Magnetic properties of a Ni–Co–Mo–Ti maraging 350 steel

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Abstract

The magnetic properties of a Ni–Co–Mo–Ti maraging steel 350 aged at different temperatures were measured. The effects of the aging time and cold deformation before aging were studied. It is found that the mechanical and magnetic hardening effects are not correlated in the maraging 350 steel. The behaviour of the saturation magnetisation and the coercive force against aging time at 440, 500, 560 and 650 °C are discussed taking into account previous results on the same material.
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1. Introduction

The Ni–Co–Mo–Ti maraging steels are ultra-high resistant steels developed for special applications from pressure vessels to aircraft and sports equipment. Maraging steels have also been studied for use as ultra-high speed rotors for hysteresis electric motors. For this purpose, not only high mechanical strength and toughness are necessary, but also suitable magnetic properties. Accordingly to Belozerov [1], the increase of the rotational speed of the disk rotors to about 10,470 rad/s (10^5 rpm) required a yield strength superior to 1300–1500 MPa. The coercive force must be low (close to the excitation field of the extractor), the saturation and residual induction must be high in fields as low as 20–60 A/cm and the squareness ratio must be at least 0.7 [1].

As quenched (or solution treated) from 850 to 900 °C the maraging steel presents a soft and deformable martensite, with hardness values between 280 and 320 HV [2]. These characteristics are attributed to the low carbon and high nickel content of the martensite. A pronounced hardening effect is produced by the aging treatment in the 400–700 °C range. Aging below 450 °C produces ordered and coherent phases (μ, S and/or ω) in martensitic matrix [2–4]. The aging

between 450 and 600 °C is more rapid and intense [2], and is attributed to the precipitation of the intermetallics compounds $Ni_3(Mo, Ti)$ and Fe_2Mo in the dislocations [2–4]. Fe_2Mo may also form at low temperatures by aging for very long times (>100 h) [4]. Aging between 500 and 700 °C promotes the formation of austenite by a diffusion-controlled decomposition reaction: $\alpha_1 \rightarrow \alpha_2 + \gamma$, where α_1 is martensite, α_2 is a low nickel bcc phase and γ is the nickel enriched austenite phase [5,6]. According to Li [7] the formation of the austenite occurs at the same time and as consequence of the partial dissolution of $Ni_3(Ti, Mo)$ and precipitation of Fe_2Mo. The austenite phase formed at high aging temperatures is totally or partially retained at room temperature depending on its nickel content.

In this paper, the magnetic properties of a Ni–Co–Mo–Ti steel were measured as function of aging temperature in the 440–750 °C range. Two initial conditions were compared: solution treated and cold rolled. The effect of aging time was also evaluated for 440, 500, 560 and 650 °C. The results are discussed taking into account previous works on the same subject [1,6,8,9].

2. Experimental

A forged maraging 350 steel with composition shown in Table 1 was cold rolled and solution treated at 870 °C three

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Table 1
Chemical composition of the steel

Element	wt.%
Ni	19.77
C	0.0075
Co	10.74
Mo	4.70
Ti	1.47
Al	0.098
S	0.003
Fe	Balance

times to produce a 1 mm plate. Solution treatments were followed by oil quenching. A final cold rolled step to 0.2 mm thickness was then realised. The true deformation was 1.61. A final solution treatment was undertaken for some samples, while others remained in the cold worked condition. Then disks with 3 mm diameter were carefully machined for the magnetic measurements in a Vibrating Sample Magnetometer EGG-PAR model 4500. The small disks were aged in vacuum at temperatures in the 440–750 °C range for different times. The magnetic measurements were taken at room temperature with maximum applied field of 200 kA/m in a time of 30 min, with 1 ms of time constant. The data were corrected for demagnetisation fields using the equations suggested by Chikazumi [10]. X-ray diffraction was carried out in a PHILLIPS® X-PERT diffractometer using Cu Kα radiation.

