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A thermomagnetic study of the martensite–austenite phase transition in the maraging 350 steel

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Abstract

A thermomagnetic analysis of the maraging 350 steel quenched from 1000 °C and cold rolled with completely martensitic structure is presented. In fast heating and cooling rate (10 °C min^{-1}) tests the start (A_s) and final (A_f) temperatures of the martensite (M) to austenite (γ) transformation were determined as 690 and 800 °C, respectively. The martensite start (M_s) and final (M_f) temperatures were 175 °C and 130 °C, respectively. In low heating rate tests, the austenite formation may happen above 510 °C, which is associated with precipitation reactions. Both $\gamma \rightarrow$M and M$\rightarrow \gamma$ may progress isothermally. The kinetics of these reactions at selected temperatures were also investigated by thermomagnetic analysis.

Keywords: Transition metal alloys; Phase transition; Magnetic measurements

1. Introduction

Maraging steels are a family of metallic materials with extremely high mechanical strength and good toughness. Maraging 350 is one of the strongest grades of this family. In the as-quenched or solution-treated condition its microstructure consists of b.c.c. martensite. This martensite containing low carbon (0.02 wt% max.), and high nickel (~18 wt%) and cobalt (~12 wt%) is soft and deformable. The strengthening effect is produced by the precipitation of fine particles of Ni_3(Mo,Ti) and Fe_2Mo in the 450–650 °C range [1,2].

Thermomagnetic analysis (TMA) involves simple experiments where a small sample is subjected to a thermal treatment and the magnetization is measured as function of temperature or time. It is an useful tool to detect magnetic transitions, phase transformations and precipitation reactions. In previous work [3,4], this analysis was used to investigate the α' martensite to austenite transformation during the heating of cold rolled AISI 304L stainless steel and a Fe–17Mn–1.9Al–0.1C (wt%) alloy. It was also applied to investigate the magnetic properties changes caused by the tempering of the AISI 420 martensitic stainless steel [5].

In this paper, the martensite (M) to austenite (γ) and the reverse $\gamma \rightarrow$M phase transition of a maraging 350 steel were investigated using TMA. The start and final temperatures for the M$\rightarrow \gamma$ (A_s and A_f) and the $\gamma \rightarrow$M (M_s and M_f) reactions were analysed and determined. The effects produced by aging and the kinetics of the above reactions were also investigated and discussed.

2. Experimental

A maraging 350 steel with composition shown in Table 1 was solution treated at 1000 °C and water quenched. After quenching, the steel was rolled from 5.5 to 1.1 mm (true deformation = 1.61) at room temperature. The solution treated and deformed steel presented a completely

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Table 1
Chemical composition of the steel

	Element							
	C	Ni	Co	Mo	Ti	Al	Mn	Fe
Wt.%	0.0073	19.77	10.74	4.70	1.47	0.98	0.01	Balance

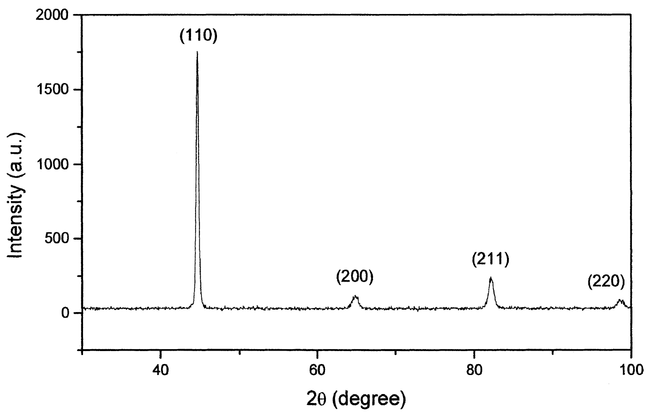

Fig. 1. X-ray diffraction of the solution treated and deformed maraging 350 steel.

martensitic structure, as observed by X-ray diffraction (Fig. 1).

Thermomagnetic analysis were performed in a thermomagnetic balance equipped with a resistance oven where magnetization could be measured as function of temperature and time. This machine (at the Laboratoire of Cristallographie of CNRS, Grenoble) is controlled by a computer where thermal treatment parameters such as heating and cooling rates could be changed. The small samples for the TMA were vacuum sealed in quartz tubes.

