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Mössbauer spectroscopy and magnetic measurements on Fe-Ni-Co-Ti shape memory alloys

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Fe-Ni-Co-Ti shape memory alloys were prepared by various techniques. A comparison between samples prepared by classical metallurgy and by melt spinning technique is performed in respect to the microscopic mechanisms responding for the shape memory effects. X-ray diffraction, thermomagnetic measurements and Mössbauer spectroscopy were applied for a complete structural and magnetic characterization. Only samples supporting an aging treatment gave evidence for shape memory effects and correlated structural transformations.

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1. Introduction

Ferromagnetic shape memory alloys are presently under investigation for their possible applications in actuation of higher magnitude, controlled by thermal as well as by magnetic field [1,2]. The mechanism of the magnetically controlled shape memory materials was suggested by Ullakko et al. [3] and is related to the fact that magnetic and martensite variants are twin related to each other and to the fact that the magnetic isotropy energy is larger than the elastic energy.

Fe-Ni-Co-Ti alloys are among the few ferrous alloys of convenient price which can exhibit simultaneously shape memory effect (SME) and ferromagnetic behavior. By comparison to other ferrous shape memory alloys, they belong to the group which shows thermoelastic martensite (together with Fe-Pt and Fe-Pd alloys), similar to the non-ferrous shape memory alloys. However, they exhibit usually a smaller thermal hysteresis, compared to non-thermoelastic ferrous alloys with large thermal hysteresis and complete or nearly complete shape memory (e.g. Fe-Mn-Si, Fe-Ni-C) [4,5].

The shape memory effect is based on the thermal or mechanical induced reversible phase transformation between a martensite and an austenite phase. In the case of Fe-Ni-Co-Ti, the martensite phase, which is present at low temperature, shows a body cubic tetragonal (BCT) structure whereas the austenitic phase (present at high temperature) has a disordered face centered cubic (FCC) one. Fe-Ni-Co-Ti alloys of atomic weight 52/32/12/4 (%) respectively, show in the first thermal cycles, after an adequate aging process, a nearly complete martensite→austenite transformation with a small hysteresis loop [6]. The temperature where the martensitic phase starts to appear (during the temperature decreasing branch of the cycle) is called M_s and that where the transformation is complete is called M_f. On the increasing temperature branch, the temperature where the austenitic phase starts to appear is called A_s and the temperature where the austenitic transformation is complete is called A_f. For the Fe-Ni-Co-Ti alloy with the above mentioned composition, M_s, M_f, A_s, A_f are about 173 K, 77 K, 143 K and 247 K, respectively [6]. It is worth to mention that after many thermally cycling processes the phase transformation knocks off to be complete and more and more martensitic phase remains retained in the austenitic phase above A_f. After several thousand cycles, the martensite is stabilized over the whole temperature range and the alloy looses completely their SME.

At this point is important to stress out that, excepting the structural transition, the morphology of each of the two main phases involved in the thermal process is very important in respect to the SME. The most important prerequisite of the effect is the formation in the austenitic phase of fine dispersed and coherent $(Ni,Co,Fe)_3Ti$ particles (FCC ordered with $L1_2$ structure) which forms the so called coherent γ' phase. Usually, the addition of Ti is the one which leads to the formation of fine γ' precipitates, resulting in a high yield stress and a large back stress for assisting the reverse-transformation [7].

The precipitation of the γ' phase, directly connected with the reversibility of the transformation, can be controlled by the aging parameters (e.g. 100 h at 500 °C are needed in order to obtain complete reversibility of the transformation, but at 600 °C only 10 min suffice). Long aging time or high temperature (e.g. 50 h at 600 °C or aging temperature $\geq$ 700 °C) lead to the precipitation of incoherent and stable η phase (Ni_3Ti – Hexagonal). The martensite in ferrous alloys can appear with lath, lenticular or thin plate morphologies but the mobile interface needed for shape memory effect is characteristic only for thin plate features. The ausaged martensite morphology of Fe-Ni-Co-Ti alloys is a thin plate one with planar interface and comprising twins that extend from one interface to the other. The $L1_2$ –type ordering of γ' precipitates favor the occurrence of tetragonal martensite and the tetragonality is increased by such ordered intermetallic precipitates generated by ausaging [8]. It is likely that for a good shape memory effect, the coherent precipitates which transform together with the austenite into martensite must also become unstable on heating. The increase η (incoherent precipitates) [9] phase leads to a deterioration of the shape recovery because it replaces part of the austenite that can transform into martensite

As can be seen from the above presentation, the magnitude of the SME depends on the completeness of the reversible martensitic-austenitic transformation, which in turn depends on the morphology of the two phases, through the structure and mobility of the phase boundaries. Such phase transformations should influence hyperfine parameters and local structure around Fe atoms in the involved phases. This work reports on a temperature dependent Mössbauer study of Fe-Ni-Co-Ti samples obtained in different conditions. The results, completed with magnetization data, are discussed in respect to phase transformation processes, reported in the literature.

