

Study of the austenite quantification by X-ray diffraction in the 18Ni-Co-Mo-Ti maraging 300 steel

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In this paper, quantifications of the austenitic phase in a maraging 300 steel heat treated at different temperatures and periods of time were carried out using the direct comparison method by X-ray diffraction. The influence of taking into account the chemical compositions of austenite and martensite phases in the results by the direct comparison method was evaluated. In order to analyze the instability of austenite under plastic deformation, the quantifications were carried out with and without previous grinding of the samples. The behavior of the austenite volume fraction against aging time at 560°C, 600°C and 650°C were determined. The variation of the martensite lattice parameter with aging time was also analyzed. The results show an increase of the austenite content with aging time at 560°C and 600°C. At 650°C, however, the austenite content present at room temperature decreases and the martensite parameter increases with the aging time above 1 h.

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1. Introduction

Maraging steels are high alloy ultra high resistant steels used for special purposes from special pressure vessels and aircraft components to sports equipments. The high mechanical resistance of these steels is attained by the precipitation hardening mechanism during the aging in the 400–700°C interval. Low temperature aging (400–450°C) promotes the formation of metastable phases S and ω , and Ni₃(Ti, Mo) for long aging times [1–3]. At higher aging temperatures, initially the hardening is produced by Ni₃(Ti, Mo) and then by Fe₂Mo particles [1–3]. Aging treatments above 500°C, promote the formation of austenite by diffusion-controlled reaction [4, 5]. The amount of austenite formed at the aging temperature is totally or partially retained at room temperature, depending on its chemical composition. The nickel content plays the major role on the stability of austenite. Peters [4] observed that the reverted nickel-enriched austenitic phase will be wholly or in part transformed into martensite upon cooling to room temperature if its nickel content is below about 30%, which corresponds to an M_s near the room

temperature. According to some authors [6–8] the unstable reverted austenite transforms into martensite ($\gamma \rightarrow M$) during cold deformations modifying the mechanical properties.

Some previous works presented quantifications by X-ray diffraction in maraging steels considering equal chemical compositions in the both phases, thus equaling atomic scattering factors [9, 10]. Analysis by EDS and APFM performed by different investigators [11, 12] reveal that the chemical compositions of austenite and martensite phases may be quite different depending on the aging conditions.

In this paper, X-ray diffraction study of a Ni-Co-Mo-Ti steel was measured as function of aging temperature in the 440–650°C range. Two types of quantification by X-ray diffraction were performed and compared. The first one was the direct comparison method considering equal atomic scattering factors. In the second type, the differences of chemical composition were taken into account to calculate the atomic scattering factors.

The precise determination of the austenite volumetric percentage in maraging steels is of great importance, since

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TABLE I Chemical composition of the studied maraging steel

Element	C	Ni	Co	Mo	Ti	AL	Mn	Fe
wt.%	0.01	17.86	9.41	4.84	0.76	0.14	0.01	balance

mechanical [7], magnetic [8, 9, 12] and tribologic [13] properties are strongly influenced by this microstructural parameter.

2. Experimental methods

Sheet samples (20 × 10 × 2.5 mm thick) of maraging 300 steel (chemical composition shown in Table I) were solution treated at 900°C for 40 min. After this heat treatment, the samples were aged at 560, 600 and 650°C for different periods of time from 15 min to 24 h. All heat treatments were conducted in vacuum-sealed quartz tubes. After these treatments, one of the faces of each sample was grinded with fine emery paper using automatic polisher with control of speed, force and time of exposure. These parameters were standardized in all samples for analysis of the austenite stability in different conditions of treatments.

X-ray diffraction analysis (XRD) was carried out in both faces (grinded and without grinding) for all conditions. All the X-ray measurements were carried out using a PHILIPS® diffractometer, model X'Pert Pro, in step scan mode with step size of 0.02°, time per step of 3s and angular interval 45°–125°. Radiation CoK α (1.7890 Å) was used with 40 kV and 40 mA without monochromator. The measurements were made at room temperature in continuous sweeping mode. Spinner was used to minimize the effect of preferential direction. In order to keep the beam completely on the sample for low incident angles, a divergence slit of 1° was used.

