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Austenite arrest in polycrystalline Ni-Mn-Co-In films

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ABSTRACT

Electrical resistivity and magnetization measurements realized on polycrystalline $Ni_{45.2}Co_{4.7}Mn_{36.2}In_{13.9}$ film showed that the austenite phase was blocked upon a magnetic field during the martensitic transformation. Besides, the shift of the temperature transition upon a magnetic field towards the lower temperature is responsible for a large magnetoresistance that can be irreproducible in the heating branch of the transformation and that was measured in this work. We studied how the magnetoresistance was changing inside the hysteresis loop depending on whether the temperature lies on the forward or reverse transformation path. The analysis is interpreted in terms of the non equilibrium state consequent to the field cooled process and how martensite is converted into austenite inside the hysteresis loop when the magnetic field is applied.

1. Introduction

Ferromagnetic shape memory alloys Ni_2MnX (X = In, Sn, Sb …) [1] exhibit a first order transition during the martensitic transformation with a stronger magnetism for the parent phase. The martensitic transformation in these alloys is associated to caloric effects [2–4], giant deformations and shape memory effects [5,6], large irreversible magnetoresistance [7,8] and piezoresistance [9,10]. Irreversibility of the martensitic transformation is taking place and is the manifestation of phase coexistence, metastability and hysteresis associated with the first order transition [11]. The irreversibility of the transformation largely depends on the cooling or heating procedure with respect to the application of the magnetic field or pressure [10].

Another important aspect of these alloys is the appearance of an arrest of the austenite phase during the martensitic transformation while cooling under a magnetic field, a phenomenon that is called kinetic arrest, thermal arrest or austenite arrest [13–18]. As for glass transition, there is no consensus on all the aspects of the arrest effect and the names given to it depend on whether it is viewed as a purely dynamical phenomenon with no relation to thermodynamic features, a mixture of both or a purely thermodynamic phenomenon. The austenite arrest deserves a special terminology if the transformation is viewed purely athermal (process with no thermal activation without time dependence) or isothermal (thermally activated) with a short incubation time so that the arrest of the transformation is not simply coming from its incomplete nature. S. Kustov showed that in Ni-Mn-Co-In alloy, the forward transformation was isothermal because the change in the magnetic order from the ferromagnetic to antiferromagnetic opposes the structural transition which is not the case in the reverse transition, thus its intrinsic athermal nature [19]. In this paper, we chose the neutral terminology “austenite arrest” with an emphasis of its connection to the isothermal nature of the forward transformation. The austenite arrest is characterized by the coexistence of both phases and is mostly studied by means of magnetization measurements. Electrical resistivity measurement under a magnetic field is suited to the study of Ni_2MnX alloys since it depends mainly on the volume fraction of austenite and martensite phases. Most of these observations were carried out on bulk samples. However, the possibility to master Heusler Ni-Co-Mn-In film growth is essential to develop microsystem devices so as to study fundamental questions [20]. In the present study, the dependence of the electrical resistivity and magnetization with the magnetic field as a function of temperature in free-standing polycrystalline $Ni_{45.2}Co_{4.7}Mn_{36.2}In_{13.9}$ films is investigated. The austenite arrest is also studied and the possibility to estimate a complete transformation upon magnetic field in the film is proposed.

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2. Method

A polycrystalline freestanding film was produced by a co-sputtering process [21]. To free the sample from the substrate, a positive photoresist buffer layer is deposited prior to the co-sputtering process by means of a rotating spin coating procedure on a glass substrate. The buffer layer is then etched away by dissolution in acetone. Co-sputtering deposition is used with a Ni-Co-Mn-In quaternary principal target and a secondary target of indium. The film crystallization is then realized with a post-annealing treatment at 700 °C. The resulting composition of the sample is $Ni_{45.2}Co_{4.7}Mn_{36.2}In_{13.9}$ following this process [21]. The stoichiometry was chosen to come close to a martensitic transformation from ferromagnetic (FM) to antiferromagnetic (AFM) close to room temperature. Indium composition must be adjusted to 13% at to obtain a room temperature transformation in $Ni_{45}Co_5MnIn$ [22]. Eventually, the magnetic state results mainly from antiferromagnetic interactions between the Mn_1 (occupying the regular Mn site) and the Mn_2 (doping the In sub-lattice) atoms. Film homogeneity was verified by analyzing different spots along the film. The deviation from the composition $Ni_{45.2}Co_{4.7}Mn_{36.2}In_{13.9}$ is lower than 0.1%. The film shows some clear delimited grains of austenite or martensite depending on the temperature history of the sample and no secondary phase could be observed from the XRD pattern or FESEM images [21]. The grain size is ranging from 2 to 30 μm.

The electrical resistivity measurements under a magnetic field were realized using a commercial PPMS device under two different protocols: on the one hand, the sample is cooled and warmed without magnetic field (rate 2K/min). On the other hand, it is cooled and warmed under a magnetic field (rate 2K/min). The length between the potential taps of the electrical resistivity measurements is 1.5 mm. The sample is 4.9 mm long and 4.5 μm thick. The magnetization M was measured by a VSM-SQUID magnetometer where the sample is cooled and then warmed under a magnetic field ranging from 0.1 to 7 T at a rate of 3K/min.