2. Experimental

The initial shape memory Fe-Ni-Co-Ti alloy (55Fe -29Ni -11Co-5Ti % at.) was obtained by melting the metallic components in an arc furnace in argon atmosphere. Homogenization of the ingot was undertaken at 1000 ^{o}C in vacuum followed by water quenching. An aging treatment at 600 ^{o}C for 1 h followed again by water quenching was subsequently performed. A piece of the material with a 2 cm × 1cm surface was then manually polished with sandpaper down to a thickness of about 50 μm, resulting in a sample, denoted in the following by FeNiCoTi_ini, suitable for XRD, Mössbauer and magnetic measurements. The rest of the initial material was rapidly quenched by melt spinning, resulting ribbons of about 30 μm thickness and 3 mm × (30 to 70 mm) surface. A new sample was prepared with a part of the as quenched ribbons, denoted by FeNiCoTi_raq. Finally, a new ageing treatment was performed on some of the as quenched ribbons, for 90 min. at 715 C, resulting the sample denoted by FeNiCoTi_rtt. All samples were analyzed by XRD at room temperature (RT), magnetometry and temperature dependent Mössbauer spectroscopy. It is worth to mention that only samples FeNiCoTi_ini and FeNiCoTi_rtt have shown SME effects when heated from 80 K to RT, whereas sample FeNiCoTi_raq did not show any effect, perhaps due to the remelting process during the melt spinning, which removed the beneficial effect of the ageing process. Because temperatures M_f and A_s are supposed to be about 80 K and 140 K, respectively, the Mössbauer measurements were performed between 80 K and 550 K. For the low temperature measurements, the samples were inserted in a static He cryostat, while for measurements above RT, the samples were inserted in an oven, under vacuum. A ^{57}Co source in Rhodium matrix was used and the calibration was made by using an α-Fe absorber at RT.

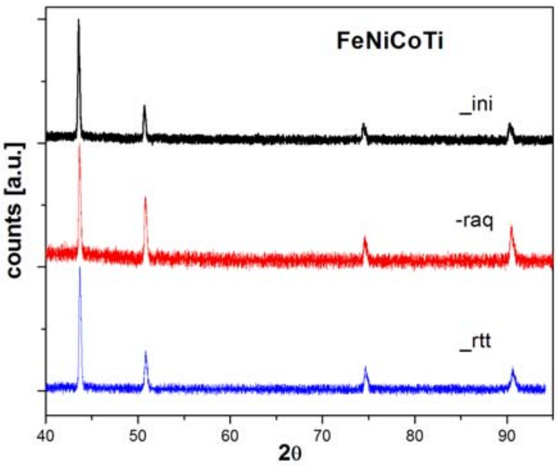


Fig. 1. X-Ray diffraction patterns for FeNiCoTi_ini alloy (prepared by classical metallurgy, FeNiCoTi_raq (as quenched ribbons) and FeNiCoTi _rtt (aged ribbons - 90 min. at 715 C).

3. Results and discussion

The XRD spectra collected at RT on all three samples are presented in Fig. 1. The diffraction peaks correspond to a typical fcc structure. However, they are relatively large and can not exclude completely the presence of additional phases with similar structure. The spectra can not be completely refined either for the thermally treated samples, where a better ordering would be expected.

Some of the Mössbauer spectra collected at different increasing temperatures on samples FeNiCoTi_ini, FeNiCoTi_raq and FeNiCoTi_rtt are presented in Figs. 2, 3 and 4, respectively.

