

An Atomic Redistribution Study of the 440°C Ageing Kinetics in Maraging-300 Steel

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Mössbauer spectroscopy, X-ray diffraction and hardness measurements were used to investigate the atomic redistribution and phase transformation of solution-treated and 440°C aged Maraging-300 steel specimens. The ageing temperature that resulted in the best mechanical properties in this steel was 480°C. At 440°C, the formation of the precipitates that assure excellent mechanical properties of the maraging steel (Ni₃Ti, Fe₂Mo) was not expected. The results indicated that Mo and Ti redistribution was severe during the first hour of ageing. The mobility of the Ni atoms probably occurred during all stages of the ageing process, and the Co atoms remained close to Fe atomic sites. An irregular behaviour of the formation of paramagnetic phases containing iron was observed, and some evidence of the formation of these phases without Fe will be discussed. The formation of metastable phases was suggested and the possibility of austenite reversion was not discarded at this ageing temperature.

Keywords: *Maraging-300, Mössbauer spectroscopy, Ageing, Intermetallic compound, X-ray diffraction.*

1. Introduction

Maraging steels are a class of Fe-based alloying steels that are age-hardened by the precipitation of finely dispersed intermetallic compounds in a low-carbon martensitic matrix. The combination of appropriate mechanical and magnetic properties makes them suitable materials for strategic applications in the aeronautical, aerospace and nuclear industries.

The main alloying elements in these steels are Ni, Co, Mo and Ti. Carbon is considered an impurity, and the high nickel content (18 wt% Ni) ensures that martensite (α') forms on air cooling¹. The low carbon bcc martensitic matrix is hardened by fine-scale precipitation of intermetallic compounds, such as the needle-like Ni₃(Ti,Mo) η -phase. Other phases, like the A₃B X-phase, A₂B ω -phase, A₈B S-phase, Fe₇Mo₆ μ -phase and Fe₂Mo Laves phase (longer ageing time) were also reported in early studies on 300 and 350 grade maraging steels at low ageing temperatures^{2,3}. Reversion to austenite (γ) was also noticed at higher temperatures and for longer ageing times^{4,6}.

Thermal processing of maraging steels commonly involves a solution treatment at 820°C (minimum temperature) for at least 30 min, and an ageing process at temperatures of 400-650°C, inducing the formation of intermetallic compounds through the redistribution of atoms. The nanometric structure of the precipitates makes them hard to analyse. Because of this, a variety of techniques have been used to

study their precipitation behaviour, including: transmission electron microscopy (TEM)⁴, small angle X-ray scattering (SAXS)⁷, small angle neutron scattering (SANS)⁸, electrolyte extraction method⁹, positron annihilation¹⁰ and Mössbauer spectroscopy¹¹⁻¹⁵. Since Maraging-300 steel has about 66 wt% Fe, Mössbauer spectroscopy becomes a powerful local technique for studying the mobility and redistribution of solute atoms during ageing.

Some authors¹¹⁻¹³ studied the early stages (≤ 1 h) of the ageing process of both Maraging-350 and a Fe-19Co-14Mo-10Ni maraging steel using Mössbauer spectroscopy. They analysed samples aged at 500°C for times varying between 2 and 60 min. It was reported that the redistribution of atoms was fast in the initial stages of ageing and then slowed down. Nunes et al.¹⁴ used Mössbauer spectroscopy to study samples aged at various temperatures above 480°C and longer ageing times (≤ 12 h). Li et al.¹⁵ studied the decomposition of Maraging-350 at low ageing temperature (430°C). The latter did not find paramagnetic components in the Mössbauer spectra until 4 h of ageing, and suggested that the embrittlement of 18Ni(350) maraging steel aged between 400 and 450°C results from Fe-Co-rich and Ni-Mo-Ti-rich zones, and not from precipitates.

Many authors have studied Maraging-350 steel through Mössbauer spectroscopy, but there are few studies that investigated Maraging-300 steel, and fewer at the low ageing temperatures using this technique. In addition, the exact nature of the precipitation behaviour at these conditions is still uncertain. In this paper, transmission Mössbauer spectroscopy (TMS), with the aid of X-ray diffraction (XRD) and Vickers

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hardness measurements, was used to investigate the effect of the atomic redistribution of the non-iron atoms on the ageing kinetics of 300 grade maraging steel aged at 440°C.