3. Results and discussion

3.1. Austenite arrest

The electrical resistivity hysteresis and magnetization loops (inset) on $Ni_{45.2}Co_{4.7}Mn_{36.2}In_{13.9}$ films as a function of temperature and magnetic field is presented in Fig. 1.

The martensitic transformation in the film possesses a hysteresis of almost 150 K. The curves of magnetization show a large drop of magnetization between the austenite and martensite phases. The resistivity is around 1 μΩ m and the increase of resistivity associated with the martensitic transformation only reaches 30% (to be compared to 300%, the usual ratio obtained in these alloys). This low value can be partly attributed to the grain boundaries resistance of a same order of magnitude than the film resistance and high internal stresses that may change the grain boundaries contribution during cooling and the grain resistivity. The magnetization behavior of the martensite is weakly ferromagnetic. It could come from an intrinsic feature of the martensite, a magnetic behavior of the grain boundaries or an incomplete transformation. This could also contribute to lower the rise of electrical resistance upon the martensitic transformation. The thermal hysteresis comes from the frictional barrier to move the interface between the austenite and martensite during the nucleation and growth of one phase. A supplementary work is consequently needed both in the cooling and heating branches to induce the transformation. Therefore, one phase has to be over-heated or under-cooled before transforming to the other phase, resulting in a hysteretic behavior.

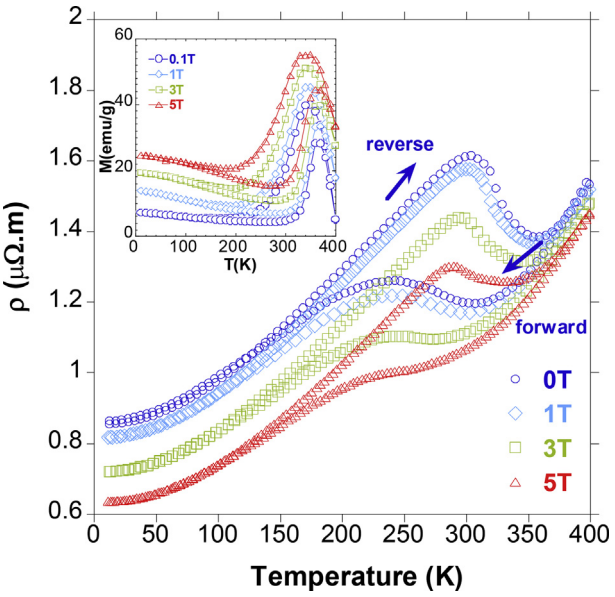

Fig. 1. Electrical resistivity measurements of $Ni_{45.2}Co_{4.7}Mn_{36.2}In_{13.9}$ film cooled and then warmed under a magnetic field up to 5 T. In inset, thermomagnetic curves for applied magnetic fields up to 5 T.

The transformation temperatures M_S, M_F, A_S, A_F are determined with the tangent methods and equal to 325 K, 225 K, 305 K and 355 K.

The decrease of electrical resistivity and the increase of magnetization below 150 K is associated to the austenite arrest of the ferromagnetic austenite phase while cooling under a magnetic field. Thermomagnetic curves under different fields were done to associate the decrease of electrical resistivity to austenite arrest and not to an anisotropy of electrical resistivity of martensitic variants. The difference of electrical resistivity below 350 K under a magnetic field is due to the martensitic transformation whereas above 350 K, in the austenite state, it is mainly attributed to the classical magnetoresistive effect.

Magnetization relaxation were done in $Ni_{45.2}Co_{4.7}Mn_{36.2}In_{13.9}$ films at different stable temperatures reached while cooling at 12K/min under a magnetic field ranging from 0.1 T to 7 T. The temperature needs around 1 min to stabilize. Normalized M versus time at 250 K under 0.1 T and 7 T is plotted in Fig. 2a. First, one can observe a relaxation occurring at 0.1 T which can be attributed to the isothermal character of the transformation while cooling. Second, the magnetization decreases more slowly under a magnetic field. Finally, the magnetization at 0.1T fits a logarithmic law which is not the case under a magnetic field. The error coming from the imprecision of the reference time $t = 0$ is estimated to reach 0.5% on normalized M after 60min. Normalized M versus time t at various temperatures under a field of 7 T is plotted in Fig. 2b. The magnetization decreases all the faster, as the temperature is high. Yet even at 10 K some relaxation of the magnetization is observed showing that even at these temperatures no stable state is reached under 7 T in our films. No substantial change in the relaxation mechanism or curve shape under a magnetic field could be noted from the relaxation happening inside the hysteretic cycles where the transformation is still occurring and at very low temperatures. It was difficult to fit the curves under a magnetic field with a logarithmic law. We modified the stretched exponential function (also called Kohlrausch-Williams-Watt (KWW)) $\exp(-(t/\tau)^{\beta})$, where τ is the characteristic relaxation time and β is a shape parameter to take into account the fact that the transformation is not complete inside the hysteresis [12,23,24]. Indeed, the magnetization at infinity must