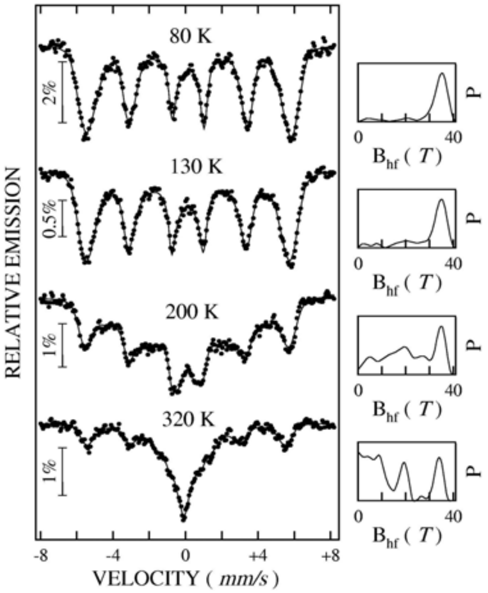


Fig. 2. Mössbauer spectra collected at different temperatures on sample FeNiCoTi_ini.

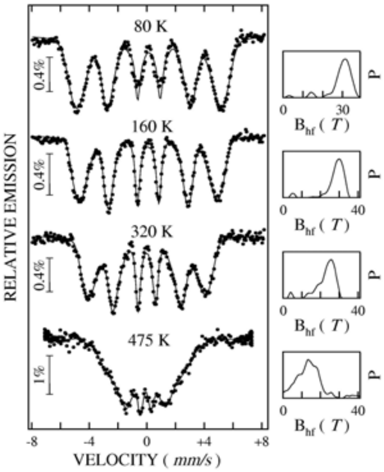


Fig. 3. Mössbauer spectra collected at different temperatures on sample FeNiCoTi_raq.

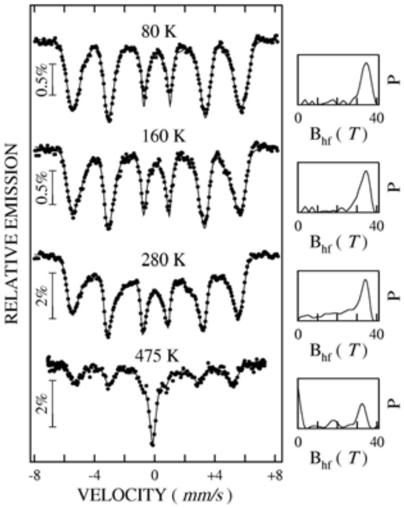


Fig. 4. Mössbauer spectra collected at different temperatures on sample FeNiCoTi_rtt.

It can be observed that the spectra at low temperature (up to about 200 K), consist in broad sextes, reminding to an amorphous magnetic phase. The initial idea was to observe the phase transformation process via different Mossbauer patterns which would be assigned to the BCT martensitic structure and respectively to the fcc austenitic one. Tacking into account that in the BCT structure, the Fe atoms are surrounded by 8 metallic neighbors, whereas in the fcc structure by 12 neighbors, a first fit of the spectra was thought in the term of a finite number of sextets respecting the binomial distribution connect with the different probabilities to have a different number of Fe atoms in the first coordination sphere around the central Fe.

Such a fitting procedure was completely unsuccessful, mainly in respect to the overall intensity of the third (and forth) absorption peak. The experimental data suggest a higher number of Fe positions than provided by this algorithm. In fact, the problem derives from the fact that the alloy composition contain many other kind of magnetic atoms (Co and Ni) with different magnetic moments, which can polarize differently the 4s electrons of the central Fe. Therefore, the number of possible combinations leading to slightly different values of the hyperfine fields is much higher (e.g. C_8^3 for the BCT structure and C_{12}^3 in the fcc structure).

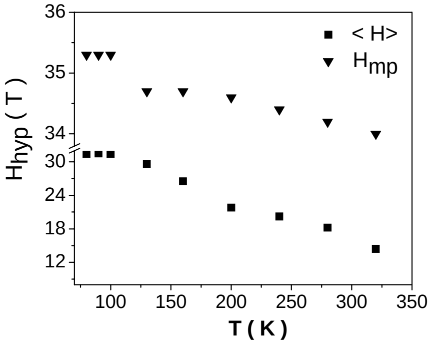


Fig. 5. Mean hyperfine field <H> and most probable hyperfine field, H_{mp}, in sample FeNiCoTi_ini

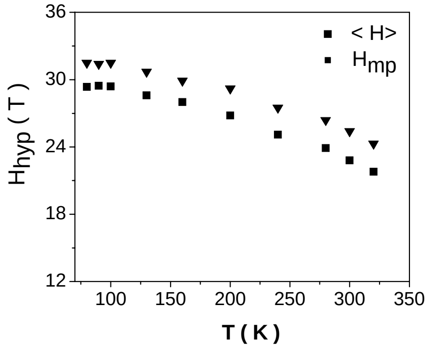


Fig. 6. Mean hyperfine field <H> and the most probable hyperfine field, H_{mp}, in sample FeNiCoTi_raq.

