Maraging-350 steel: Following the aging through diffractometric, magnetic and hyperfine analysis

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ABSTRACT

Plates of solution annealed Maraging-350 steel were submitted to aging under an inert atmosphere, varying the time and temperature. The aged samples were characterized by X-ray diffraction and Mössbauer spectroscopy. The results revealed that the aging treatments induced the reversion of austenite, in amounts that vary with the time and the temperature of the heat treatment. The lattice parameters of the martensite and austenite phases, as well as their hyperfine parameters, were obtained at all aging conditions. No intermetallic compounds were identified in any of the aged samples, but a poorly crystallized phase fraction, the consequence of an incomplete martensite ⇒ austenite reversion transformation, was observed for some samples. The tetragonal distortion from cubic symmetry presented by the martensite in the solution annealed steel was not eliminated after aging.

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1. Introduction

Maraging steels constitute a class of ultra-high strength and magnetic steels that have several applications, ranging from sporting equipment to aeronautic components. They also have applications as high velocity rotors and are used in hysteresis motors.

Heat treatments are applied for tempering and hardening of Maraging steels, aiming to provide these alloys with desirable mechanical or magnetic properties. Knowing the final structural and magnetic state of a steel, heat-treated at specific conditions of time and temperature, is essential for the intended application. This is especially important for the Maraging steels.

This family of low-carbon high alloy steels has as main alloying elements Ni (18 wt%), Co, Ti and Mo and, sometimes, Al or Cr [1,2]. They are divided into sub-classes – 200, 250, 300, 350 and 400, according to their yield strength (in ksi) [3]. Particularly, Maraging-350 has the second highest content of cobalt – first is Maraging-400 – and the highest content of titanium, which are responsible for increasing the formation temperature of reversed austenite [3].

The metallurgical routine of its fabrication involves, after the proper fusion alloying, a solubilization step – usually performed at 820 °C, for 1 h – to dissolve the alloy elements in the iron austenite matrix [2,4]. After that, the steel is cooled to room temperature (RT), in time varying from minutes to a few hours. This temperature path leads to a martensitic transformation of which the final product is a metastable structure, with the alloy elements forming an extended solid solution in iron, supposedly crystallized in the *bcc* structure.

Further, heat treatments in the 480–650 °C temperature range – a process of so-called *aging* – induce changes in the local chemical composition and may even favor the precipitation of intermetallic compounds. The tribological, mechanical or magnetic properties may be thus modified, according to several studies [4–6]. A large number of results, regarding the structural and magnetic changes that occurred as a result of an aging treatment, have been reported previously [7–10].

The aim of this study was to identify the aging effects – structural and magnetic – on the Maraging-350 steel, starting from samples solution annealed and stabilized in the martensitic state. This investigation was carried on with extreme care in the preparation of the specimens for characterizations in order to avoid or, at least, to minimize mechanical effects commonly observed from cutting, sieving or grinding the steel. This procedure is essential when searching exclusively for thermal effects; otherwise, mechanically induced transformations may mask the appropriate results. We took the same precautions in the description of a *virgin* (i.e. not aged) steel sample [7].

Here, the aging effects were followed through diffractometric and hyperfine analyses of samples aged under specific conditions (i.e., time and temperature) usually applied in the aging of the

Maraging-350 steel. The phase(s) present in the heat-treated samples were identified by X-ray diffraction and Mössbauer spectroscopy. Both characterization techniques were conducted using new approaches, concerning the mathematical models for fitting experimental curves. The methodology applied led to a more precise description of the physical and chemical properties of a heat-treated Maraging-350 steel. This shall provide key information for the processing of this useful material.

2. Experimental details

The raw material used in this investigation was a commercial Maraging-350 steel (i.e., a forged billet), made by a Brazilian steel company. Details on the steel composition and about the preparation of samples for the characterizations may be found elsewhere [7]. In the present study, pairs of plates – a thin one ($\phi \leq 100\ \mu m$) and a thick one ($\phi \approx 1\ mm$) – taken from the solubilized specimen were simultaneously submitted to heat treatments, i.e., each of the pairs was annealed at 480 °C, 580 °C and 650 °C, for periods of 3 h, 6 h and 12 h, under an argon atmosphere. After each heat treatment, the plates were polished again, with the same care taken as before. The thin plates were reduced to a final thickness of ~50 μm.

