25th ABCM International Congress of Mechanical Engineering
October 20-25, 2019, Uberlândia, MG, Brazil

COB-2019-1914
X- RAY DIFFRACTION STUDY IN MARAGING 300 AGED IN SEVERAL CONDITIONS

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Abstract. *The main aim of this work was performing a study of microstructural characterization by X- ray diffraction (XRD) in maraging 300 steel in distinct aging conditions. The austenite volume fraction precipitated versus aging time at 510, 560, 600 and 650°C were determined by using Rietveld Method through Fullproof ® free software. The change of martensite lattice, considering cubic and tetragonal structures, was also analyzed comparing with the residues (χ^2) obtained in each condition. The results obtained revealed similar austenite precipitation kinetics behavior, but with a greater amount in high temperatures and aging times in 510, 560 and 600°C interval. Additionally, it was noticed a decrease in the c/a ratio of the martensite lattice parameters, justified by the material aging kinetics and the elements segregation of the supersaturated martensite matrix. In addition, the analyses have shown the relationship between the aging kinetics progress with the dislocation density and the microstrain of the martensite matrix for each temperature. Finally, this work enabled a detailed microstructural characterization in this class of steel, being of great relevance for the evaluation of the mechanical and magnetic behavior during the processing of these materials.*

Keywords: *Maraging steels; Phase quantification; Lattice parameters; Dislocation density; Microstrain.*

1. INTRODUCTION

Commercial maraging steels are based on the Fe-18Ni-Co-Mo quaternary system and, when heat-treated, achieve remarkable ductility, toughness and ultra-high strength values. These qualities granting for this class an illustrious position in strategic industries such as military and nuclear purposes.

Due to the extra low carbon percentage, the martensitic matrix, in solution annealed condition is ductile body centered cubic structure (b.c.c) with up to 17% elongation with yield limit of 790 MPa (Rao, 2016). The strengthening effect is achieved by the substitutional precipitation of elements such as Ni, Ti and Mo (Habiby et al., 1996) during treatments in the 400-700°C range (Pardal et al., 2006), reaching high resistance limit values near to 2100 MPa (Rao, 2016). Aging treatments above 500°C dissolve precipitates such as Ni_3Mo, in the boundaries of the lath martensite, a phenomenon that causes a local Ni enrichment that enables the formation of austenite by a controlled- diffusion reaction (Viswanathan et al., 1993). The presence of austenite modifies the mechanical, electrical and magnetic properties of maraging steel (Vasudevan et al., 1990; Viswanathan et al., 2005; Tavares et al., 2003), being a subject for several scientific works.

The X- ray diffraction (XRD) technique enable identify presents phases in a material, with excellent precision, being widely used in material characterization works. In the matter of phase quantification, an accurate method is the Rietveld Method. It’s based on a theoretical fit to the experimental diffractogram by least squares method. In reason of using all the diffractogram obtained experimentally, this method is more accurate when compared with the internal standard method and the direct comparison method. However, this methodology requires knowledge of the approximate crystal structure and all phases of interest present in the mixture (Jenkins and Snyder, 1996).

In this paper, XRD study of maraging 300 steel was measured as function of aging temperature in the 510-650°C range. Two types of quantification by XRD were done and compared. The first one was considering b.c.c martensite microstructure. In the second type, martensite t.b.c was considered. An assessment of the fit quality (χ^2) parameter was made for each one of the two considerations and compared to determine the most accurate percentage of present austenite.

With all fit diffractograms with the lowest residues, it was possible to estimate the crystallite size (D), dislocation density (δ) and microstrain (ε) through the Scherrer relation on equation 1 and the Williamson-Smallman relations (Subhash and Dhaka, 2016) on equations 2 and 3, respectively:

$$D = \frac{K.\lambda}{FWHM_{hkl}.\cos(\theta_{hkl})} \tag{1}$$

$$\delta = \frac{1}{D^2} \tag{2}$$

$$\varepsilon = \frac{FWHM_{hkl}}{4.\tan(\theta_{hkl})} \tag{3}$$

Where:

K: Shape factor;

λ: Wavelength;

$FWHM_{hkl}$: Full width at half maximum in plane hkl (rad);

θ_{hkl}: Diffraction angle (°).