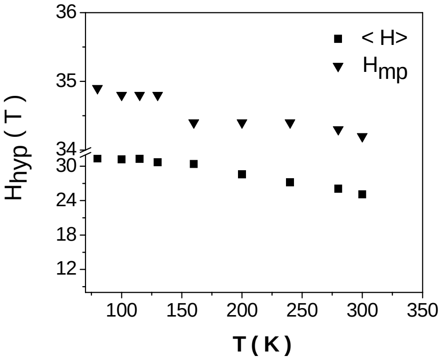
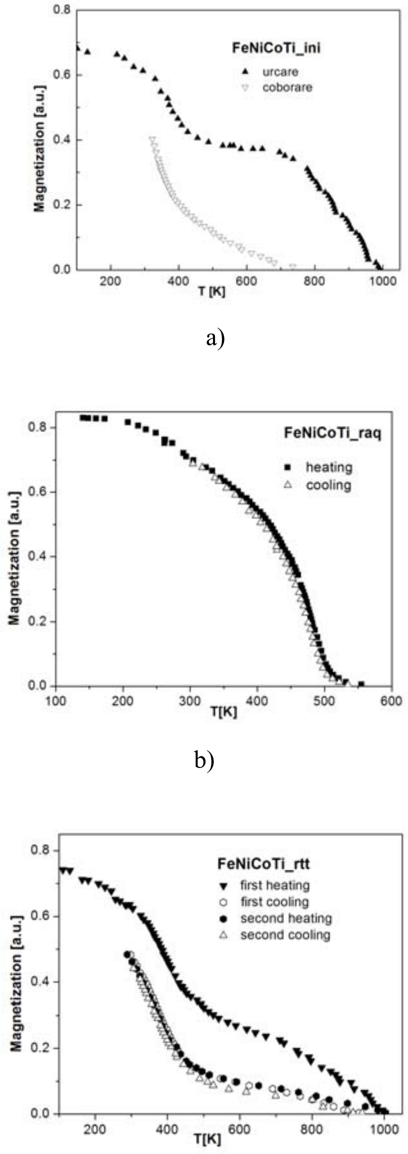


Fig.7. Mean hyperfine field <H> and the most probable hyperfine field, H_{mp}, in sample FeNiCoTi_rtt.



a)

b)

c)

Fig. 8. Thermomagnetic results on a) FeNiCoTi_ini, b) FeNiCoTi_raq , c) FeNiCoTi_rtt.

That involves a quasi-continuum distribution of the hyperfine fields and consequently, the fitting procedure involving a distribution of hyperfine fields was finally chosen. The distribution probabilities corresponding to the spectra are presented on the right hand of the figures. In spite of the fact that the fitting procedure is successful in this case, the interpretation of the data in terms of an eventual phase transition seems to be more difficult. However, a phase transition should be accompanied by a jump of some of the distribution parameters. The mean hyperfine field, <H>, and the most probable field, H_{mp} (the hyperfine field at the maximum probability), are shown in Figs. 4, 5, 6, for the considered samples in Figs. 1, 2, 3, respectively. Whereas the mean hyperfine field show a continuous decrease vs. temperature for all the three samples, the most probable hyperfine field shows a jump only for samples FeNiCoTi_ini and FeNiCoTi_rtt, where the SME was evidenced. Moreover, H_{mp} follow very closely the temperature dependence of <H> in sample FeNiCoTi_raq, with no SME, but for the other two samples, the decrease of the most probably field after the jump is less pronounced as compared with the decrease of <H>. The magnitude of the jump is of only about 0.7 T in sample FeNiCoTi_ini and 0.5 T in sample FeNiCoTi_rtt, but however, much higher than the error range of H_{mp} (included in the magnitude of the scatter points in the figures) or than the scattering of the H_{mp} in the adjacent points. We consider this aspect as a prove of a phase transition, appearing at about 120(10) K in sample FeNiCoTi_ini and at about 140(10) K in sample FeNiCoTi_rtt (the mentioned temperatures should be considered as A_s points). On the other hand, a general view if the three series of spectra presented in Figs. 1,2,3, show a similitude of the magnetic relaxation regime of samples FeNiCoTi_ini and FeNiCoTi_rtt, which is in contrast with the magnetic relaxation regime of sample FeNiCoTi_raq.