2. Experimental

The raw material used in this study was a Maraging-300 steel (composition in Table 1) obtained as a forged billet at 825°C for 10 h and then oil cooled. This was the solution-treated condition, as informed by the manufacturer. The material was cut into small pieces of about 15 x 12 x 2 mm, austenitized at 820°C for 30 min and then water cooled to room temperature (RT), presenting a fully martensitic matrix. The samples were aged for periods of 1, 3, 10, 50 and 100 h at 440°C and water cooled.

For each ageing condition, the same specimen was used for each of the analytical techniques performed. All samples were ground to 1 mm thickness, then immersed for 30 s in a solution of 5% hydrofluoric acid in hydrogen peroxide to eliminate the surface layer, thus eliminating any possible phase transformation ($\gamma \rightarrow \alpha'$) caused by mechanical grinding, as reported by Pardal et al.⁵

X-ray measurements were carried out using a PANalytical® diffractometer, model X'Pert Pro. All diffractograms were measured at RT using Co-K α radiation ($\lambda = 1.78901 \text{ \AA}$) with 40 kV and 45 mA, a step size of 0.02°, step time of 2 s and an angular interval of 45-130° with a monochromator. A divergent slit of 2° and a receiving slit of 1.5° were used at the measurement. The PANalytical® software X'Pert HighScore was used for data treatment.

For Vickers hardness measurements, the same samples used for XRD were then mounted and polished. The measurements were carried out in a Shimadzu TH710 tester using a 1 kg load and 15 s indentation times. Each result was obtained as an internal average of 4 out of 6 impressions.

TMS measurements were carried out at RT from a constant acceleration spectrometer with a ⁵⁷Co(Rh) source. The same samples were ground to a thickness of about 0.06 mm. After grinding, the previously described acid solution was used with the same aim, in addition to further reducing the thickness of the material. The largest Doppler velocity was 8 mm/s. The equipment was calibrated with metallic iron (α -Fe) at RT.

3. Results and Discussion

3.1 X-ray diffraction

The diffractograms of both the solution-treated and all aged samples are shown in Figure 1. Reverted austenite peaks

Table 1. Chemical composition of Maraging-300 steel.

	Ni	Co	Mo	Ti	Al	Cr	Fe
wt%	18.33	9.41	4.99	0.78	0.10	0.11	Bal

*Mn, Si, Cu, V, C less than 0.1 wt%

were not identified, resulting in a monophasic martensitic diffraction pattern, as expected for this temperature according to previous studies^{6,16}. Due to the very low volume fraction of precipitates, they cannot be identified by X-ray analysis. No significant changes were observed in the diffractograms from the solution-treated condition until 100 h of ageing.

The variation of the bcc martensitic lattice constant value was completely attributed to the atomic redistribution of alloying elements as the ageing proceeded. The zone formation of alloying elements, or intermetallic compound precipitation, or even the reversion of austenite in quite small amounts (below the resolution limits of XRD) will be directly reflected in lattice constant values of the martensitic matrix.

For this paper, the martensite lattice constant at each condition was computed using the extrapolation method suggested by Cullity¹⁷, and is plotted in Figure 2. The value of this parameter decreased quickly during the first hour of ageing, and became a bit smaller after 10 h.

When a certain amount of alloying elements leaves the martensitic matrix to form other phases, their positions are occupied by other atoms of different atomic volume¹⁸. This fact implies a change in the unit cell volume of Fe-rich bcc martensite, and therefore in its lattice constant. Note that Mo and Ti atoms are much larger than Fe atoms, whereas Ni and

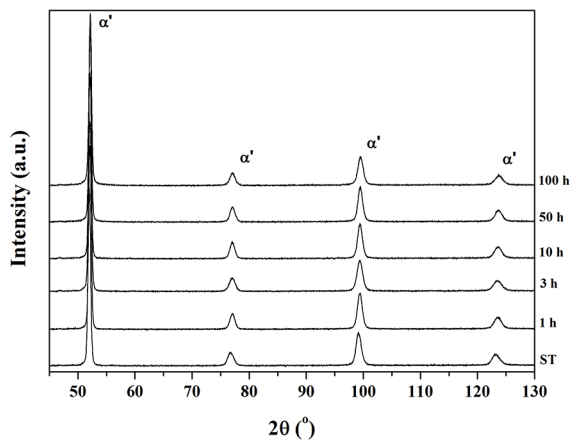


Figure 1. XRD patterns of solution-treated and aged Maraging-300 steel specimens.