2. MATERIAL AND EXPERIMENTAL METHODS

The material used in this investigation was the maraging grade 300 with the chemical composition exhibited in Tab. 1. All sheet samples (20 x 10 x 2.5 mm thick) were solution annealed at 900°C for 40 min. Then, the samples were aged at 510, 560, 600 and 650°C for periods of time in the rage of 15 min to 24 h. The entire heat treatments that were done in this research were conducted in vacuum-sealed quartz tubes.

Table 1. Chemical composition of the received maraging 300 steel

Element	C	Ni	Mo	Ti	Al	Mn	Fe
wt%	0.01	17.86	4.84	0.76	0.14	0.01	balance

The X- ray diffractograms were obtained by using a PHILIPS® diffractometer model X'Pert Pro with CoKα radiation (λ=1.7901 Å). The analysis was executed at room temperature, with step-scanning of 0.02°, 3 s time per step and angular interval 45 – 125°. A spinner apparatus was used to minimize the effect of preferential direction as well as a divergence slit of 1°, to keep the beam completely on the sample surface in cases that were low incident angles.

For the initials approaches for the Rietveld Method, lattice parameters of martensite and austenite were calculated with the experimental data. All identified peaks from each phase were used in this determination. In austenite and martensite considered b.c.c structure, equation 4 was used (Cullity and Stock, 2013). On martensite considered t.b.c structure condition, the graphical method for indexing pattern of non-cubic crystals was implemented (Cullity and Stock, 2013; Klug and Alexander 1974) – based on equation 5 and applying the logarithmic.

$$a_{hkl} = d_{hkl}\sqrt{h^2 + k^2 + l^2} \tag{4}$$

$$\frac{1}{{d_{hkl}}^2} = \frac{1}{{a_{hkl}}^2}\left[(h^2 + k^2) + \frac{l^2}{(c/a)^2}\right] \tag{5}$$

For each identified peak was calculated the values of "a" and, in some cases, "c". In order to determine the most accurate lattice parameter, Nelson and Riley (1945) [$a_{hkl}\ vs\ \frac{cos^2\theta}{2}\left(\frac{1}{sin\theta} + \frac{1}{\theta}\right)$] and Cullity and Stock (2013) [$a_{hkl}\ vs\ cos\theta\ cotan\theta$] function associated with least square methods were used to fit a linear function. The mean value obtained by these two last functions, for each aging treatment condition, were used as the initial approaches.

The refinement of the crystalline structure was achieved by the FullProf® program (Rodriguez-Carvajal, 1998), considering Im–3m group for cubic and I4 for tetragonal structures. Austenite and martensite were considered with similar chemical composition, inferring that the absorption coefficient of each phase were almost equal.

The Full width at half maximum (FWHM) was obtained by the equation 6 (Cagliotti et al., 1958).

$$FWHM_{hkl}^2 = U.tan^2(\theta) + V.\tan(\theta) + W \tag{6}$$

3. RESULTS AND DISCUSSION

Nunes et al. (2015) considered the cubic structure for all heat treatment conditions in their quantifications and suggested that the martensitic phase stabilizes with another structure. However, Nunes et al. (2017) did the same analyzes, but in this case with a tetragonal structure for all the aging conditions. Thus, in this work, analyses of χ^2 residues obtained in the Rietveld Method for each heat treatment condition with the assumption of cubic and tetragonal martensite structure were done.

For initials aging times the residues of both premises were close. However, for the prolonged ones, the residues of the martensite considered with tetragonal structure were lower, indicating a structural change as shown in Figure 1 (a), (b), (c) and (d).

