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Influence of Additional Annealing on Properties of Ni-Mn-In-Co Heusler Alloy.

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A promising class of solid materials for magnetic cooling at room temperatures is that in which a first order metamagnetostructural phase transition (PT) is induced by the magnetic field [1]. In this case, so-called inverse magnetocaloric effect (MCE) originates from a structural PT from the paramagnetic or antiferromagnetic martensite phase to the ferromagnetic austenite phase on the application of a magnetic field. Recently, much interest is attracted to Ni-Mn-In-Co alloys due to large magnetic-field-induced strains [2] and giant inverse MCE [3,4]. We created the new series of Ni-Mn-In-Co alloys with 43 at. % of Ni and 7 at. % of Co. The samples from this series were prepared by arc melting under an argon atmosphere with subsequent homogenizing annealing during 48 hours at 900 ^{0}C. Metamagnetic alloy $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ was chosen for further research. We investigated the properties of this alloy by electrical resistance measurements (ERM), differential scanning calorimetry (DSC) and energy-dispersive X-ray spectroscopy (EDX). After that, samples of this alloy were exposed to additional annealing during 50 hours at 750 ^{0}C and all measuring procedures were repeated.
It was determined, that electrical resistance of annealed samples is less on 30% than before annealing in martensite and austenite state too (see Fig. 1). In addition we observe a narrowing of hysteresis curve almost on 40% (from $\Delta T_{hyst} = 40^0$ downto 25^0) and a shift of curve on 15^0 to higher temperatures.
The martensitic transformation temperatures and the latent heat during the PT were determined by DSC at heating and cooling rates of 10 K/min. As seen from Fig. 1, DSC scans of the sample demonstrate exothermic and endothermic peaks which are associated with the martensitic PT occurring in the sample. The characteristic transition temperatures M_s, M_f and A_s, A_f corresponding to start and finish temperature of direct and reverse martensitic transformation, respectively, before and after additional annealing. The transition temperatures were determined as a crossing point between the extrapolation lines of the peaks and the base line. For our alloy transformation's temperatures before annealing were found: martensite start $M_s = 6$ ^{0}C, martensite finish $M_f = -10$ ^{0}C and austenite start $A_s = 32$ ^{0}C, austenite finish $A_f = 45$ ^{0}C. Transformation's temperatures after annealing: $M_s^A = 26$ ^{0}C, $M_f^A = 14$ ^{0}C and $A_s^A = 39$ ^{0}C, $A_f^A = 54$ ^{0}C. The Curie temperature of austenite state does not depend on heat treatment: $T_C = 150$ ^{0}C. Calculated from the DSC data the latent heat upon direct (cooling) and reverse (heating) PT are $L_C = +3.8$ J/g and $L_H = -4.3$ J/g in both cases (differences ~ 10% - in limits of error).
The EDX analysis of samples before and after annealing was conducted; SEM micro-photos of investigated fields are presented on Fig. 2. The black areas are flaws. The white areas (martensite plates) have the following average composition in at. %: $Ni_{42.4}Mn_{37.2}In_{13.9}Co_{6.5}$. The grey area (main body) has the similar composition. The significant difference in composition observed in dark-grey areas (the second phase): $Ni_{37.4}Mn_{40.0}In_{1.0}Co_{21.6}$. These areas have little 1% of In and a lot 21.6% of Co. One can see that annealing increases grain size and helps to reveal additional information about inner structure.