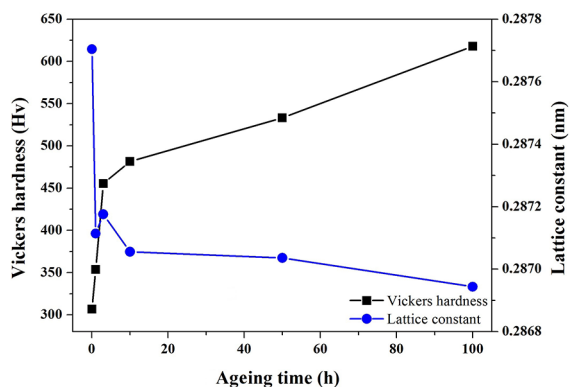


Figure 2. Age hardening and bcc martensitic lattice constant values of solution-treated and aged Maraging-300 steel specimens.

Co atoms are a little bit smaller. The lattice constant change reflects that a certain amount of alloying elements, most likely Mo and Ti, leaving the martensitic matrix, mainly during the first hour of ageing. After this, the Mo and Ti output slowed down. In Maraging-300 steel, Co does not form precipitates itself and only substitutes a few percent of Ni and Fe in Ni_3Ti and Fe_7Mo_6 intermetallic phases, respectively¹⁹. The amount of Ni that leaves the martensitic matrix to form paramagnetic phases with other alloying elements is compensated by a higher Co concentration around Fe sites, and then no significant changes can be noted in lattice constant value because of this Ni and Co rearrangement. This is a reasonable explanation for the lattice constant curve behaviour. Thus, there is a possibility that Ni left the martensitic matrix in all stages of ageing on this study.

3.2 Hardness measurements

Vickers hardness of all samples is also shown in Figure 2. At this temperature, two stages of the hardening process may be defined. The steel presented a fast increase in hardness values at initial ageing times (≤ 3 h), and then a continuous slow increase was observed until 100 h of ageing. As in the studies of Lecomte et al.²⁰ and Servant and Bouzid²¹, the over-ageing phenomenon did not occur at this temperature until 100 h of ageing.

Finely distributed precipitates present an effective barrier to the motion of dislocations²². Precipitate size, shape and spacing seem to be very relevant factors in the age hardening mechanism of the material. Following Magnée et al.³, the hardening that results from holding at temperatures below 450°C is probably due to the formation of ordered precipitates, 1 to 5 nm in diameter, that are coherent with the martensitic matrix. This coherency indicates that at initial stages of ageing at this temperature, strengthening is related to the stress required for dislocations to cut through precipitates. This result in higher hardness values due to the increase in shear stress required to cut through the precipitates, in addition to the stress generated in the matrix by the simple presence of precipitated phase particles.

Tewari et al.² reported the formation of metastable phases in Maraging-350 when aged at low temperatures. Thus, in the present study, with increasing ageing time at this temperature, the formation of increasingly strong precipitate particles (different phases) can occur, enabling Orowan's mechanism and greatly hindering the dislocation movement in the material. In this case, the formation of successive phases finely dispersed in the steel occurred until equilibrium was reached, as the phases formed.

As the ageing proceeded (> 3 h), the precipitate size increased, precipitate coarsening occurred and interparticle distance also increased, causing a slowdown in the strengthening of the material. The progressive formation of incoherent particles with the matrix was an additional fact to explain this. The hardness curve behaviour in Figure 2 reflects this.

Despite the notable strength gain of the material at this temperature in the initial stages of ageing (≤ 3 h), the hardness values found at these conditions were relatively lower than those found at higher ageing temperatures (i.e. at 480°C). This suggests that the precipitates that formed during these ageing stages at this temperature would not be the same as found at higher temperatures. However, for longer ageing times, the hardness behaviour found in this study was similar with previous results⁶ reported for maraging steels.

3.3 Mössbauer analysis

The Mössbauer spectra of the solution-treated sample and those aged for various times at 440°C are shown in Figure 3. A hyperfine field distribution, and in some cases a singlet, were used for best fitting. A ferromagnetic behaviour was observed in all of them, other than a paramagnetic contribution at 3 and 50 h of ageing. The distribution belongs to the martensitic phase. The singlet suggests that there is a paramagnetic phase (or phases) containing a fraction of Fe in these two specimens. This paramagnetic peak is likely due to the precipitation of intermetallic compounds that contain some Fe. However, although the reversion of austenite is not common at this temperature for maraging steels and was not detected by XRD in this work, the presence of austenite in quite small amounts cannot be excluded in this case.