The thick and thin plates were used for X-ray diffraction and transmission Mössbauer spectroscopy, respectively. Other basic details about the characterization techniques, such as equipment and numerical analysis, may also be found in Ref. [7]. In the present investigation, a cobalt tube (not a copper tube as in [7]) was used for the X-ray measurements, aiming to minimize the effects of the fluorescence, which is significant when the copper radiation is used.

The diffractograms were refined by the Rietveld method (FullProf program), considering the $I4$ and $Fm-3m$ space groups, attributed respectively to the martensite (α') and austenite (γ) phases, eventually present in the samples characterized. The $I4$ space group was chosen for martensite since, according to our earlier studies, this phase presents a tetragonal distortion [7]. For the refinements, both phases were considered to have the same nominal sample composition.

3. Results and discussions

3.1. X-ray diffraction

Fig. 1 shows the diffractograms for some selected samples. Refined lattice parameters ($a=b$ and c) and phase molar fractions are presented in Table 1, which includes data for all samples characterized. The diffractometric profile of the 480 °C/12 h sample (Fig. 1a) is analogous to that of the solution annealed steel (see Fig. 1 of Ref. [7]). It is characteristic of a monophasic sample, corresponding to the martensite structure. As for the as-received steel – and for the samples annealed at 480 °C for 3 h and 6 h (diffractograms not shown) – no extra peaks could be identified, which means that no secondary phases have precipitated in the sample in significant amounts (i.e., within the resolution limits of the X-ray diffraction technique).

In contrast, the diffractogram of the 580 °C/12 h aged sample (Fig. 1b) shows peaks of a minor phase, which by its structure (fcc) may be identified as belonging to austenite. Indeed, this phase is recurrently found in aged or even just annealed solution Maraging-350 steels [1,3,8,11]. Austenite is also (is not) present in 580 °C/6 h (3 h) aged sample (diffractograms not shown).

The lattice parameters of the martensite phase change slightly from one sample to other. As a general trend, a decreases whereas
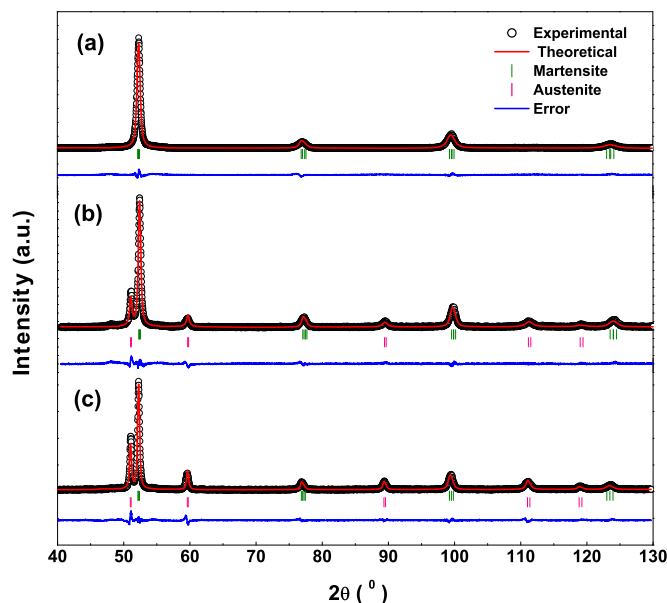

Fig. 1. Refined diffractograms for the 480 °C/12 h (a), 580 °C/12 h (b) and 650 °C/12 h (c) aged Maraging-350 samples.

Table 1
Lattice parameters and molar fractions of the phases identified in the as-received and aged steel samples.

	Sample	Phase	$a=b$ (Å)	c (Å)	Phase fraction (%)
As-received		Martensite	2.8842 (2)	2.8688 (4)	100
		Austenite	–		–
480 °C	3 h	Martensite	2.8812 (3)	2.8604 (4)	100
		Austenite	–		–
	6 h	Martensite	2.8796 (2)	2.8611 (4)	100
		Austenite	–		–
	12 h	Martensite	2.8794 (3)	2.8608 (4)	100
		Austenite	–		–
580 °C	3 h	Martensite	2.8670 (5)	2.8569 (9)	91.5 (4)
		Austenite	3.5962 (6)	–	8.5 (1)
	6 h	Martensite	2.8736 (2)	2.8605 (4)	88.4 (2)
		Austenite	3.5995 (5)	–	11.6 (1)
	12 h	Martensite	2.8720 (2)	2.8587 (4)	74.0 (2)
		Austenite	3.5965 (2)	–	26.0 (1)
650 °C	3 h	Martensite	2.8739 (3)	2.8652 (6)	57.7 (1)
		Austenite	3.5964 (2)	–	42.3 (1)
	6 h	Martensite	2.8754 (5)	2.8703 (9)	65.7 (2)
		Austenite	3.5975 (2)	–	34.3 (1)
	12 h	Martensite	2.8789 (2)	2.8665 (4)	63.7 (2)
		Austenite	3.5992 (2)	–	36.3 (1)

c is more or less constant, as the temperature raises for isochronical aging treatments.