3. Results

Figs. 1 and 2 show the saturation magnetisation (m_s) and the coercive force (H_c) as function of aging temperature, respectively. The aging time was 1 h. Aging between 560 and 700 °C increases the coercive force and decreases the saturation magnetisation. This is attributed to the formation of Ni-rich reverted austenite in this temperature range. The minimum value of m_s and the maximum value of H_c are obtained at 650 °C both for solution treated and cold rolled samples. After the aging at 650 °C the reverted austenite present at room temperature is maximum. In fact, the amount of austenite formed increases with the aging temperature, but as the nickel content of the austenite decreases above 650 °C, the M_s and M_f tempeatures for the $\gamma \rightarrow \alpha_1$ transformation are raised. As result, the amount of residual austenite decreases as the aging temperature increases from 650 to 750 °C. This explains why the m_s increases and H_c decreases after 650 °C in Figs. 1 and 2.

The cold rolling prior to aging does not change significantly the behaviour of m_s and H_c with the aging temperature. Only a small decrease in the H_c till 560 °C (Fig. 2), and an increase of hardness and mechanical strength may be provided by plastic deformation before aging. The influence of the cold working prior aging on the coercive force is a controversial point. Ahmed et al. [8] observed an increase of H_c when a reduction ratio of 85% was applied by cold rolling before aging. Belozerov et al. [1] found an increase of H_c which the cold deformations above 40%. According to Garabellis [11], however, the maraging steels show the unusual characteristic of having their lowest values of H_c in the cold worked condition and the highest in the annealed condition, in agreement with the results of this work. In general, the mechanical strengthening mechanisms tend to increase the coercive field and the residual induction, but in maraging steels this general rule will be rarely observed.

Fig. 3 shows that the squareness ratio (B_r/B_s) tends to increase slightly when the plastic deformation is applied before aging, except for the samples aged between 500 and 560 °C. Ahmed et al. [8] also observed this effect, but in their
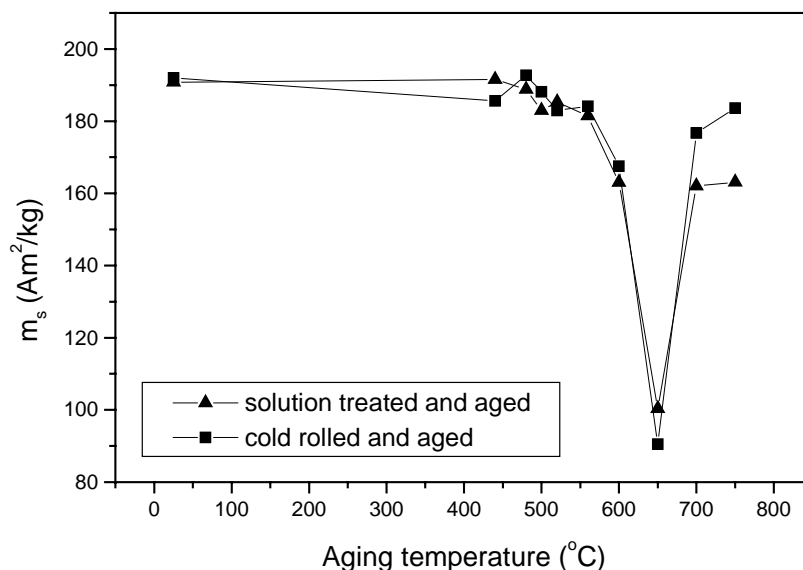

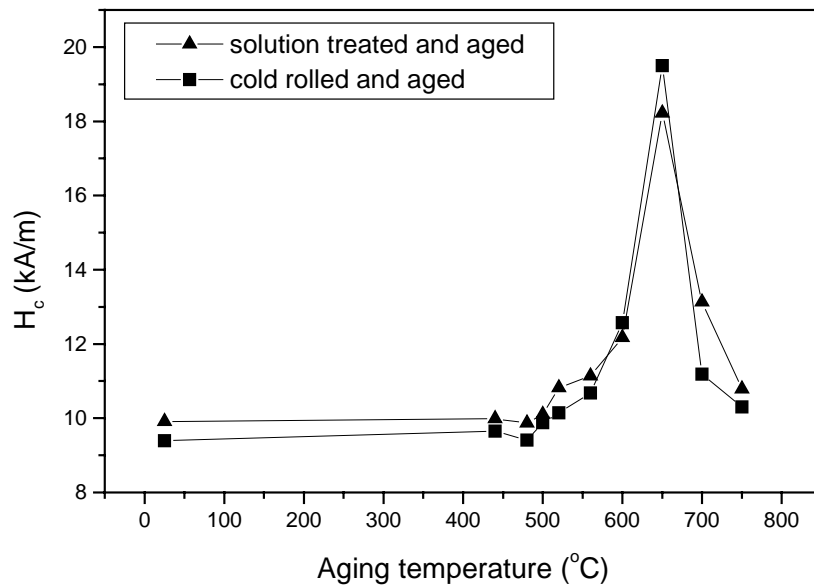Fig. 1. Magnetisation saturation (m_s) vs. aging temperature of solution treated and cold rolled samples.