The expression for the intensity diffracted by a single phase specimen in a diffractometer is:

$$I = \left(\frac{I_o \cdot e^4}{m^2 \cdot c^4} \right) \left(\frac{\lambda^3 \cdot A}{32 \cdot \pi \cdot r} \right) \left(\frac{1}{v^2} \right) \times \left[|F|^2 \cdot p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta} \right) \right] \left[\frac{e^{-2M}}{2\mu} \right] \quad (1)$$

Where I = integrated intensity per unit length of diffraction line; I_o = intensity of incident beam; e , m = charge and mass of electron; c = velocity of light; λ = wavelength or incident radiation; r = radius of diffractometer circle; A = cross section area of the incident beam; v = volume of unit cell; F = structure factor; p = multiplicity factor; θ = Bragg angle; e^{-2M} = temperature or Debye-Waller factor and $1/2\mu$ is the absorption factor. The term $\left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)$ is the Lorentz polarization factor.

The value of the temperature factor (e^{-2M}) is a function of $(\sin \theta)/\lambda$. In this work we took the value of iron at 20°C using the graph presented by Cullity [14]. The p value depends on the type of structure and the hkl of the

diffraction plane. The structure factor (F) is $2f_\alpha$ for the martensite (bcc structure) and $4f_\gamma$ for the austenite (fcc structure), where f_α and f_γ are the atomic scattering factor done by the sum of the scattering factors of the elements in each phase:

$$f_{\alpha,\gamma} = f_{Fe} + f_{Ni} + f_{Co} + f_{Mo} + f_{Ti} \quad (2)$$

The scattering factor of the elements is a function of their concentration in the phase to a given temperature, Bragg diffraction angle (θ) and wavelength (λ). For instance, the scattering factor of nickel content into austenite phase is given by:

$$f_{Ni} = \frac{[\%at.] Ni_\gamma}{100} \cdot F_{Ni}(\theta, \lambda) \quad (3)$$

Where $F_{Ni}(\theta, \lambda)$ is a function obtained by fitting the data published by Cullity [14]. From equation (1) we can write:

$$R = \left(\frac{I_o \cdot e^4}{m^2 \cdot c^4} \right) \left(\frac{\lambda^3 \cdot A}{32\pi \cdot r} \right) \quad (4)$$

$$K = \frac{1}{v^2} \left[|F|^2 \cdot p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta} \right) \right] \left[\frac{e^{-2M}}{2\mu} \right] \quad (5)$$

Quantitative analysis by X-ray diffraction is based on the fact that the intensity of the diffraction pattern of a particular phase in a mixture of phases depends on the concentration of that phase in the mixture. Austenite and martensite phases depend on the concentration of that phase in the mixture. For austenite and martensite phases, we can write respectively:

$$I_\gamma = \frac{R \cdot K_\gamma}{2\mu_m} C_\gamma \quad \text{and} \quad I_\alpha = \frac{R \cdot K_\alpha}{2\mu_m} C_\alpha \quad (6)$$

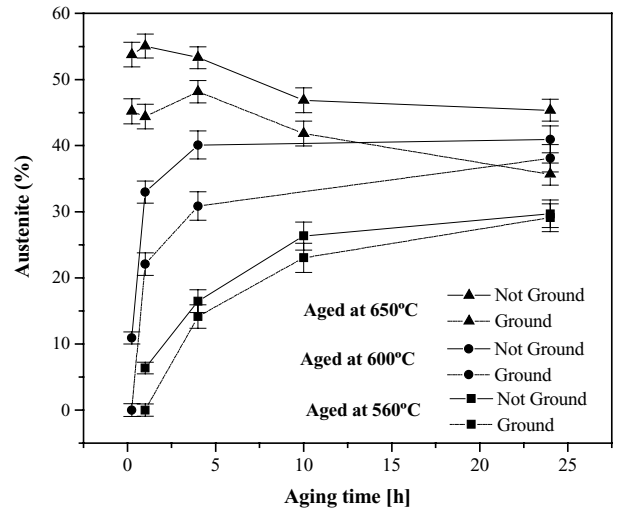


Figure 1 Austenite volumetric percentage versus aging time at 560°C, 600°C and 650°C. Samples with and without previous grinding.