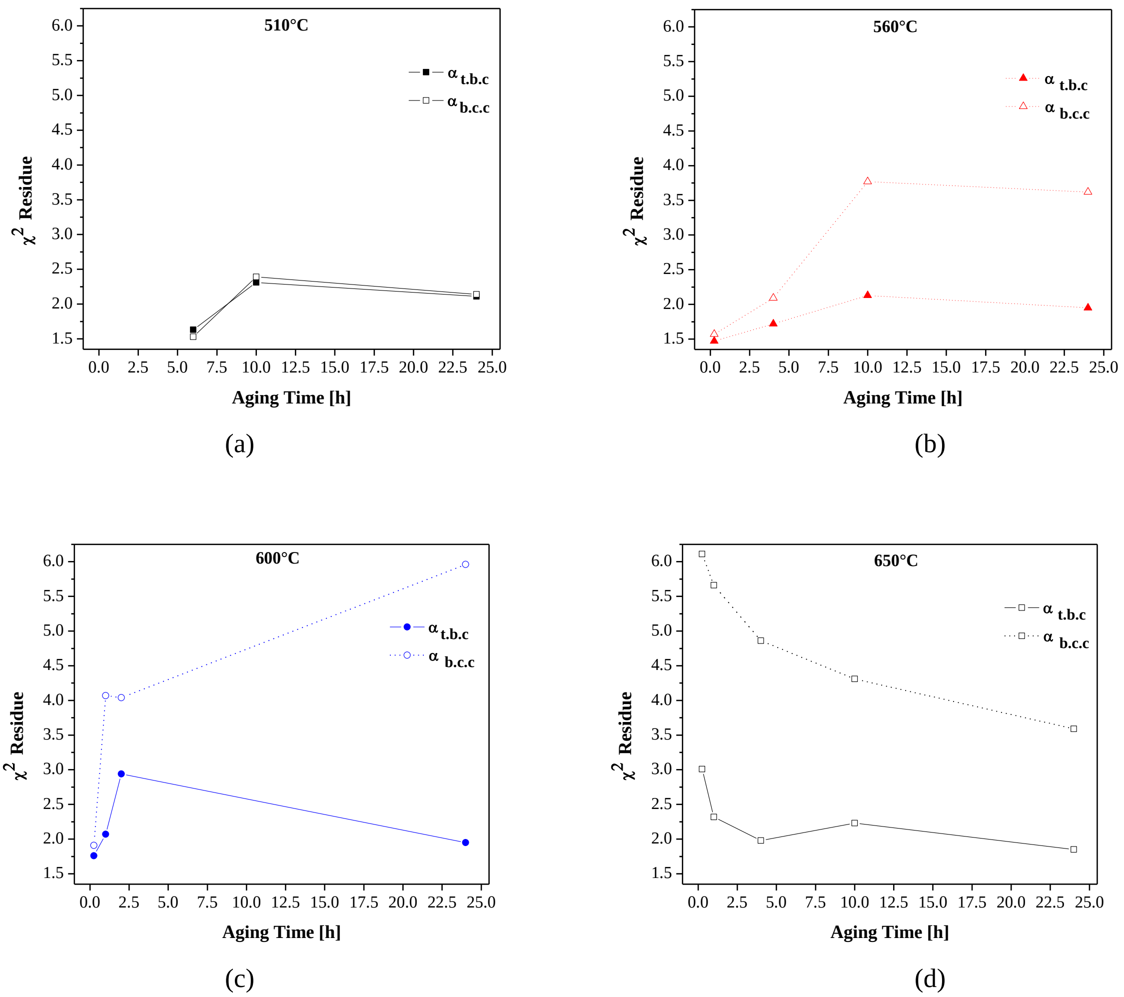


Figure 1. χ^2 residues comparison for aging treatments at: (a) 510°C, (b) 560°C, (c) 600°C and (d) 650°C.

Regarding the results of χ^2, with the lower residues, Figure 2. shows the volume of austenite quantified in each aging condition. An initial increase in these values was noticed followed by a decrease. This fact was evidenced at 510, 560 and 600°C conditions. Therefore at 650°C conditions, this bias wasn't so visible, reasoned by the accelerated phase precipitation kinetics.

At first, curves appear to have behavior fit by exponential function. However, repetition of tests is needed for larger statistical sampling and more conclusive statements.