Fig. 2. Coercive force (H_c) vs. aging temperature of solution treated and cold rolled samples.

experiments the squareness ratio of the deformed sample was much superior than that of solution treated ones, and the maximum B_r/B_s was obtained in the samples aged at 650 °C. At this temperature we found the minimum B_r/B_s values, probably related to the austenite precipitation.

Fig. 4 shows the aging curves (hardness *versus* aging time) at 440, 500, 560 and 650 °C. The hardness increases abruptly in the first hour of aging at 440, 500 and 560 °C. During the aging at 440 °C the hardness increases slowly but continuously after 1 h. During the aging at 500 °C the hardness achieves a maximum value (708 HV) after 4 h and remains stable after this. The peak value at 560 °C is obtained at 1 h and after this the hardness decreases slightly (overag-

ing). The lowest hardness values are obtained by the aging at 650 °C. The peak value at this temperature is attained at about 15 min (600 HV), and after this time the material softens obeying a second order exponential decay law.

The strengthening at low temperatures is mainly attributed to the coherent phases (μ, S and/or ω), but for long aging times the λ(Fe$_2$Mo) phase can occur contributing to the increase of hardening. At 500 °C the strengthening is due to the Ni$_3$(Mo, Ti) and Fe$_2$Mo phases.

The decrease of hardness in the overaged samples is related to the austenite precipitation and also to the coarsening of strengthening precipitates [12]. During the aging at 650 °C the austenite formation precedes the precipitation
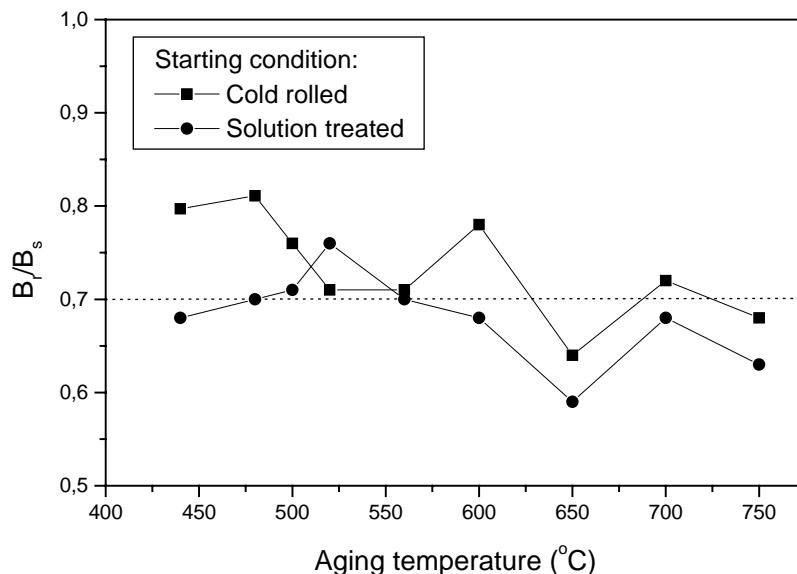