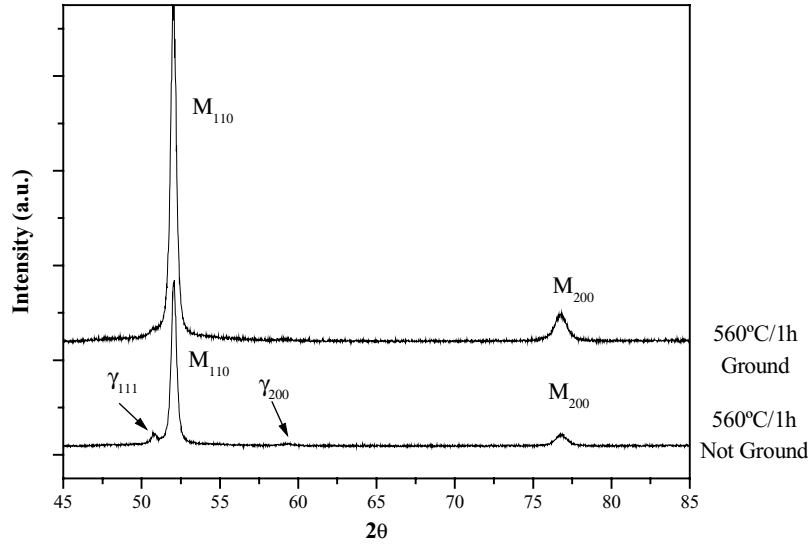


Figure 2 X-ray diffractogram of the sample aging at 560°C for 1 h, with and without previous grinding.

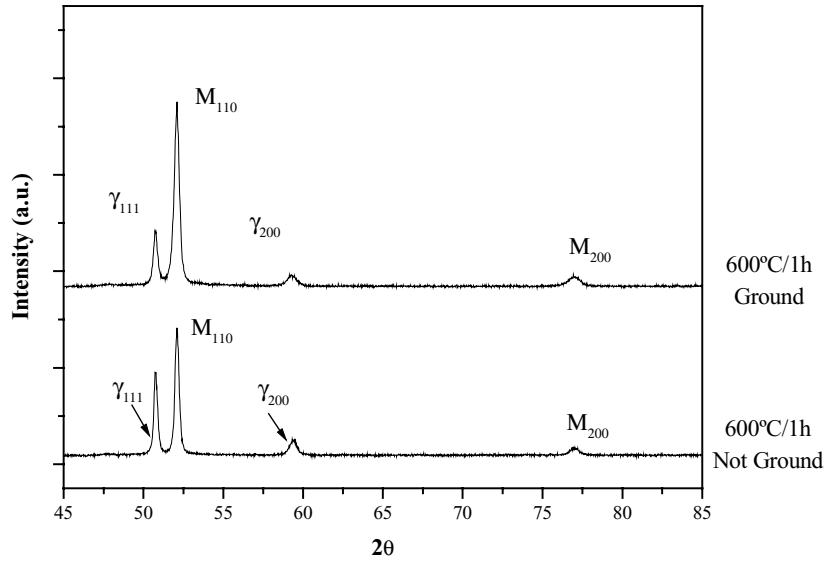


Figure 3 X-ray diffractogram of the sample aging at 600°C for 1 h, with and without previous grinding.

Where, μ_m is the absorption coefficient of the mixture. By division of these equations and considering the relation $C_\alpha + C_\gamma = 1$, we can obtain the basic equation relating the diffracted intensities and the austenite volume fraction (C_γ) by the direct comparison method in an alloy containing only two phases[14]:

$$C_\gamma = \frac{1}{\frac{I_\alpha \cdot K_\gamma}{I_\gamma \cdot K_\alpha} + 1} \quad (7)$$

The diffraction peaks corresponding to the planes of each phase were compared to one another. The analyzed peaks were: $(111)_\gamma$, $(110)_\alpha$, $(200)_\gamma$, $(200)_\alpha$, $(220)_\gamma$, $(211)_\alpha$, $(311)_\gamma$, $(222)_\gamma$, and $(220)_\alpha$, respectively. The average value of all the compared diffraction peaks was calculated to minimize the effect of preferential direction, as suggested by Ahmed *et al.* [9].

Although the aging of maraging steels promotes the precipitation of intermetallics compounds such as Fe_7Mo_6

and Ni_3Ti , the diffractograms obtained in this work did not present any peak of these phases, probably because their contents were lower than 5% [14]. For instance, Sha *et al.* [11] found 3% Ni_3Ti and 4% Fe_7Mo_6 in a C-300 maraging steel aged at 510°C for 128 hours. Aside from this, these precipitates form from the martensite and not from the austenite phase. Based on these points, it is possible to affirm that the procedure described in equations (1) to (6) for austenite quantification gives a very good estimation of the real austenite content.