The evolution with aging time of the tetragonal distortion may be perceived from Fig. 2. The c/a ratios for the 650 °C and 580 °C temperatures initially grow and then further decrease, both converging after 12 h of heat treatment to ~0.9955.

In Ref. [7], we argued that the distortion in the as-solubilized state may be attributed to the different atomic sizes of the alloy elements present in the steel composition. Now, it is clear that heat treatments, which may produce precipitation of titanium or molybdenum (i.e., the elements with the largest atomic radii) compounds, do not eliminate the distortion from the cubic symmetry. The variation of the c/a ratio for the 480 °C condition, although also slight, reveals that some atomic re-arrangement takes
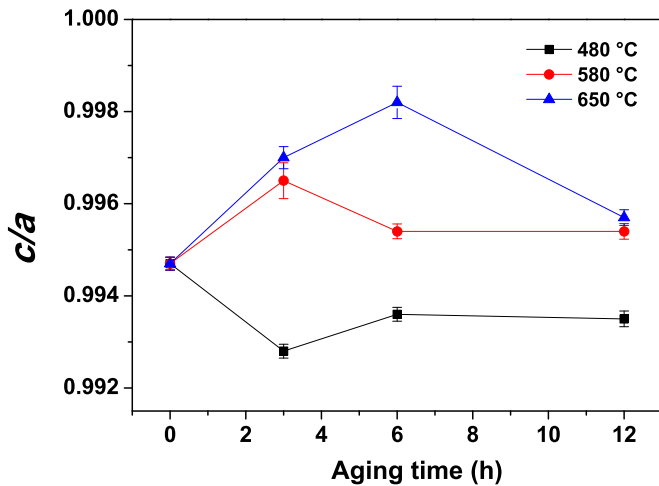
Fig. 2. The c/a ratio for the martensite phase, in samples heat treated at different temperatures.

place in the steel in despite of there being no evidence for a second phase presence in the respective diffractograms. The lattice parameters obtained for austenite are, in general, consistent with earlier reported data [12].

The austenite molar fraction increases with time: monotonically for the 580 °C heat treated samples and more effectively for 650 °C heat treated samples (in spite of a fluctuation after 3 h). These fractions must be regarded as just as an estimation, since in the refinement process the austenite was always considered as having the same composition of the solution annealed sample. In this sense, one has to impose an approximation, because both martensite and austenite change their compositions along the heat treatment in an unpredictable exact way.

3.2. Mössbauer analysis

The Mössbauer spectra measured for the same aged samples (i.e., those in Fig. 1), plus the one for the 650 °C/3 h sample, are shown in Fig. 3. All of them present a clear magnetic aspect – consistently with earlier investigations [4,7,13] – plus a central unsplitted contribution.

The 480 °C/12 h spectrum – as well as the 480 °C (3 h/6 h) and 580 °C (3 h/6 h) spectra (not shown) – were fitted considering three discrete sextets and a singlet. The hyperfine parameters fitted and subspectral areas for these and other samples characterized in this investigation are shown in Table 2.

According to our earlier work on the solution annealed Maraging-350 steel [7], the discrete sextets belong to the martensite phase. They are related to iron atoms with atomic neighborhoods that may consistently be classified and handled in three groups, depending on the number of nickel and cobalt nearest neighbors. Inside determined limits, the higher the number of neighboring Ni and Co atoms, the larger the hyperfine magnetic field at the iron site [5].