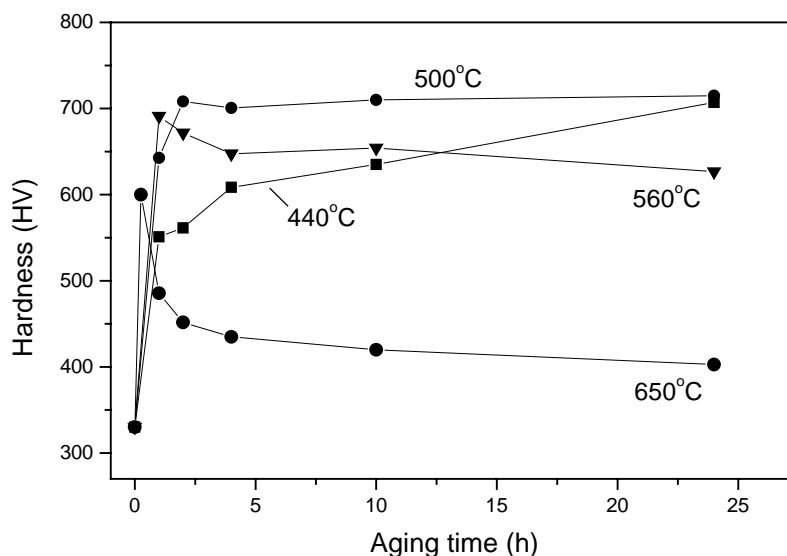Fig. 3. Squareness (B_r/B_s) vs. aging temperature of solution treated and cold rolled samples.

Fig. 4. Hardness vs. aging time curves.

of intermetallic compounds [12] and at this temperature softening can be mainly attributed to the austenite precipitation. At 560 °C, however, the austenite formation is preceded by $Ni_3(Ti, Mo)$ precipitation and partial dissolution. Fig. 5 shows the X-ray diffractograms of the samples aged at 560 °C for 4 h, 650 °C for 1 and 4 h. As reported
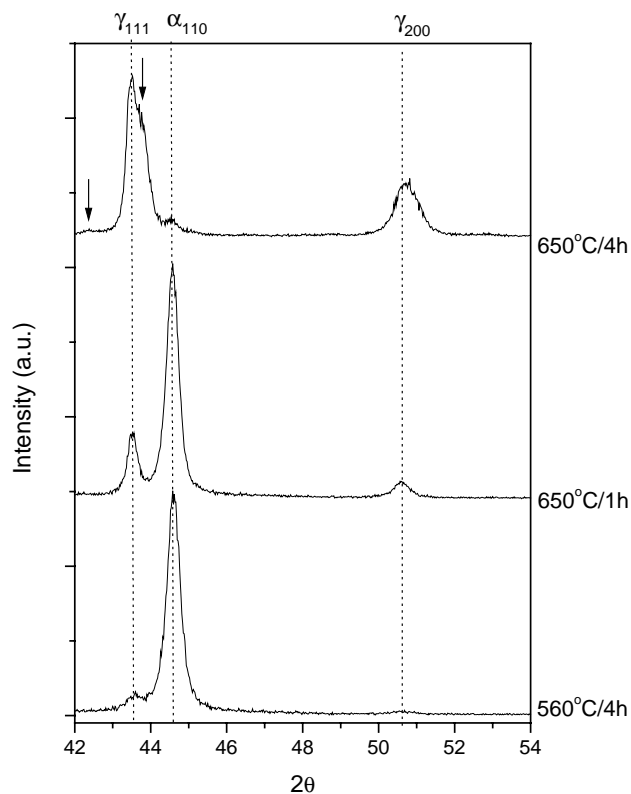

Fig. 5. X-ray diffractograms of the samples aged at 560 °C for 4 h, 650 °C for 1 h and 650 °C for 4 h.

before [13], the austenite formation at 650 °C is much more intense and rapid than at 560 °C. The diffractogram of the samples aged at 650 °C for 1 and 4 h are quite different. The increase of aging time has promoted an increase of the austenite peaks, the decrease of martensite ones and the appearance of Fe_2Mo and Ni_3Ti lines (indicated by arrows). Austenite peaks were not present in the diffractograms of samples aged at 440 and 500 °C for long times.

