COBALT BASED FERROMAGNETIC SHAPE MEMORY ALLOYS

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Abstract

Great success in Ni_2MnGa derived alloys attracted attention to similar Heusler alloys including cobalt based alloys. The article describes the progress in work on $Co_{38}Ni_{33}Al_{29}$ alloy. After long struggle the defined crystals with single-crystalline matrix were prepared. The influence of annealing on martensitic transformation in these crystals was investigated. The martensitic transformation using magnetic susceptibility measurements we found to be $M_S \sim -73$ °C. The complex interaction between martensitic lathes and A2 particles was found. The discrepancy between transformation temperatures obtained by magnetic susceptibility measurements and resonant ultrasound spectroscopy will be discussed together with the results of the quasistatic and dynamic nanoindentation.

Introduction

Ferromagnetic shape memory alloys (FSMAs) took a lot of attraction in the past decade [1]. The structural transition initialized by the magnetic field or just shape change due to martensitic variant's reorientation give wide possibilities of applications as sensors or actuators. The NiMnGa based alloys were the most studied among FSMAs and they also have the biggest potential. The ferromagnetic shape memory effect was described in stoichiometric compound Ni_2MnGa at first [2]. Later various effects (as magnetically induced transformation or magnetically induced reorientation) were described in non-stoichiometric alloys and shape change grew from approx. 0,2 % for stoichiometric alloy up to 14 % in off-stoichiometric one (for review see Ref. 1).

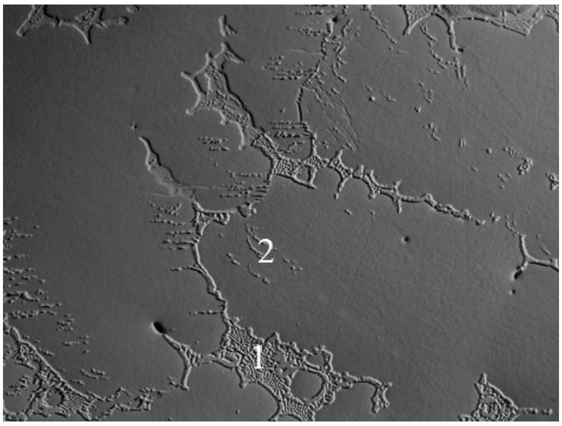


Figure 1. The structure of the samples observed by light microscope metallography. In B2 ordered matrix there are the precipitates - interdendritic A2 fcc cobalt solid solution particles (marked 1) and the ordered precipitates $L1_2$ of the phase $(Co,Ni)_3Al$)marked 2).

Great success in Ni_2MnGa derived alloys attracted attention to similar Heusler alloys including cobalt based CoNiAl and CoNiGa alloys. As the NiMnGa alloys suffer due to their strongly intermetallic state (brittleness, poor creep and fatigue properties) the cobalt based alloys seemed to be the interesting candidate for the mechanically stronger and more resistant FSMAs.

The presentation will describe the progress in work on $Co_{38}Ni_{33}Al_{29}$ alloy. After long struggle we have managed to prepare the defined crystals with single-crystalline matrix. The influence of annealing on martensitic transformation in these crystals was investigated.

Structures

The structure of the investigated material $Co_{38}Ni_{33}Al_{29}$ is composed of three phases – an ordered matrix (Co,Ni)Al with space group $Pm\bar{3}m$, structure type B2, and a disordered face centred cubic cobalt solid solution with space group $Fm\bar{3}m$, structure type A2 [3], Fig. 1. According to the phase diagram $L1_2$ structure $(Co,Ni)_3Al$ (space group $Fm\bar{3}m$) exits in samples with sufficient amount of nickel. The B2 phase matrix undergoes martensitic transformation into the tetragonal $L1_0$ structure (space group P4/mmm). The transformation mechanism is very similar to the Ni-Al alloy including precursors, tweed structure and softening of the phonon modes [4].

The structure analysis was performed using analytical electron microscopy including electron back-scattered diffraction (EBSD) as our samples are usually directionally crystallized structures with extremely large/coarse grains. The set of the in-situ measurements as a function of temperature on powders was performed on neutron source at HZB - E9 high resolution powder diffractometer.

Crystal growth

In order to study and to apply ferromagnetic shape memory effect (FSME), it is very convenient to have single-crystalline samples. The samples for crystallization study were prepared using vertical floating-zone method and Bridgman method [5, 6]. The findings from it can be summarized in the points:

1. The samples grown with a growth rate of 17 mm h^{-1} or lower have tendency to get split into a two-phase mantle (B2 matrix plus A2 interdendritic precipitates) and a single-phase (only B2) core. Such structures have tendency to crack during cutting and polishing.

2. The composition of the matrix and precipitates seems to be stable within three categories: Floating-zone sample; Bridgman sample grown with a growth rate of 17 mm h^{-1} and Bridgman samples grown with a growth rate higher than 17 mm h^{-1}. Both phases in respective categories have the uniform composition. The last category appears to be interesting for our investigation, since a variation of the chemical composition along the Bridgman crystal is realized through the change of the A2/B2 phase's ratio.

Sample annealing

A kind of metastable (quenched) equilibrium is necessary for the SME performance in these alloys. It was described in literature that this equilibrium can be reached by quick cooling after homogenization annealing, but significant changes are observed mainly in the matrix [7]. Nanoprecipitates of various phases are created by quenching, which can later support spreading of the habit plane of martensite. The fcc- and hcp-cobalt solid solution precipitates with a diameter below 100 nm were observed in samples grown with a growth rate 28 and 38 mm h^{-1} [8, 9]. Other nanoprecipitates were described in literature [7].

The material is very sensitive to the annealing temperature. The sample's phase composition change significantly as the composition of the sample is driven by the A2/B2 phase's ratio and annealing temperatures are close to the dissolving limit of A2 phase (Fig. 2).