Metallographic samples were prepared and etched with Picral modified reagent, as suggested by Farooq *et al.* [15] to reveal austenite phase in the martensite matrix.

3. Results and discussion

Fig. 1 shows the austenite volumetric percentage as a function of aging time at 560°C, 600°C and 650°C, with and without grinding. In this figure it is observed

TABLE II Chemical composition data used in the calculations of the atomic scattering factors at 560°C, 600°C and 650°C. $f_{\gamma, \alpha}$ and $K_{\gamma, \alpha}$ values in these conditions

Condition	Phase	Atomic weight (%)					110 (α) – 111 (γ)			200 (α)–200 (γ)				
		Fe	Ni	Co	Mo	Ti	f_{γ}	K_{γ}	f_{α}	K_{α}	f_{γ}	K_{γ}	f_{α}	K_{α}
560°C/1 h	γ	58.6	32.6	4.6	1.9	2.3	f_{γ}	18.29	K_{γ}	157.84	f_{γ}	17.14	K_{γ}	72.23
	α	73.8	13.5	11.4	0.8	0.5	f_{α}	16.05	K_{α}	167.27	f_{α}	13.46	K_{α}	24.67
600°C/1 h	γ	61.8	28.2	6.4	1.7	1.9	f_{γ}	17.80	K_{γ}	150.51	f_{γ}	16.66	K_{γ}	68.41
	α	71.5	14.2	12.6	0.9	0.8	f_{α}	15.88	K_{α}	165.20	f_{α}	13.31	K_{α}	24.23
650°C/1 h	γ	64.8	22.4	9.7	1.4	1.7	f_{γ}	16.99	K_{γ}	137.46	f_{γ}	15.90	K_{γ}	62.49
	α	68.7	15.1	14.0	1.0	1.2	f_{α}	15.68	K_{α}	160.74	f_{α}	13.14	K_{α}	23.61

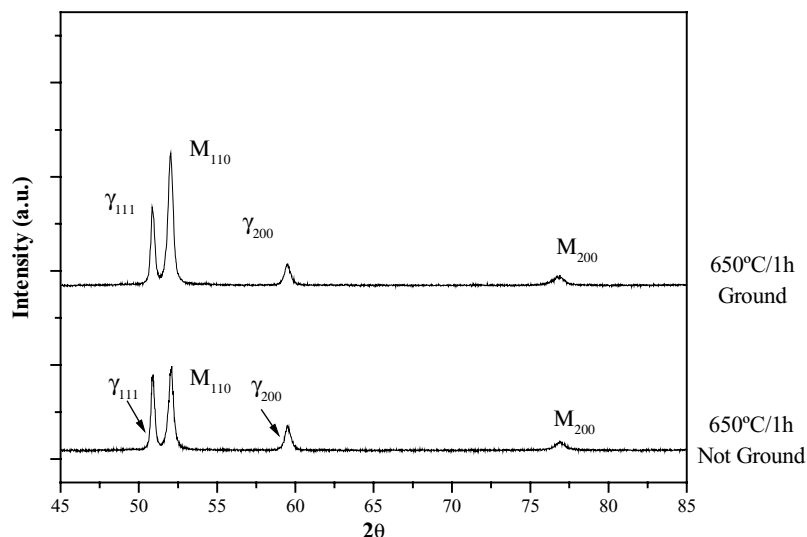


Figure 4 X-ray diffractogram of the sample aging at 650°C for 24 h, with and without previous grinding.

that the austenite volume fraction of grinded samples is lower in all aging conditions. This is attributed to the instability of the austenite phase, which transforms into martensite in the surface layers sheared by grinding. Fig. 2 shows the X-ray diffractograms with and without grinding of the sample aged at 560°C for 1 h. Due to grinding, the austenitic peaks disappear and the intensity of the martensite peaks increase. The results of austenite quantification by direct comparison method in this condition were 6.35% without grinding and 0% with previous grinding.