Fig. 6 shows the behaviour of the coercive force against the aging time at 440 and 500 °C. The precipitation at 440 °C does not increase the coercive force, but some magnetic hardening is produced by the aging at 500 °C. From the results of Figs. 4 and 6 it can be concluded that the effect of the precipitation on the magnetic hardening is much less important than the mechanical hardening. Fig. 7 shows that a small magnetic hardening effect is also produced during the aging at 560 °C, although at this temperature the mechanical hardness decreases with aging time (Fig. 4). This is probably associated with the lath or plate-like austenite precipitation [7]. The samples aged at 650 °C presents a high coercive force value due to the intense austenite precipitation. However, H_c tends to decrease for long aging times at 650 °C, probably due to composition changes of the martensitic matrix as will be discussed later.

Fig. 8 shows the behaviour of m_s with aging time for solution treated samples. The saturation magnetisation of the samples aged at 440 and 500 °C remain stable at almost the same value of the solution treated condition. The samples aged at 650 °C show an interesting behaviour. The m_s value decreases from 191 to 100 A m^2/kg in the first hour, which could be attributed to the reverted austenite formation. However, although the austenite volume fraction increases with the increase of aging time from 1 to 4 h, as suggested by the diffractograms of Fig. 5, m_s does not present any change.
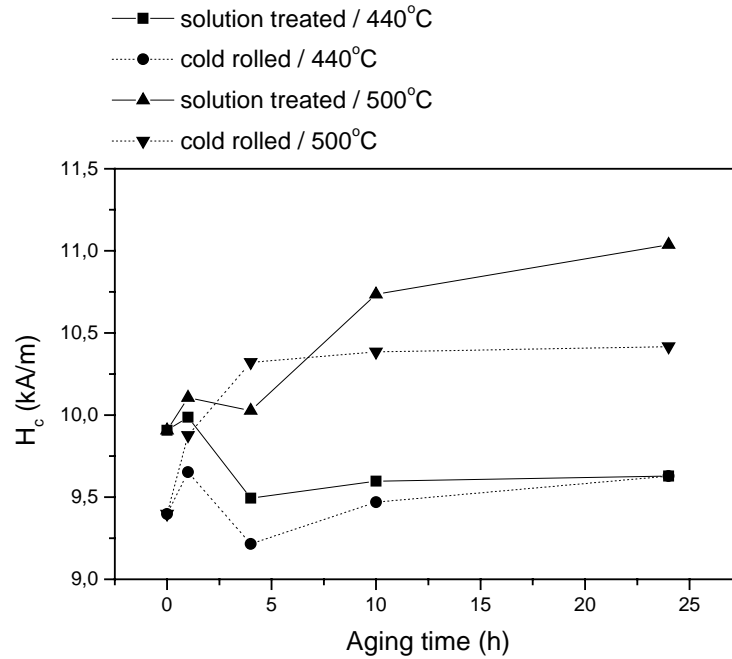
Fig. 6. Coercive force (H_c) vs. aging time at 440 and 500 °C.

Moreover, the m_s value show a tendency to increase with further increase of aging time. Some workers [7–9,14] determined the chemical composition of the reverted austenite and the martensite matrix for the aged 18Ni maraging steels, and in all cases, the reverted austenite presented Ni, Mo and Ti contents higher and Co content lower than the martensite matrix. It means that during the progress of precipitation the Ni and Mo contents of the martensite are decreased and the Co content is increased. The influences of Co and Ni on the magnetic moment of Fe alloys are such that the decrease of Ni and Mo and the increase of Co content promotes an increase of the magnetisation saturation of the solid solution
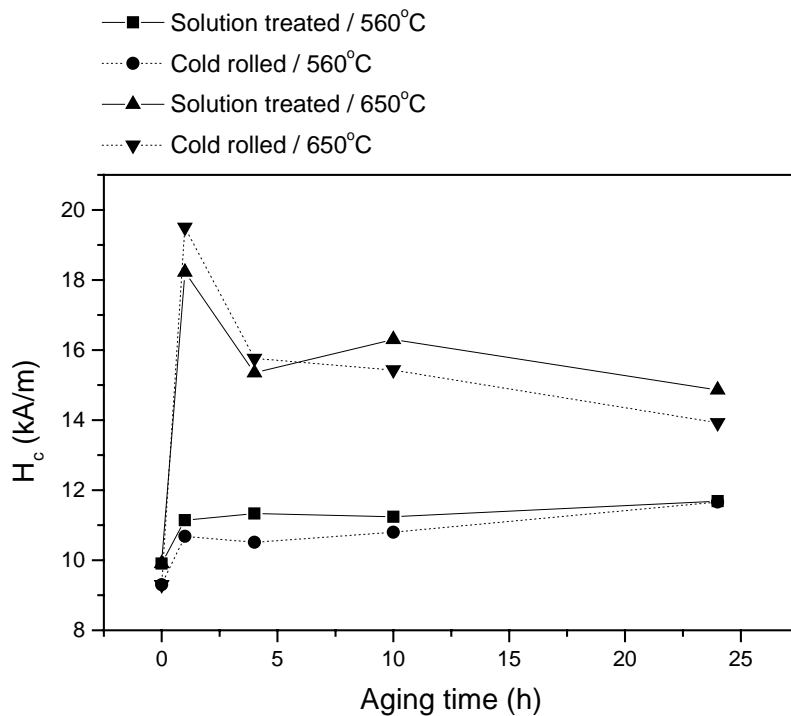