3. Results and discussion

Fig. 2 show the TMA measurement of the material obtained with heating and cooling rates of 10 °C min^{-1}. It is found that, up to about 690 °C, the magnetization does not change significantly with temperature. After this temperature, the magnetization starts to decrease, reaching to zero at about 800 °C. For decreasing temperatures, the magnetization was not reversible until 175 °C, where it starts to recover the initial room temperature magnetization which is obtained at about 130 °C.

A TMA experiment to 730 °C with a stop of 5 min at this temperature was carried out (Fig. 3). In this experiment, the magnetization is not reversible with cooling, which implies that the magnetization decrease between 690 and 800 °C is due to the M→γ reaction. From the results shown in Figs. 2 and 3 we can determine the temperatures A_s (690±10 °C), A_f (800±10 °C), M_s (175±10 °C) and M_f (130±10 °C) of the steel for the heat treatment rates used.

Some authors [2,6,7] have reported the formation of retained austenite during aging below the A_s found in this work. Li and Yin [6] observed the formation of lath like austenite at prior grain boundaries and between the martensite lath boundaries in the 500–570 °C range. After aging at 570 °C for 4 h, plate like austenite was observed and at 640 °C Widmanstätten austenite was formed. Retained austenite is rarely observed in samples aged up to 500 °C. It seems that the austenite formed below the A_s temperature of the steel is due to the local enrichment of γ-stabilizing elements such as Ni. Li and Yin [6] suggested that the austenite results from the partial dissolution of Ni_3(Mo,Ti) and Fe_2Mo formation. Since the austenite formed by aging in the 500–700 °C range is enriched with Ni, it is very stable and does not transform on cooling to room temperature. All these observations are useful to understand the TMA curve obtained with low heating rate, shown in Fig. 4. The high speed TMA is also plotted for

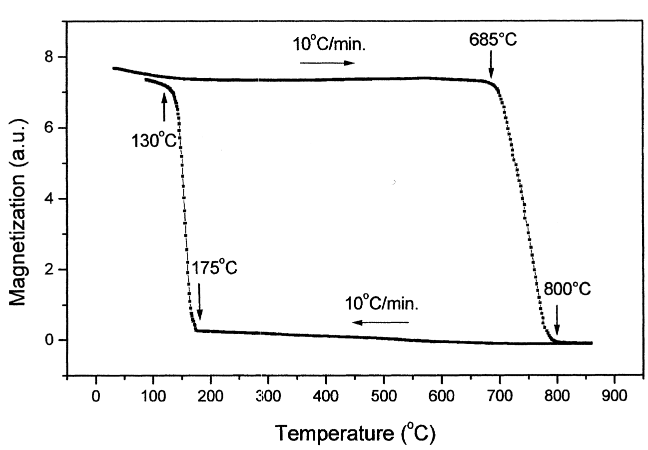

Fig. 2. TMA curve of the maraging 350 steel.

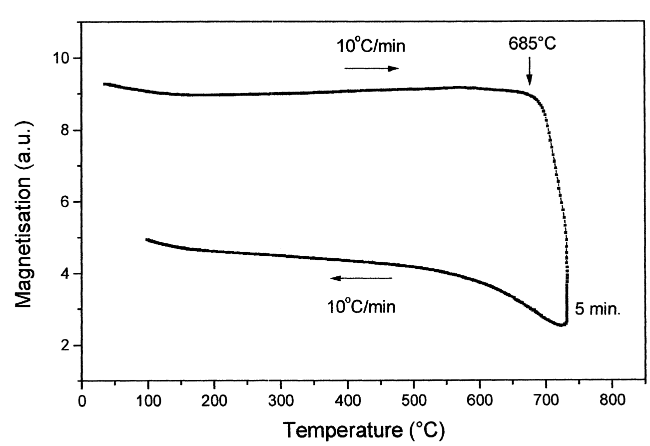

Fig. 3. TMA curve up to 730 °C of the maraging 350 steel. The sample was kept for 5 min at 730 °C.