Fig. 3 shows the comparison between the X-ray diffractograms of the sample aged at 600°C for 1 h with and without grinding. The influence of grinding is similar to that of sample aged at 560°C for 1 hour (Fig. 2). The difference between the % γ with and without grinding becomes smaller in the samples aged for long periods (24 h) at 560°C and 600°C, which suggests that the austenite is less unstable with these prolonged agings. A comparison between the curves of 600°C and 560°C in Fig. 1 shows that the austenite formed at 600°C is more unstable than that formed at 560°C, which is in agreement with the higher nickel content observed in the austenite formed at 560°C [5].

Fig. 1 also shows the % γ versus aging time at 650°C, with and without grinding. A part of the austenite formed

at this temperature has already transformed on cooling, since its nickel content must be less than 30% according to previous results [4]. As observed in samples aged at 560°C and 600°C, grinding before measurement also decreases the % γ in the surface layers (see Fig. 4). However, the increase of aging time does not reduce the instability of the austenite phase.

In many works a common simplification is adopted in the direct comparison method by considering equal scattering factors for both phases [9, 10]. However, as the chemical composition of both phases may be quite different in this case, the calculation of scattering factors should give more precise results. Table II shows examples of the chemical composition data used in the calculations of the atomic scattering factors at 560°C, 600°C and 650°C. The chemical compositions were compiled from references [5, 11, 12] and converted to atomic percentages. Table III shows the results of quantification comparing each pair of peaks of the samples aged at 560°C for 1 h, 4 h, 10 h and 24 h.

Fig. 5 shows the comparison between austenite quantification results obtained considering equal and different scattering factors in samples measured without previous grinding for 560°C, 600°C and 650°C conditions. In this case, the differences between values of austenite volumetric percentage (% γ) considering equals

TABLE III Quantifications comparing each pair of peaks of the samples aged at 560°C for 1 h, 4 h, 10 h and 24 h

N°	Planes to compare		Austenite (%) at 560°C			
	α	γ	1 h	4 h	10 h	24 h
1	110	111	6,80	16,80	28,35	27,23
2	200	200	5,79	24,19	33,35	26,42
3	211	220	8,44	18,30	17,42	32,43
4	220	311	4,35	12,18	25,74	38,00
5	220	222	—	8,93	26,68	31,88
6	200	111	7,55	22,38	35,67	24,50
7	211	111	7,63	22,49	32,00	25,68
8	220	111	7,26	14,74	32,17	35,59
9	110	200	5,20	17,41	26,30	29,27
10	211	200	5,86	24,30	29,80	27,65
11	220	200	5,57	16,05	29,96	37,94
12	110	220	7,52	12,82	15,06	34,20
13	200	220	8,35	18,21	19,91	31,08
14	220	220	8,04	11,77	17,53	43,43
15	110	311	4,06	13,26	22,43	29,32
16	200	311	4,53	18,79	28,84	26,46
17	211	311	4,58	18,89	25,59	27,70
18	110	222	—	9,76	23,29	24,06
19	200	222	—	14,06	29,85	21,56
20	211	222	—	14,14	26,54	22,64
Average value γ (%)			6,35	16,49	26,33	29,70
Error values (%)			$\pm 0,98$	$\pm 2,60$	$\pm 3,22$	$\pm 3,27$

and different scattering factors vary between 3 and 7%, depending on the aging time and temperature.

Now analyzing the variation of $\% \gamma$ as function of aging time in samples not previously grounded, it is found that the curves for 560°C and 600°C are similar in shape, but the increase of austenite is more intense and rapid at 600°C. Considering the direct comparison method with different scattering factors, the $\% \gamma$ increases converge asymptotically to 30% and 40% at 560°C and 600°C, respectively. In this way, the precipitation of austenite in the maraging steel class 300 at 560°C and 600°C can be mathematically described by equation (8), obtained

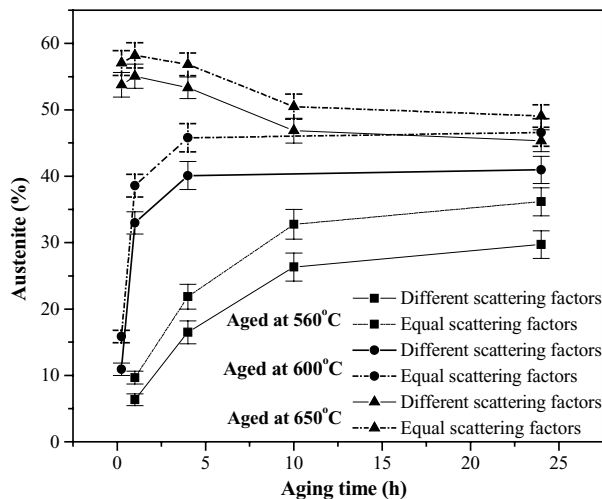


Figure 5 Austenite volumetric percentage versus aging time at 560°C, 600°C and 650°C obtained by the direct comparison method considering different and equals scattering factors, without previous grinding.