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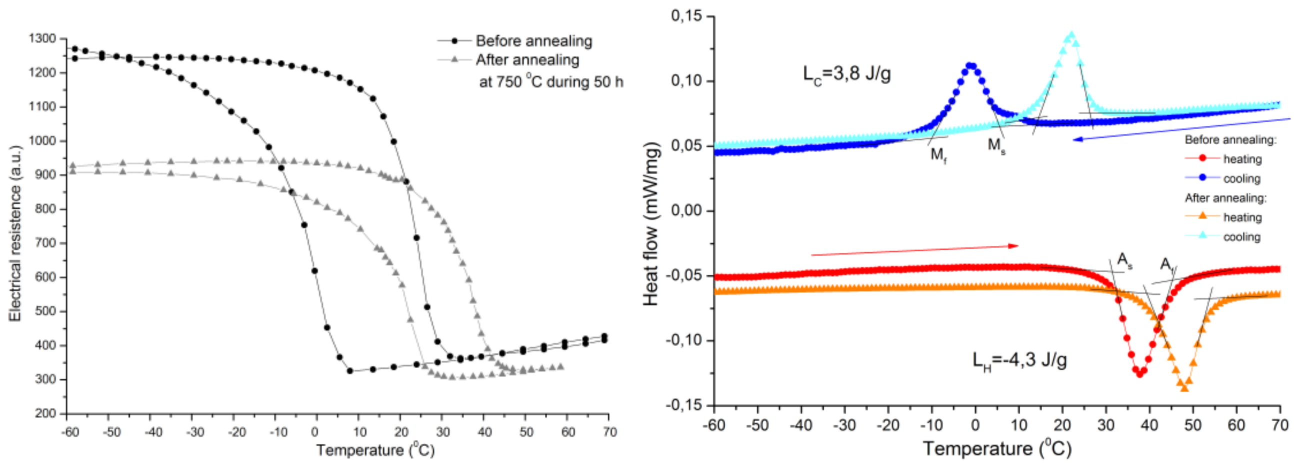

Figure 1. ERM and DSC investigations of metamagnetic $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ alloy before and after additional annealing during 50 hours at 750 ^{0}C.

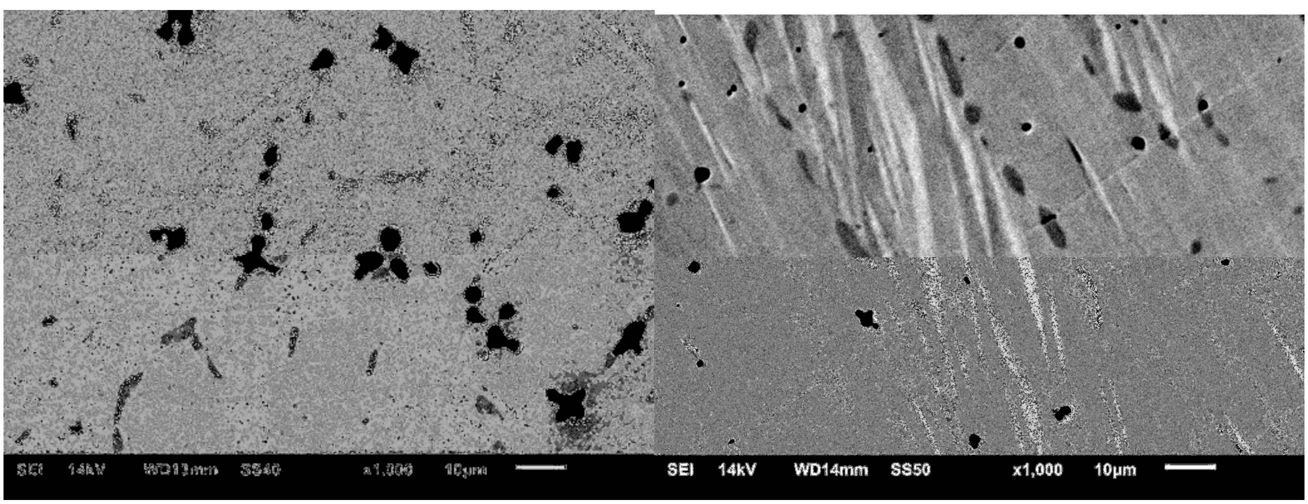

Figure 2. SEM micro-photos of region of EDX analyses of metamagnetic $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ alloy before and after additional annealing during 50 hours at 750 ^{0}C.