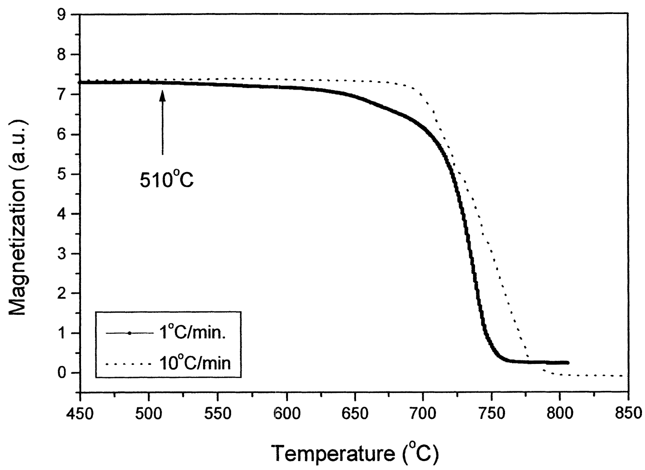

Fig. 4. TMA heating curves obtained at 1 and 10 °C min^{-1}.

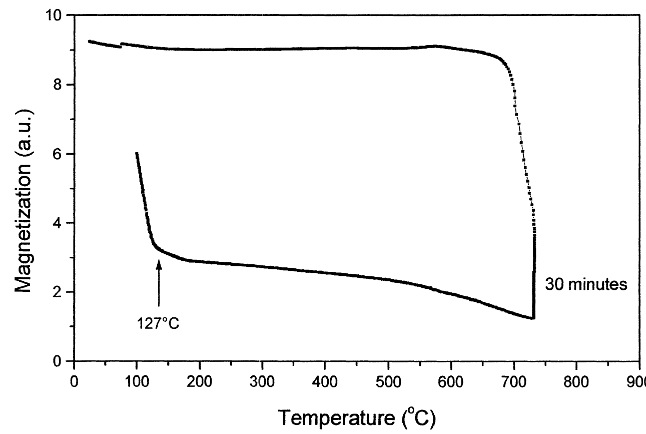

Fig. 6. TMA curve up to 730 °C of the maraging 350 steel. The sample was kept for 30 min at 730 °C.

comparison. When the TMA is performed with 1 °C min^{-1} a small decrease of magnetization is observed before the A_s temperature, which is attributed to the austenite formation associated with Fe_2Mo precipitation and $Ni_3(Mo,Ti)$ dissolution. Comparing the high and low speed curves it is possible to conclude that this Ni-enriched austenite starts at about 510 °C, which is consistent with previous work [2].

Fig. 4 suggests that the A_s and A_f temperatures are lower in the low speed curve. It is rather an effect caused by the rate of test than due to the precipitation during the TMA. Fig. 5 shows the TMA data obtained with heating rate of 10 °C min^{-1} for three samples: unaged, aged at 560 and 650 °C for 5 h each. It is found that the A_s temperature is not affected by the aging at 560 °C but is significantly increased by the aging at 650 °C. The formation of Ni-rich stable austenite during the aging retards the beginning of the M→γ reaction. The M_s temperature is not affected by the aging.

In Fig. 3, it can be seen that after 5 min at 730 °C the M→γ transformation progressed isothermally. During the cooling, however, the γ→M did not occur till 100 °C. This is probably because the austenite formed was enriched with stabilizing elements. Fig. 6 show a TMA curve similar to that of Fig. 3, but with a higher holding time at 730 °C. In this case, the M_s temperature could be measured (127 °C), but M_f was placed below 100 °C. The increase of time at 730 °C promoted a higher homogenization of the austenite formed and, as a consequence, M_s increased.

Figs. 7 and 8 show the data of magnetization as function of time obtained in isothermal experiments at 560, 650 and 730 °C. The normalized magnetization (NM) was obtained dividing the magnetization values by that of the completely martensitic sample. NM is roughly proportional to the volume fraction of magnetic phase (martensite) and the NM vs. time curves give a picture of the kinetics of M→γ reaction in each temperature. The kinetics is very slow at 560 °C and becomes faster at higher temperatures, specially above 690 °C (A_s temperature). All curves present an exponential behaviour, that is, the rate of reaction is proportional to the amount of martensite present. Although the γ→M reaction progresses isothermally at the three temperatures (560, 650 and 730 °C) a complete transformation is not allowed. Table 2 show the fitted equations for the three curves of Fig. 8.