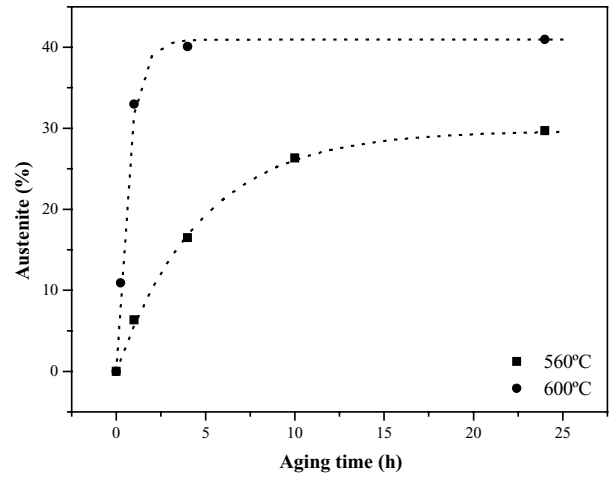


Figure 6 Fittings of the austenite volumetric percentage versus aging time curves at 560°C and 600°C.

TABLE IV Values of γ_{\max} and b .

Temperature [°C]	b	γ_{\max} (model)	γ_{\max}	R
560	-0.21	29.9	29.7	0.99
600	-1.49	40.8	41.0	0.99

through the fitting of exponential curves as shown in the Fig. 6:

$$\gamma(t) = \gamma_{\max} \cdot (1 - e^{b \cdot t}) \quad (8)$$

Where γ : percentage of austenite, γ_{\max} : maximum percentage of austenite in this condition, b : exponent negative of time, and t : aging time [h].

Table IV presents the values of the parameters γ_{\max} and b of the equation (8) and respective correlation coefficients for each aging temperature. The values of max obtained by the model and the experimental ones (also shown in the Table IV) are very close, which validates the model.

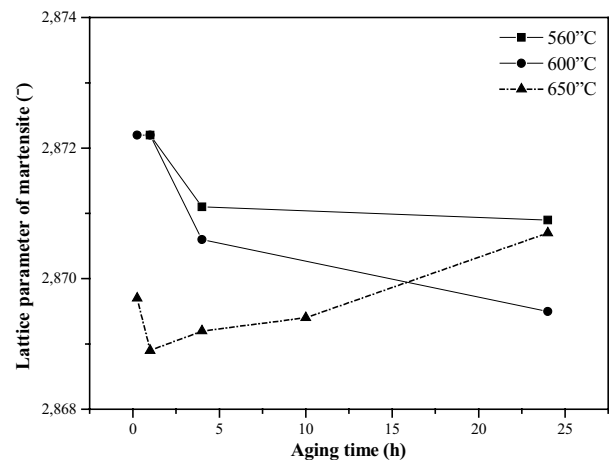
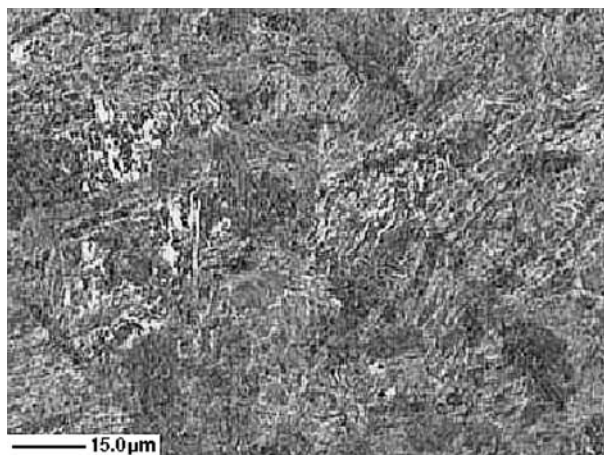
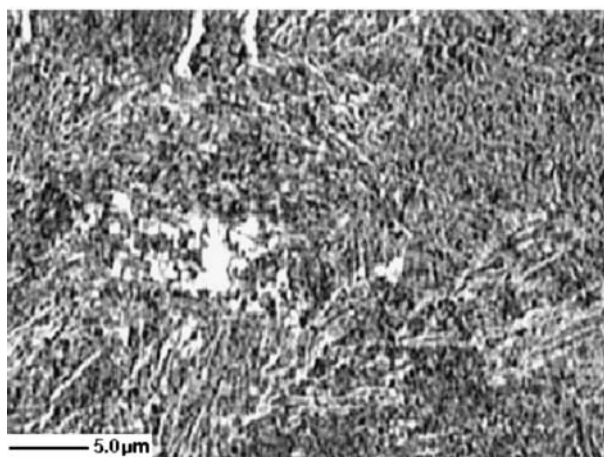