Fig. 7. Coercive force (H_c) vs. aging time at 560 and 650 °C.
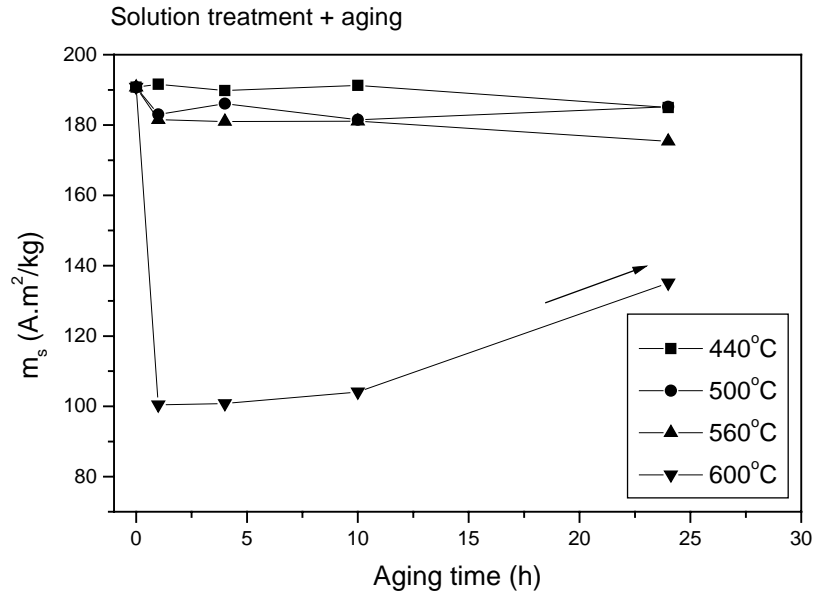
Solution treatment + aging

Fig. 8. Magnetisation saturation vs. aging time of the samples aged at 440, 500, 560 and 600 °C.

[15]. These observations may be the explanation for the m_s increase for longer aging times at 650 °C.

Composition changes can also explain why the samples aged at 560 °C maintain a relatively high m_s level, besides the austenite precipitation. At this temperature, Ni and Mo content of the reverted austenite are even higher and the Co content is lower than at 650 °C [7,9,14]. The decrease of magnetisation due to the austenite phase is probably counterbalanced by the increase of the intrinsic magnetisation of the martensite matrix phase as consequence of its higher Co and lower Ni and Mo contents. Although further investigation is necessary, this effect of increase of the intrinsic

magnetisation saturation of Co-rich martensite seems to be the explanation for the behaviour shown in Fig. 8.