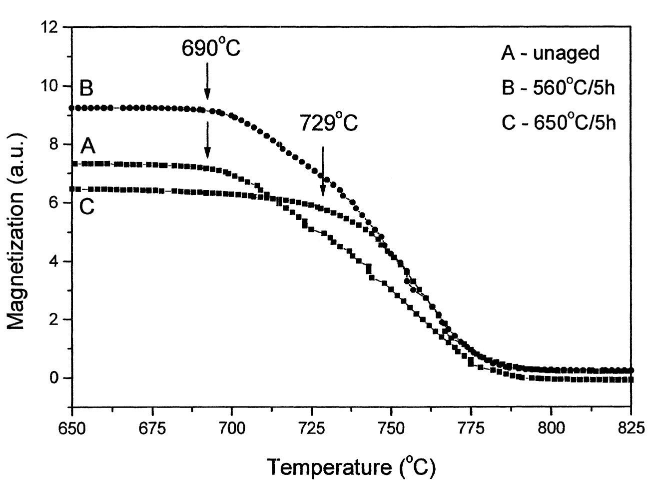

Fig. 5. TMA heating curves of samples unaged, aged at 560 °C, and aged at 650 °C for 5 h.

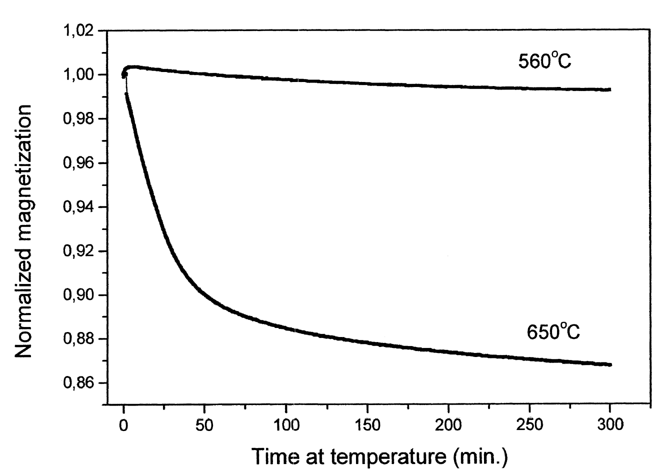

Fig. 7. Normalized magnetization vs. time curves at 560 °C and 650 °C.

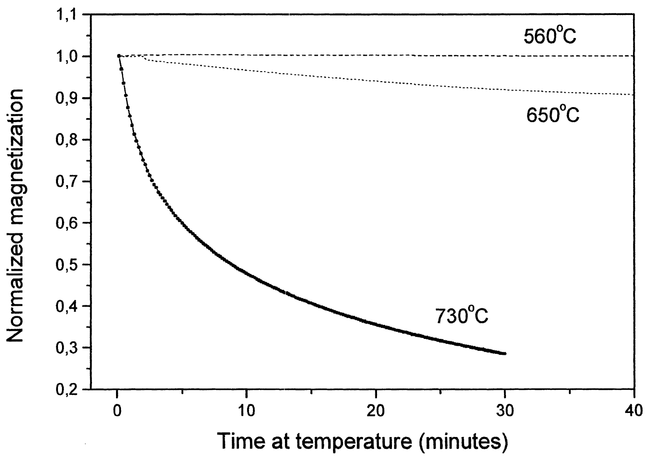

Fig. 8. Normalized magnetization vs. time curves at 560, 650 and 730 °C.