The paramagnetic (PM) contribution (i.e., the singlet), which was not observed for non-aged samples, may be attributed to (reversed) austenite, according to the X-ray results. However, we cannot exclude the possibility that the austenite subspectrum be superimposed on other paramagnetic (minor) components, from iron intermetallic compounds (nanostructured and superparamagnetic) precipitated from the aging process. Usually, the $Ni_3(Ti, Mo)$ and Fe_2Mo intermetallic compounds have been identified in aged samples [1,6,12] and these phases could, plausibly, be present here (with iron dissolved in the A_3B phase) but in quite small amounts.
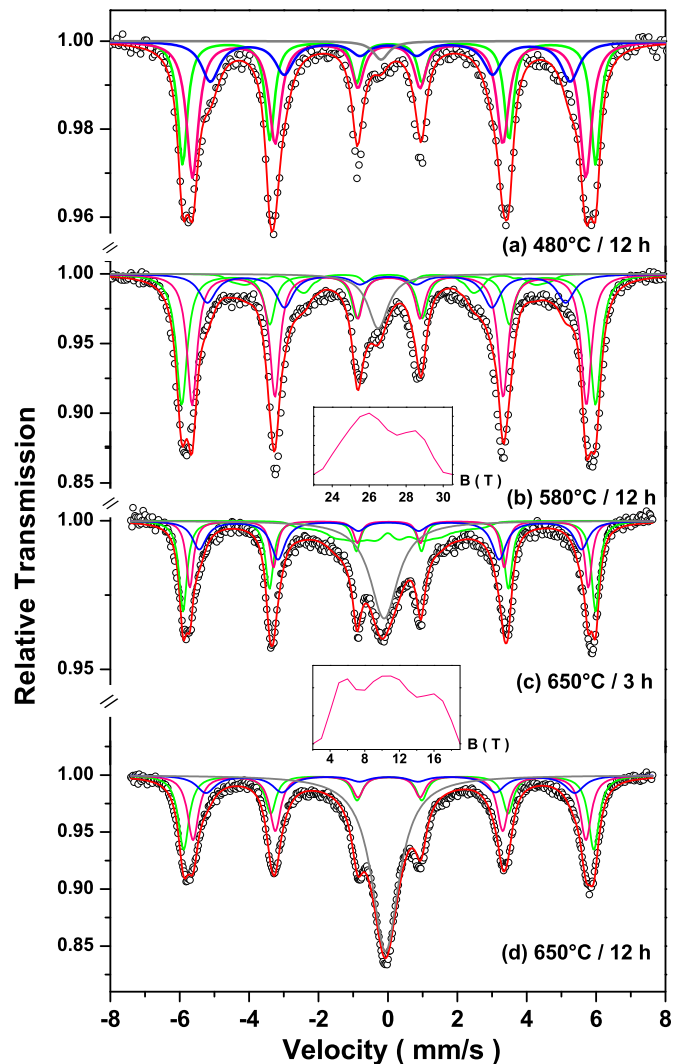

Fig. 3. Mössbauer spectra for the 480 °C/12 h (a), 580 °C/12 h (b), 650 °C/3 h (c) and 650 °C/12 h (d) aged samples. Inserts in (b) and (c) represent the hyperfine magnetic field distributions.

Although appearing as an unequivocal spectral contribution for the 480 °C aged samples, the singlet presents small relative areas (i.e., from 1% to ∼2%), whereas the X-ray diffraction does not identify this phase in the same samples. This may be explained by recalling that Mössbauer is a "microscopic" technique. Besides being selective to iron, it is able to identify and quantify phases from small crystallites (eventually, nanostructured) while X-ray diffraction only sees "larger" crystallites. This is exactly the great achievement of the [57]Fe Mössbauer spectroscopy technique, which affords a fine characterization where iron alloys and compounds are present. For higher aging temperatures the PM spectral component becomes much more evident, reaching ∼40% for the 650 °C/12 h aged sample (Fig. 3d).

The 580 °C/12 h spectrum (Fig. 3b) was fitted with an additional hyperfine magnetic field distribution – as well as the spectra of the 650 °C/3 h (Fig. 3c) and 650 °C/6 h (spectrum not shown) samples – besides the same discrete components of the previous samples.

These hyperfine magnetic field distributions (B_{hf} Dist.) account for the 'wings' appearing between the main lines, especially between the lines 2 (4) and 3 (5) in the above cited spectra. This contribution is related to the fraction of martensite in transformation to austenite, at the grain boundaries of the more nickel-

Table 2

Hyperfine parameters and subspectral areas for the as-received and aged steel samples.