Figure 7 Lattice parameter of martensite phase versus aging time at 560°C, 600°C and 650°C.



(a)



(b)

Figure 8 Microstructure of the sample aged at 650°C for 1 h observed by optic microscopy: low (a) and high (b) magnification.

The behavior observed in samples aged at 650°C is quite different. According to the results of the direct comparison method, the austenite volumetric percentage increases and reaches a maximum value in an hour and then decreases with the increase of aging time. This decrease of the austenite content was observed by the two methods employed. This result must be analyzed in conjunction with the plot of martensite lattice parameter variation against aging time (Fig. 7). The decrease of lattice parameter at 560°C and 600°C was also observed by Habiby *et al.* [16], and is found to occur as consequence of the depletion of alloying elements in the martensite, while the amount of the Ni-rich austenite increases. On the other hand, the increase of the lattice parameter at 650°C after 1 h is due to the enrichment of alloying elements in the martensite phase as a consequence of the austenite retransformation in the cooling process. Thus, the increase of the martensite lattice parameter is related to the decrease of austenite content at 650°C. This result seems to be independent of cobalt content since it was also observed by Sinha *et al.* [10] in a Co-free maraging steel.

Some features of the methods of austenite quantification may be analyzed. Zhao *et al.* [17] compare the different techniques for austenite quantification in steels. According to them, optical microscopy (MO), scanning electron microscopy (SEM) and dilatometry give low accuracy. Figs 8a and b show the microstructure of the sample aged at 650°C for 1 h revealed by Picral modified etch. Austenite precipitates are revealed as light particles. Optical and scanning electron microscopies are very useful to show morphology and distribution of the reverse austenite. However, quantification using these techniques is very imprecise and difficult, since the reverse austenite of maraging steels is very fine and not uniformly distributed, as shown in Fig. 8a. Mössbauer spectroscopy and magnetization measurements give high accuracy. Mössbauer spectroscopy is usually applied to thin foils, which restrict its applicability to this problem. Quantification by magnetization measurements in maraging steels needs further investigation since the composition variations with temperature and time of aging cause important changes of the intrinsic saturation magnetization of the martensite phase. Neutron and X-ray diffraction (XRD) are classified as intermediate accuracy techniques. However, the XRD is the most applied method to austenite quantification in maraging steels.

4. Conclusions

The instability of the austenite phase by grinding with fine emery paper depends on the aging time and temperature. Austenite becomes more stable with prolonged agings at 560°C and 600°C. At 650°C the increase of aging time does not reduce the instability of the austenite phase.

The results obtained by the two methods of quantification are similar and show the same trends. However, the direct comparison method comparing all reflections against all and taking into account the chemical composition of both phases is the most accurate and precise method.

The curves of austenite volumetric percentage variation against aging time at 560°C and 600°C were similar in shape. Austenite increases with aging time and converges to about 30% at 560°C and to about 40% at 600°C. The behavior at 560°C and 600°C can be mathematically described by expressions of type $\gamma_{(t)} = \gamma_{\max} \cdot (1 - e^{-bt})$.

At 650°C the austenite amount decreases with aging time after 1 h. This result has relation to the martensite lattice parameter decrease, also observed in this work.

Part of the austenite formed at 650°C retransforms into martensite on cooling. This process turns the martensite richer in alloy elements increasing the lattice parameter of this phase.

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