Table 2
Fitted equations of the normalized magnetization (NM) vs. time (t) (Units: time in minutes and NM is adimensional)

Reaction	Temperature (°C)	Expressions
$M \rightarrow \gamma$	560	$NM = 0.991 + 0.130 \cdot \exp(-0.0067 \cdot t)$
$M \rightarrow \gamma$	650	$NM = 0.873 + 0.122 \cdot \exp(-0.0284 \cdot t)$
$M \rightarrow \gamma$	730	$NM = 0.280 + 0.616 \cdot \exp(-0.1168 \cdot t)$
$\gamma \rightarrow M$	164	$NM = 0.609 - 0.513 \cdot \exp(-0.2402 \cdot t)$

Fig. 9 shows the cooling portion of a TMA constructed with stop at 164 °C (below M_s). The $\gamma \rightarrow M$ of the maraging 350 can also progress isothermally (isothermal martensite [8]). The rate of transformation can be observed in the data of normalized magnetization as function of time (Fig. 10). The curve shows that the rate of the $\gamma \rightarrow M$ has also an exponential behaviour and the complete transformation is not allowed at this temperature. The fitted equation for this curve is also shown in Table 2. This equation suggests that a maximum of about 61% of magnetic phase can be formed isothermally at 164 °C.

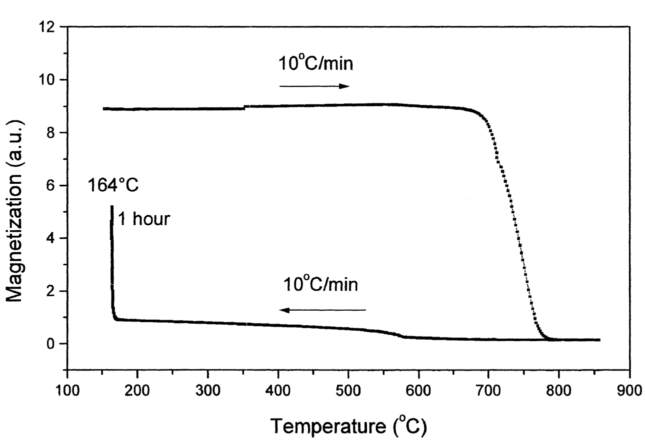

Fig. 9. TMA curve with stop at 164 °C. The sample was kept for 1 h at this temperature.

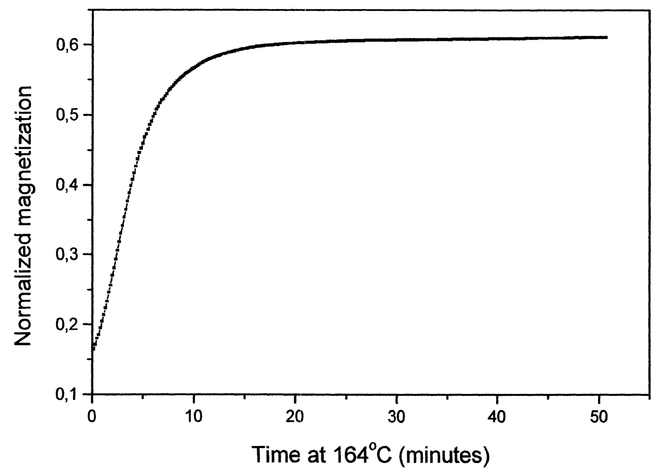

Fig. 10. Normalized magnetization vs. time curve at 164 °C, after austenitization at 860 °C.

4. Conclusions

The A_s, A_f, M_s and M_f temperatures of the maraging 350 steel analysed are 690, 800, 175 and 130 °C, respectively. The incomplete homogenization of the austenite phase formed during the heating decreases M_s.

Austenite phase precipitation occurs below the A_s point and above 510 °C when a low heating rate is employed. This is reported in the literature as an effect associated to the precipitation of Fe_2Mo and dissolution of $Ni_3(Mo,Ti)$. This Ni-rich austenite is stable at room temperature.

It was observed that the $M \rightarrow \gamma$ reaction progresses isothermally at 560, 650 and 730 °C. The martensite volume fraction is approximately equal to the normalized magnetization (NM). NM vs. time curves were determined for each temperature. These curves are fitted by exponential decay laws.

The $\gamma \rightarrow M$ reaction also progresses isothermally between M_s and M_f. The kinetics of transformation at 164 °C was studied and it was found that the NM vs. time curve also obeys an exponential law. The complete reaction is not observed at 164 °C, even after 5 h. The maximum amount of martensite obtained at this temperature is about 61%.

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