Sample		Síte	B_{hf} (T) (± 0.1)	δ [a] (mm/s) (± 0.01)	2ε (mm/s) (± 0.01)	Γ (mm/s) (± 0.01)	Area (%) (± 0.7)
RT							
As-received[b]		Sextet 1	34.8	0.04	−0.02	0.42	35.9
		Sextet 2	32.5	0.04	0.01	0.40	27.8
		Sextet 3	29.2	0.02	0.00	0.60	36.3
		Singlet	–	–	–	–	–
		B_{hf} Dist.	–	–	–	–	–
480 °C	3 h	Sextet 1	36.5	0.04	−0,02	0.36	33.7
		Sextet 2	34.8	0.04	0.01	0.38	41.6
		Sextet 3	31.1	0.01	−0.02	0.62	23.7
		Singlet	–	−0.09	–	0.30	1.0
		B_{hf} Dist.	–	–	–	–	–
	6 h	Sextet 1	36.5	0.04	−0.02	0.36	38.1
		Sextet 2	34.8	0.04	0.01	0.37	41.9
		Sextet 3	31.1	0.02	−0.02	0.58	18.5
		Singlet	–	−0.12	–	0.37	1.5
		B_{hf} Dist.	–	–	–	–	–
	12 h	Sextet 1	36.9	0.04	−0.01	0.33	33.1
		Sextet 2	35.1	0.03	0.01	0.42	44.4
		Sextet 3	32.2	0.04	0.05	0.63	20.6
		Singlet	–	−0.20	–	0.54	1.9
		B_{hf} Dist.	–	–	–	–	–
580 °C	3 h	Sextet 1	36.7	0.05	−0.04	0.42	41.8
		Sextet 2	35.2	0.04	0.01	0.28	25.7
		Sextet 3	33.4	0.05	0.05	0.41	26.5
		Singlet	–	−0.19	–	0.72	6.0
		B_{hf} Dist.	–	–	–	–	–
	6 h	Sextet 1	36.6	0.03	−0.02	0.37	39.4
		Sextet 2	35.0	0.04	0.01	0.34	36.6
		Sextet 3	32.5	0.03	0.03	0.63	17.7
		Singlet	–	−0.24	–	0.65	6.3
		B_{hf} Dist.	–	–	–	–	–
	12 h	Sextet 1	36.8	0.04	0.00	0.41	32.4
		Sextet 2	35.4	0.04	0.01	0.40	39.8
		Sextet 3	–	–	–	–	–
		Singlet	–	−0.22	–	0.55	6.3
		B_{hf} Dist.	30.9	0.05	0.05	0.28	21.5
650 °C	3 h	Sextet 1	36.9	0.04	−0.02	0.28	26.1
		Sextet 2	35.6	0.03	0.03	0.25	17.3
		Sextet 3	34.1	0.04	0.05	0.51	18.9
		Singlet	–	−0.12	–	0.97	23.7
		B_{hf} Dist.	10.6	0.05	0.09	0.28	14.0
	6 h	Sextet 1	37.1	0.03	−0.02	0.26	10.1
		Sextet 2	35.8	0.04	−0.02	0.28	18.9
		Sextet 3	34.4	0.04	0.02	0.49	28.8
		Singlet	–	−0.07	–	0.97	34.0
		B_{hf} Dist.	13.5	0.14	0.05	0.28	8.2
	12 h	Sextet 1	37.1	0.03	−0.03	0.29	11.5
		Sextet 2	35.8	0.03	−0.01	0.32	19.5
		Sextet 3	34.4	0.04	0.02 a	0.52	28.8
		Singlet	–	−0.07	–	0.96	40.2
		B_{hf} Dist.	–	–	–	–	–

[a] Relative to α-Fe.
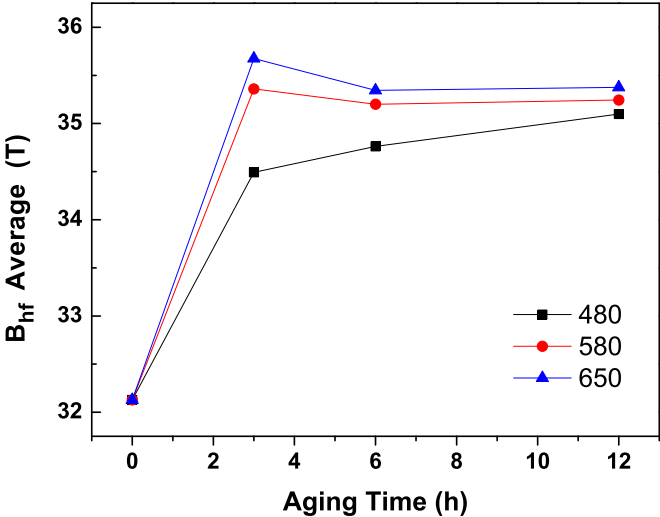[b] Data compiled from Ref. [7].