The paramagnetic phase(s) accounted for about 1.59 and 1.31% of the total Fe in the specimens aged for 3 and 50 h, respectively. For the sample aged for 10 h, the presence of a singlet for fitting the results may be possible. However, with values so small that they can be considered within the margin of error. This possible singlet was disregarded in this work. This irregular behaviour of paramagnetic phase(s) suggests the formation of metastable paramagnetic precipitate (or precipitates) that contains Fe as a compositional element. This is in accordance with what was discussed in the previous section.

As the paramagnetic peak was not detected for the samples aged for 1, 10 and 100 h, it is reasonable to think that intermetallic compounds that contain Fe did not exist at these conditions. This is an important result, because it showed that Fe containing phases like Fe_2Mo Laves or Fe_7Mo_6 μ -phase did not exist at these ageing times. This is not in agreement with what was found for Maraging-350 by Tewari et al.², who suggested the existence of Fe_2Mo Laves phase after ageing for about 45 h at this temperature. According to Sha et al.¹⁹, the activity of Mo is raised by the presence of Co in maraging steels. Therefore, the driving force for the precipitation of Mo-rich phases is increased. The higher amount of Co for Maraging-350 steel explains the difference in Mo-rich phase kinetics for these two grades of maraging steels.

As expected for a Fe^0 metallic alloy, the isomer shift (δ) of martensite was close to zero. Because of the low carbon content of this steel, quadrupole splitting (2ϵ) was

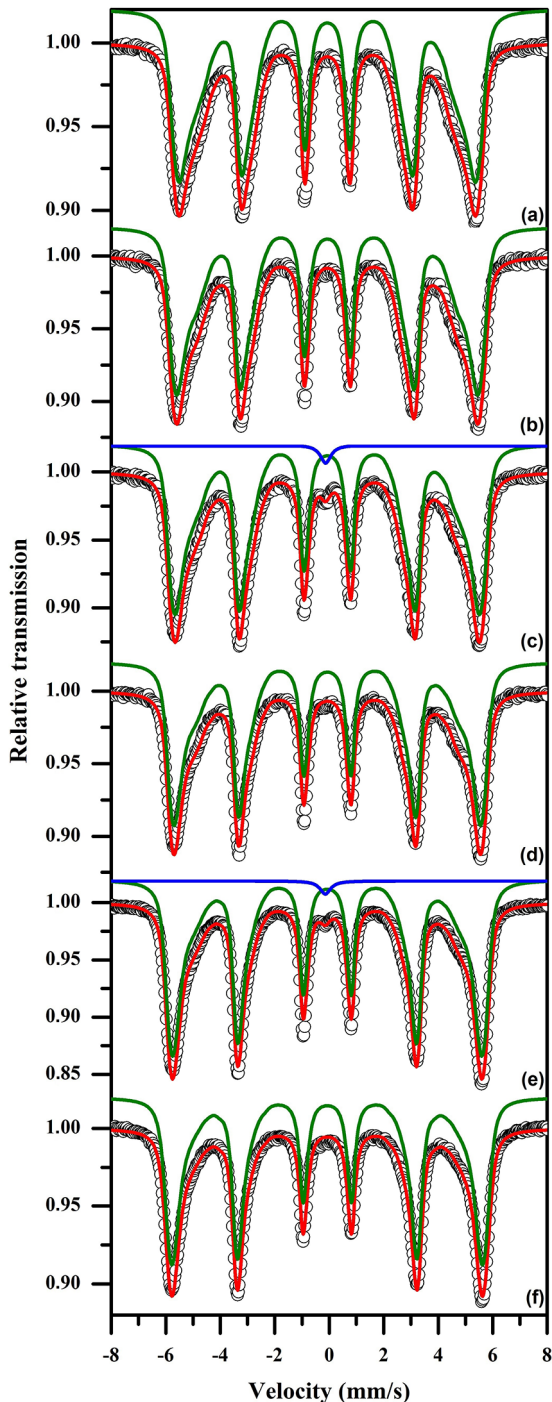


Figure 3. Mössbauer spectra of Maraging-300 steel solution-treated at 820°C for 30 min and aged at 440°C for various times: (a) as solution-treated; (b) 1 h; (c) 3 h; (d) 10 h; (e) 50 h; (f) 100 h.

also close to zero, confirming that the martensitic matrix can be considered as bcc in this case. The sextet linewidth decreased from Figure 3(a) to (f), indicating a reduction in the number of configurations around ferromagnetic Fe sites as ageing proceeds.