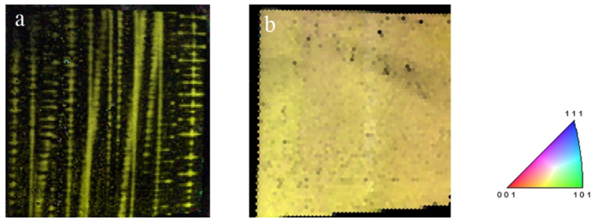
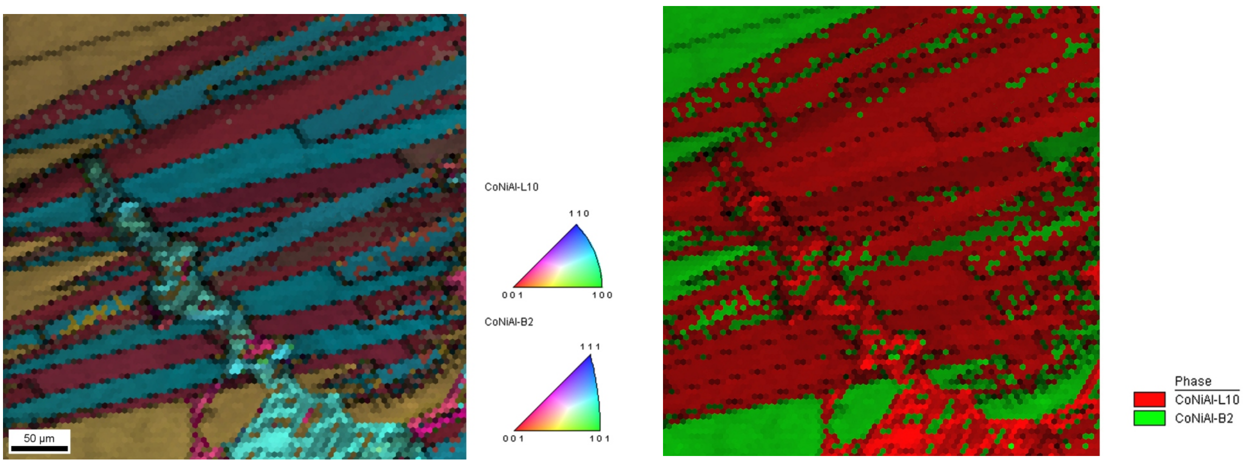


Figure 2. The dendritic microstructure of the sample unidirectional grown with a growth rate 104 mm·h^{-1} (a) was dissolved during annealing at 1275 °C / 4 h (b). The color of both maps is given by inverse pole figure for cubic structure at the right side.

Martensitic transformation

Older works [10] reported quite high temperatures of the martensitic transformation, but using magnetic susceptibility measurements we observed $M_S \sim -73$ °C. The annealing temperature depends only slightly on annealing temperatures from 1250 °C up to 1350 °C. The hysteresis of the martensitic transformation enlarges with decreasing of the annealing temperature. Although the martensitic transformation was indicated by magnetic measurement at temperatures below -73 °C, the martensitic structures were observed in various samples at room temperature. The small amount of martensitic lathes was observed in sample annealed at 1250 °C, mainly in stressed areas close to cracks. The sample annealed at 1350 °C contains compact areas of martensitic lathes confirmed by EBSD (Fig. 3). The complex interaction between martensitic lathes and A2 particles was found. The martensitic lathes are partly pinned on the grain boundaries and A2 particles, but some of them surround A2 particles developing hierarchical structures close to particle's surfaces in order to lower elastic energy, see Fig. 4.

The transformation temperatures obtained by magnetic susceptibility measurements do not agree with the results of resonant ultrasound spectroscopy on the same samples.



a) b)

Figure 3. The martensitic lamellae appear widely at the sample annealed 1350 °C / 1 h and quenched. The orientation of the particular points shows figure 4a, whereas the phase shows figure 4b. The color of map is given by inverse pole figures at the right side. The particular phase should be found from comparison with Fig 4b. The rounded particle at the middle bottom of figure has the A1 (fcc) structure, although it is evaluated as $L1_0$ structure. This is due the similarity between both structures (the tetragonality of $L1_0$ is given by site ordering). Some lamellae of $L1_0$ itself were evaluated incorrectly due to the surface relief.

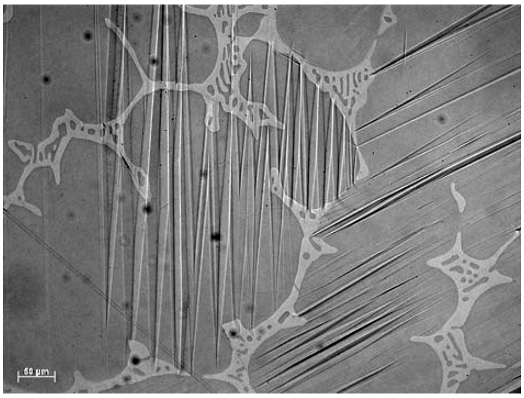


Figure 3. The sample annealed at 1350 °C for 1 h and quenched to the ice-cold water. The martensitic lather are partially pinned on the A2 particles and partially surround them.

This discrepancy is evaluated now together with the results of the quasistatic and dynamic nanoindentation.

Summary

Progress in the study of $Co_{38}Ni_{33}Al_{29}$ is described. After preparation of homogeneous unidirectional solidified material the annealing temperature and its effect on martensitic transformation was investigated. The complex interaction of martensitic lathes with A2 (fcc cobalt solid solution) was found. The transition temperatures and region of superelasticity are widely driven by annealing temperature, but clear explanation was not proven yet.

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