The results of this work show that the aging in the 600–700 °C range is very detrimental to the soft magnetic properties of the steel, since it promotes the increase of H_c and the decrease of m_s and B_r/B_s. Good options for aging treatment are 560 °C for 1 h and 500 °C for 4 h. At these conditions the material also presents excellent mechanical hardness. The service temperature must not exceed 500 °C, since the magnetic properties are stable at this temperature. Aging at 560 °C for long times may cause the increase of the coercive force.
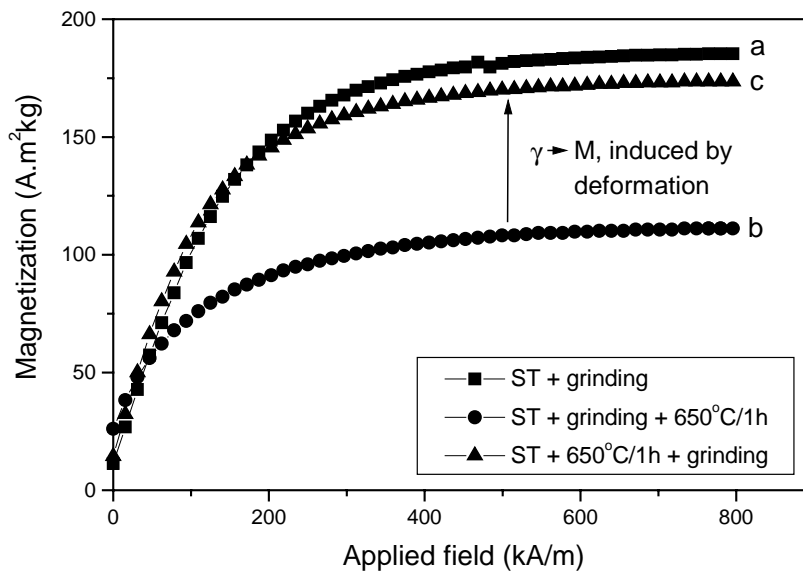

Fig. 9. Magnetisation curves of powder samples produced by grinding: a, solution treated (ST) grinded; b, solution treated, grinded and aged at 650 °C for 1 h; c, solution treated, aged at 650 °C for 1 h and grinded.

The austenite phase formed during the aging at 650 °C remains stable at room temperature due to its high nickel content. However, this phase can be transformed into martensite by cold working after the aging. Fig. 9 shows this effect comparing the magnetisation curves of three powders: curve a is from a sample obtained by grinding a solution treated bulk sample; curve b is from the same powder that was heat treated at 650 °C for 1 h after grinding; and curve c is from the powder obtained by grinding a bulk sample aged at 650 °C for 1 h before grinding. The aging at 650 °C promotes the decrease of magnetisation

due to austenite formation, but when the cold deformation by grinding is applied after the aging the magnetisation increases due to the γ → M transformation.