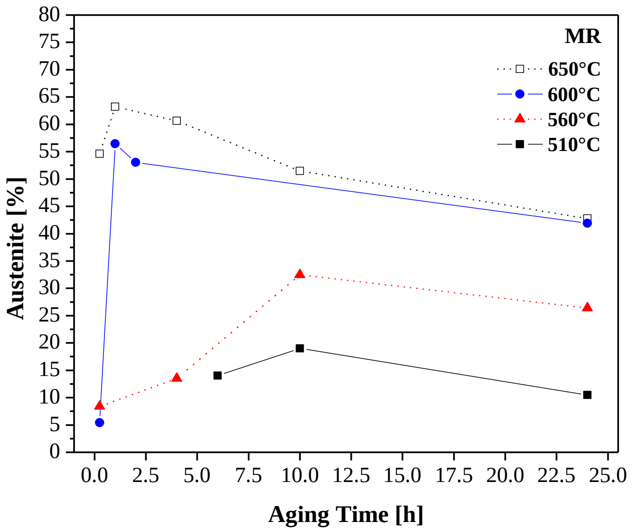
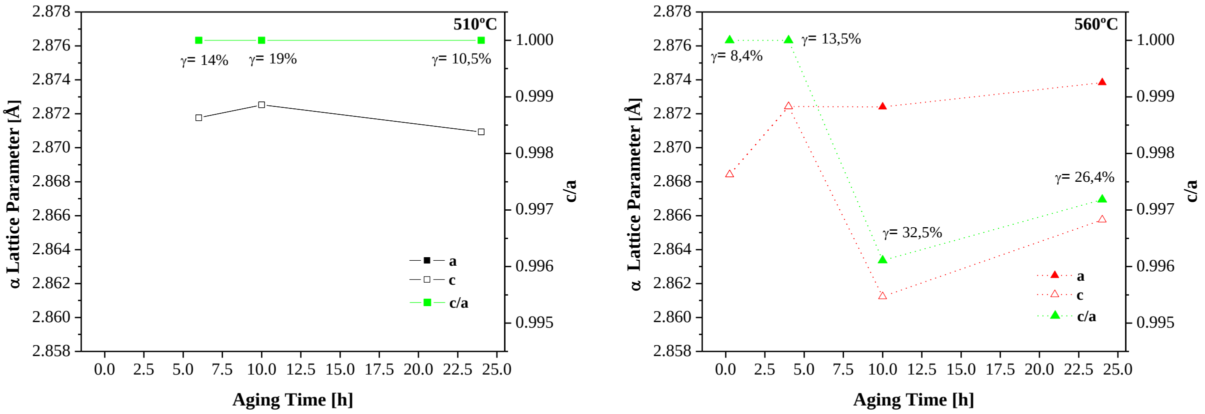


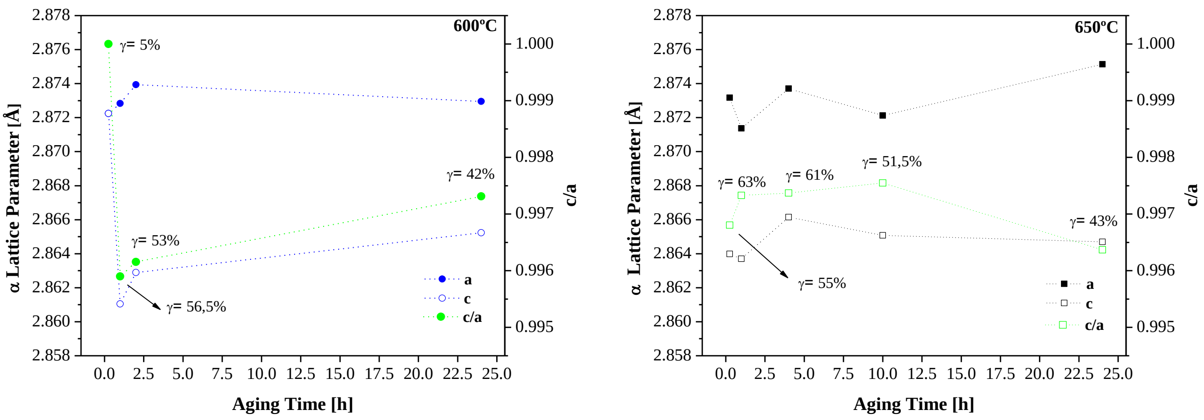
Figure 2. Volume of austenite quantified considering the lowest residues in all conditions.