The probability distribution curves of the magnetic hyperfine field (B_{hf}) for all samples are shown in Figure 4. The graphics show a notable continuous change at both high and low hyperfine field regions until 100 h of ageing, suggesting that an intense atomic rearrangement occurred at all ageing stages. The continuous severe changes at low and high hyperfine field regions were related to atomic alterations at the first coordination spheres around iron sites. Experiments by Vincze and Campbell²³ pointed out that while most of the chemical elements, including Mo and Ti, have a negative contribution (-3.87 and -1.91 T at the first coordination sphere), Ni and Co have the opposite effect (0.94 and 1.33 T) on the magnetic hyperfine field of a ^{57}Fe nucleus. As Co does not form precipitates itself, this B_{hf} behaviour can be explained by a continuous output of alloying elements from the martensitic matrix - in this case Ni, Mo, and Ti - to form paramagnetic phases, creating Fe-Co and Ni-Mo-Ti rich zones. The fact that the absolute value contributions of Mo and Ti to B_{hf} were higher than the Ni contribution is an additive effect to explain the displacement of the B_{hf} average value (see Figure 4) towards the high hyperfine field region. As the Co contribution to B_{hf} is higher than Ni contribution, an additional effect occurs when Co atoms replace previous Ni atoms sites. This is in agreement with the results discussed in the X-ray section, and the same explanation about Mo, Ti and Ni atom mobility in all stages of ageing can be applied here.

The highest probability values at each condition were related to the increasing values of B_{hf} , and all of them were always higher than the magnetic hyperfine field expected for $\alpha\text{-Fe}$. This suggests that Fe sites for the ferromagnetic martensite were more and more surrounded by alloying elements with positive contribution to its B_{hf} - in this case Ni and mainly Co - as ageing time increased.

Although the singlet appears only at some of the ageing times, there is some evidence that precipitation (without Fe atoms) occurred continuously besides these ageing times,

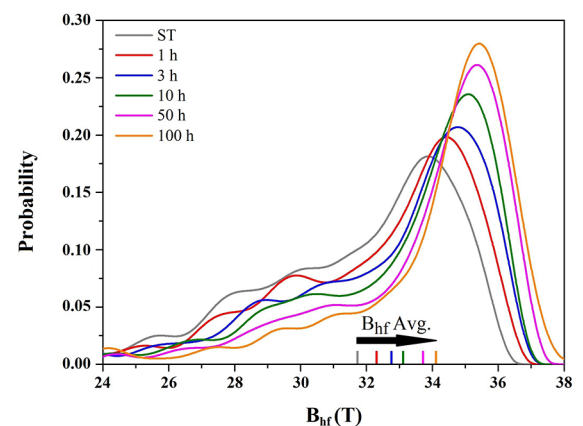


Figure 4. Probability distribution curves of the magnetic hyperfine field of Maraging-300 steel solution-treated and aged at 440°C for various times.

as indicated by the behaviour of the probability distribution curves.

4. Conclusions

The atomic redistribution of Maraging-300 steel aged at 440°C was intense and occurred continuously until 100 h of ageing. The Mo and Ti atom mobility was severe during the first hour of ageing and then slowed down. The Ni atom mobility likely occurred during all stages of ageing, and the Co atoms remained close to Fe atom sites. Paramagnetic phases, with some amount of Fe, only existed at 3 and 50 h of ageing, and possibly at 10 h. The possibility of formation of quite small amounts of reverted austenite cannot be disregarded at these conditions. Intermetallic compounds containing a fraction of Fe, for instance the Laves or μ -phase, did not exist at 1 and 100 h of ageing. This indicates that Mo atoms probably left the martensitic matrix to form some precipitate other than Laves or μ -phase at these conditions. Precipitates formed at this temperature were not probably the same as those found at higher ageing temperatures. The compilation of results suggests the formation of metastable phases during all stages of ageing that were investigated in this paper.

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6. References

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