Accordingly to some authors [2,8] only a small portion of the reverted austenite can be transformed into martensite by sub-zero cooling. Ahmed et al. [8] observed an increase of 10% in the saturation magnetisation by dipping in liquid nitrogen for 15 min the sample previously aged at 680 °C. They have also observed an increase of 5% in the coercive force value. In the present work we repeated this experience by dipping in the liquid nitrogen the samples aged at 650 °C
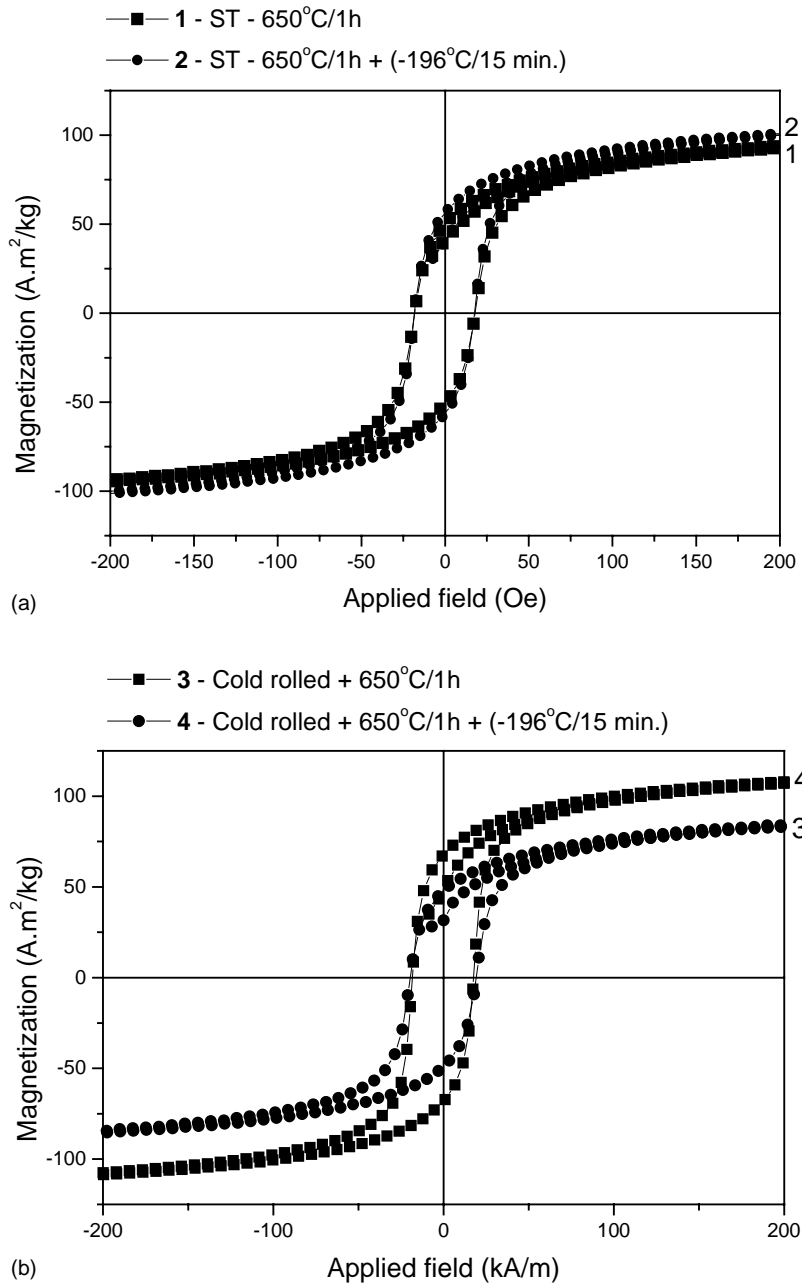

Fig. 10. Hysteresis loops before and after dipping in liquid nitrogen for 15 min. (a) Sample solution treated and aged at 650 °C for 1 h; (b) sample solution treated, cold rolled and aged at 650 °C for 1 h.

with and without previous cold deformation. The cold rolled sample has undergone a much higher increase of magnetisation saturation than the sample solution treated before aging, as shown in Fig. 10a and b. The m_s value increased from 90.5 to 113.0 A m^2/kg in the cold rolled sample and from 100.5 to 107.0 A m^2/kg in the solution treated one. The explanation for this is that the aging at 650 °C promotes only a partial recrystallization of the cold rolled sample, and the residual deformation acts favouring the martensitic transformation.

4. Conclusions

The saturation magnetisation of solution treated and cold rolled samples of Ni–Co–Mo–Ti maraging 350 steel decreases with the aging between 560 and 700 °C by 1 h, showing a minimum value at 650 °C. The coercive force increases in the same interval and reaches a maximum value also at 650 °C.

The investigation of the hardness and coercive force as function of aging time show that the mechanical hardening due to precipitation at 440 and 500 °C is much more important than the magnetic hardening at these temperatures. The aging at 440 °C does not produce any magnetic hardening effect, while at 500 °C a small increase of the coercive force is observed. The aging at 560 °C also produces a small increase of the coercive force, which is attributed to austenite precipitation. At 650 °C the coercive force increases in the first hour and slightly decreases for longer aging times. At this temperature the hardness of the material decreases obeying a second order exponential law.

The saturation magnetisation at 650 °C shows an interesting behaviour. The m_s value decreases in the first hour due to the austenite precipitation, but, for longer aging times the m_s show a tendency to increase. At the same time the austenite content has also increased. A possible explanation for this is that with the progress of the $\alpha_1 \rightarrow \alpha_2 + \gamma$ transformation the α_2 phase becomes more magnetic

due to its higher cobalt and lower nickel and molybdenum contents.

For application as high strength and soft magnetic material the maraging 350 steel may be aged at 500 °C for 4 h or 560 °C for 1 h. The aging between 600 and 700 °C must be avoided.

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