Fig. 4. B_{hf} Avg. vs. aging time, for different temperatures.

expected for a Fe^0 metallic alloy. The quadrupole splitting is nearly zero for all sites, for all samples, reflecting the symmetry of the iron sites, which is very close to the cubic, in either the martensite or the austenite phases. This is somewhat intriguing, especially for martensite which shows a tetragonal distortion and where, as well as for austenite, the iron sites present different configurations of nearest neighbors.

The evolution with the annealing time of the hyperfine magnetic field averaged for the discrete magnetic components (i.e., sextets 1, 2 and 3), B_{hf} Avg., is shown in Fig. 4, for each aging temperature. It can be seen that the B_{hf} values of the heat-treated samples increase considerably relative to that of the B_{hf} of the as-received sample, after the first three hours of aging. The higher the aging temperature, the more substantial is the initial growth. This growth in B_{hf} provides evidence that an alteration takes place around the iron atoms because of the thermal treatment, without changing the crystallographic structure of the martensite. The change may be described as a progressive enrichment of nickel and/or cobalt atoms around the iron, which must contribute positively to the B_{hf} [5].

However, according to the metastable phase diagram proposed by Schmidt *et al.* for the Fe–Ni system [6], reversed austenite has a higher nickel concentration than martensite in aged samples, although this superiority diminishes increasing the temperature of the aging process (see Fig. 2a of Ref. [6]). Thus, it can be inferred that cobalt is the element that most reconcentrates around iron atoms during the aging process and is the main agent responsible for increasing B_{hf}. Cobalt atoms in the iron neighborhood even compensate for some reduction of the nickel concentration in martensite, thus justifying why B_{hf} increases with aging.

The line widths (Γ's) also change with the temperature and time of aging. It is particularly manifest that for the samples treated at 650 °C, the line width decreases significantly. This decrease means that the thermal treatment reduces the number of configurations around the iron atoms, while the nearest neighborhood becomes richer in cobalt atoms.

The Mössbauer subspectral area and molar fraction (as obtained from refinements) respective to the austenite phase, as functions of the aging time, are shown in Fig. 5 for the two highest temperatures. An apparent discrepancy in the values provided by the two techniques for the evolution of the austenite fraction may be observed, mainly for the 580 °C aging condition. To understand this, we should recall that the Mössbauer subspectral area gives the fraction of iron atoms in the phase and not the molar (or volume) phase fraction directly.
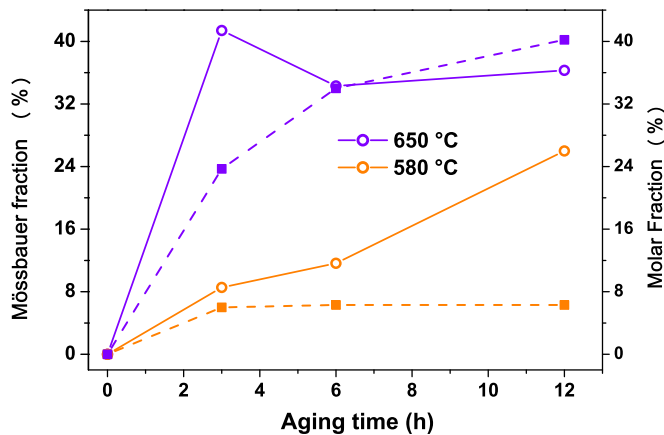
rich regions [4,13]. The sextets are collapsing to a singlet, revealing that the austenite reversion has not been completed for any of these specific aging conditions. In comparison, the reversion transformation that occurred for the 650 °C/12 h aging condition is complete (Fig. 3d), since no 'wings' are visible in the spectrum, meaning that the sample reached the (meta)equilibrium state at that temperature.