At relatively high temperatures, the spectra of the FeNiCoTi_ini and FeNiCoTi_rtt present a superposition of two magnetic phases which relax independently (one being already relaxed as compared with the other one which is still magnetic, with a significant hyperfine splitting) whereas the 475 K spectrum of sample FeNiCoTi_raq shows a relaxation behavior specific to an unique phase. Consequently, we should mention above A_s the presence of two different magnetic phases in the first two samples and the presence of only one magnetic phase in sample FeNiCoTi_raq. Therefore, the present results stand for a partial phase transformation at A_s in samples FeNiCoTi_ini and FeNiCoTi_rtt and the lack of any phase transformation in sample FeNiCoTi-raq. Having in mind that FeNiCoTi_raq does not show SME and presents a fully fcc structure at RT (as evidenced by XRD), we should assign the large sextet pattern in the Mössbauer spectra of this sample to the usual austenitic structure, with random ocupationbu Fe, Co, Ni and Ti atoms, not involved in the martensitic-austenitic transformation. This phase is present over the whole temperature interval and shows a most probable hyperfine magnetic field of about 31 T in the range of temperatures close to A_s in samples with SME. Samples FeNiCoTi_ini and FeNiCoTi_rtt, presenting SME, show H_{mp} of about 35 T before the phase transition and about 34.5 T after the transition. Because H_{mp} represents for these samples an averaged value over two most probable hyperfine fields, a hyperfine field higher than 36 T has to be expected for the involved additional phase. Based on the XRD data pointing for an fcc structure for sample FeNiCoTi_rtt at RT, we may assume that this additional phase with high hyperfine field should be attributed to the fine dispersed and coherent $(Ni,Co,Fe)_3Ti$ particles with fcc structure, responsabile for the SME effect. According to the Mössbauer data, only these particles transform in martensite at low temperatures. The H_{mp} of the martensitic phase should be slightly higher

(0.5 to 0.7 T) than H_{mp} of the coherent fcc phase. A much slower relaxation mechanism (due to stronger magnetic interactions) has to be considered for the coherent phase at higher temperatures, as compared with the relaxation mechanism in the rest of the fcc austenitic phase, not involved in the SME.

The presence of one magnetic phase in FeNiCoTi_raq and two in the aged samples is confirmed by the thermomagnetic measurements. For FeNiCoTi_raq, it was observed a normal reversible ferromagnetic behavior with the Curie temperature at 512 K. The thermomagnetic curves for both aged samples reveal two different magnetic phases obtained as effect of atomic thermo-diffusion and reorganization in more stable positions. The first magnetic phase has the Curie temperature close to those of the ferromagnetic phases evidenced in the a.q sample and may be attributed to the phase not involved in the austenite – martensite transition; the second magnetic phase, with Tc~980 K, can be ascribed to the fine dispersed (FeNiCo)3Ti phase directly connected with the reversibility of the austenite-martensite transformation (which favor the occurrence of tetragonal martensite). A supplementary reason for this assignation is the thermal irreversibility of this magnetic phase; on the cooling thermomagnetic curve this second phase is less present or simply vanishes. At slowly heating and then cooling the γ' phase, these could become unstable and transform in η (incoherent precipitates) phase, leading to a deterioration of the shape recovery.

4. Conclusions

Three ferromagnetic Shape Memory alloy samples (55Fe -29Ni -11Co-5Ti % at.) were prepared by classical metallurgy (one sample) and rapid quenched techniques (two samples). On one of the rapidly quenched samples was applied an ageing treatment at 715 C for 90 min .The sample prepared by classical metallurgy involve also an ageing treatment at 600 C for 60 min. All the three samples were studied by XRD, thermomagnetic measurements and Mössbauer Spectroscopy

XRD at room temperature evidences only an fcc-like structure, typical to an austenite phase. Thermomagnetic measurements between 100 K and 1000 K evidence the presence of two different magnetic phases in the aged samples and of only one phase in the as quenched ribbons. They were not able to give evidence for a structural phase transformation at low temperatures. Through its high sensitivity to the local structure around Fe atoms, Mössbauer spectroscopy succeeded to evidence the martensite – austenite transformation by a jump at the austenite start temperature, via the temperature dependence of the most probable hyperfine field. This jump appears only for the aged samples, where the shape memory effect was evidenced.

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