm shows clearly the transition threshold from one structure ($Al_{45}Mn_{55}$) to the formation of another ($Al_{11}Mn_{14}$) at the expense of its content. The X-ray patterns taken before and after this heat treatment confirm well the results of the isothermal analysis.
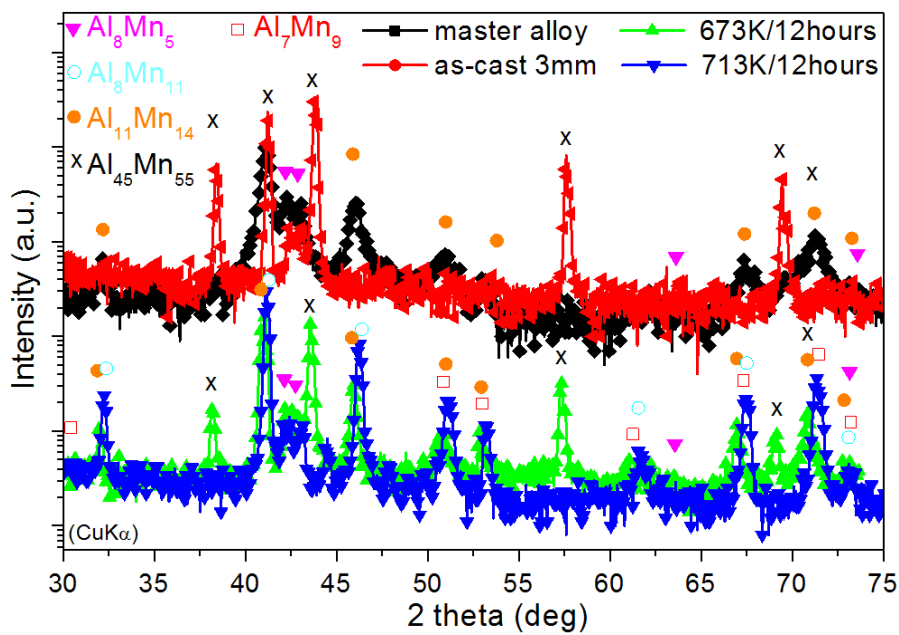

Fig. 4 *XRD patterns of $Al_{45}Mn_{55}$ sample in different states after heat treatment.*
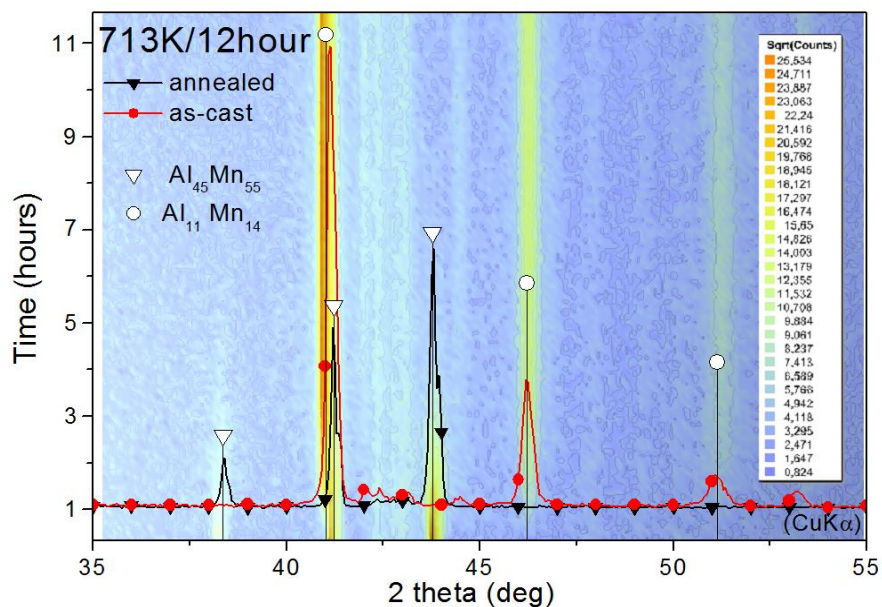

Fig. 5 *XRD of in-situ annealed $Al_{45}Mn_{55}$ isothermally annealed at 713K for 12 hours; X-ray patterns taken before and after isothermal annealing are also plotted.*

4. Conclusion

The metastable binary combination of post-transition and transition metal - Al-Mn rapidly quenched systems were prepared in form of ribbons by PFC and consequently used for elaboration of semi-hard permanent magnets. Samples subjected to appropriate heat treatments form phases with attractive ferromagnetic properties. The effect of alloying of constituting elements (in ratio about 1/1) on the changes of physical properties caused by structural transformations was studied. The structure transformation (T_x, E_{akt} and T_c) from as-cast state was analyzed by thermal analysis, DSC and TGA measurements. The formation and evolution of crystalline grains is shown by direct structure observation using transmission electron microscopy in as cast state and by X-ray diffraction methods. In-situ X-ray isothermal annealing at temperatures selected according to the results of DSC analysis has shown the process of formation of $Al_{11}Mn_{14}$ and Al_8Mn_{11} at the expense of the original $Al_{45}Mn_{55}$ phase. The experiment allowed to map the thermal processing for achieving structure with the highest content of τ-AlMn by the transformation from the existing ε-AlMn phase.

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