Analyzing the hyperfine parameters, we can see that the isomer shifts (δ's) of the martensite phase are close to zero, which is

Fig. 5. Mössbauer subspectral area (filled square symbols/left axis) and molar fraction (empty round symbols/rigth axis) of the austenite phase *vs*. aging time at 580 °C (orange lines) and 650 °C and (blue lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Thus, considering the molar fractions estimated by XRD for reversed austenite at 580 °C, for example, we see that the respective Mössbauer relative areas are always smaller, for isochronical treatments. This difference implies that the martensite matrix is richer in iron than the reversed austenite, otherwise the curves should coincide. This superposition is barely found for 650 °C (i.e., except for the 3 h points), meaning that martensite and austenite reversed have similar iron concentration after aging at this temperature.

4. Conclusions

Aging Maraging-350 steel produces an atomic rearrangement in the martensite phase, involving change in the composition and lattice parameters, and the reversion of austenite, to an extent that depends on the temperature and time of the heat treatment.

The resultant martensite is richer in cobalt and poorer in nickel, relatively to its initial composition.

The martensite lattice parameters, (c) and (a), remain constant or decrease slightly, respectively, on increasing the temperature of aging.

The tetragonal distortion from the cubic symmetry presented by the martensite phase oscillates with the heat treatments, but does not disappear whatever the temperature or aging time.

No intermetallic compounds were identified in the aged samples, but the reversion of austenite was noted, the amount of which is greater the longer is the time or higher is the temperature of annealing.

Reversed austenite is richer in nickel and poorer in iron than the original martensite monophase, the lower is the aging temperature. By or beyond six hours of aging at 650 °C, it has the same iron composition as martensite.

Acknowledgments

References

[1] A. Magnée, J.M. Drapier, J. Dumont, D. Coutsouradis, L. Habraken, Cobalt containing High-strength Steels, Centre D'information du Cobalt, Centre D'information du Cobalt, Bruxelles, 1974.
[2] R.F. Decker, Notes on the development of maraging steels, in: Source Book Maraging Steels, 1979, pp. XI–XV.
[3] F. Habiby, N. Siddiqui, H. Hussain, A. Ul Haq, A.Q. Khan, Lattice changes in the martensitic phase due to ageing in 18 wt% nickel maraging steel grade 350, J. Mater. Sci. 31 (1996) 305–309.
[4] X.D. Li, Z.D. Yin, H.B. Li, T.C. Lei, M.L. Liu, X.W. Liu, M.Z. Jin, Mössbauer study of the early stages of aging in 18Ni(350) maraging steel, Mater. Chem. Phys. 33 (1993) 277–280.
[5] I. Vincze, I.A. Campbell, Mössbauer measurements in iron based alloys with transition metals, J. Phys. F: Met. Phys. 3 (1973) 647–663.
[6] M. Schmidt, K. Rohrbach, Heat treating of maraging steels, in: R.N. Menezes et al., ASM Handbook: Heat Treating, IV, 1991, pp. 528–548.
[7] G.C.S. Nunes, P.W.C. Sarvezuk, V. Biondo, M.C. Blanco, M.V.S. Nunes, A.M. H. Andrade, A. Paesano Jr., Structural and magnetic characterization of martensitic Maraging-350 steel, J. Alloy. Compd. 646 (2015) 321–325.
[8] F.G.A. Hamilton, J.J. Silva, M.R. Silva, M.J.G. Silva, Influence of reverted austenite on the texture and magnetic properties of 350 maraging steel, J. Magn. Magn. Mater. 393 (2015) 99–104.
[9] S.S.M. Tavares, H.F.G. Abreu, J.M. Neto, M.R. da Silva, I. Popa, A magnetic study of the maraging 350 steel, J. Magn. Magn. Mater. 272–276 (2004) 785–787.
[10] S.S.M. Tavares, M.R. da Silva, J.M. Neto, J.M. Pardal, M.P. Cindra Fonseca, H.F. G. Abreu, Magnetic properties of a Ni–Co–Mo–Ti maraging 350 steel, J. Alloy. Compd. 373 (2004) 304–311.
[11] X. Li, Z. Yin, Reverted austenite during aging in 18Ni(350) maraging steel, Mater. Lett. 24 (1995) 239–242.
[12] R. Tewari, S. Mazumder, I.S. Batra, G.K. Dey, S. Banerjee, Precipitation in 18 wt% Ni maraging steel of grade 350, Acta Mater. 48 (2000) 1187–1200.
[13] X. Li, Z. Yin, Mössbauer study of the aging behavior of 18Ni(350) maraging steel, Mater. Lett. 24 (1995) 235–238.