Due to structure change phenomena, comparisons graphs were constructed relating the volume of austenite, "a" and "c" parameter and the c/a ratio. At 510, 560 and 600°C conditions (Fig. 3 (a), (b) and (c)) denoted the same particular behavior. Underneath a specific range of value of austenite volume, martensite can be considered cubic structure without losses of precision. Above this range, austenite volume and c/a ratio of martensite comported inversely proportional manner.

As well as noticed by Nunes et al. (2017), the "a" parameter didn't vary significantly. Nevertheless, "c" parameter suffered a strong variation in function of the aging conditions. Instead of the other conditions, 650°C (Fig 3. (d)) didn't present a specific bias, probably because of the reversion of a part of austenite in martensite.



(a) (b)



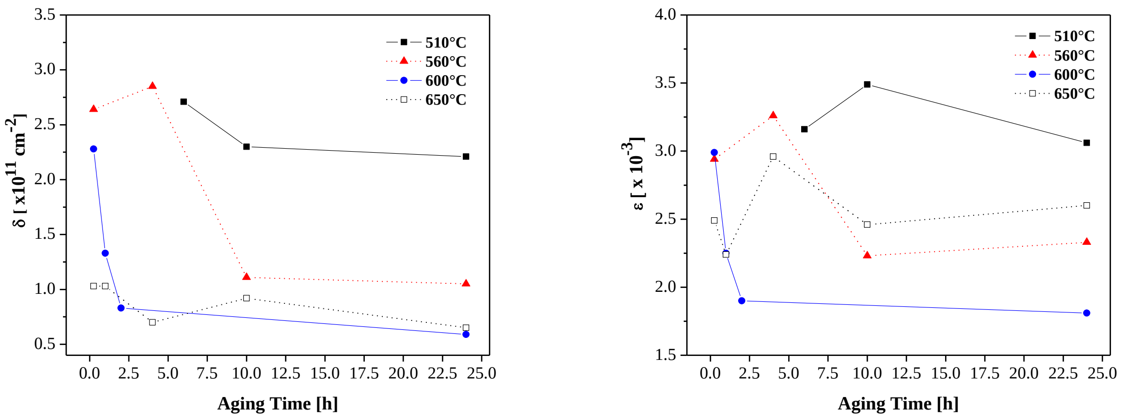
(c) (d)

Figure 3. Relationship between α lattice parameters, the c/a ration and the volume of austenite for aging conditions at: (a) 510°C, (b) 560°C, (c) 600°C and (d) 650°C.

Figure 4. (a) illustrate that the dislocation density in martensite matrix is higher in aging conditions at 510°C as well as in initial conditions at 560°C. Was observed an intense decrease in the range between 10 and 24 h at 560°C, the same behavior was notice between 15 min and 2 h at 600°C. At 650°C conditions dislocation density exhibited low values, regardless of the aging time, explained by the intense alloy elements segregation.

Figure 4.(b) shows the relationship between the microstrain of martensite matrix and the aging condition. At 510°C conditions values of microstrain stay high, caused by the precipitation of intermetallics compounds that strain the lattice. However, at 560 and 600°C there was a strong bias to decrease the values, explained by the presence of incoherent precipitates on the matrix. At 650°C an intermediate behavior was noticed.

Even adopting a crystallite size estimative methodology different from that used in this work, the calculated values for this parameter were close to those determined by Macek et al.(1996) in their analysis on maraging steel.



(a) (b)

Figure 4. Relationship between dislocation density (a) and microstrain (b) for the martensite for all aging conditions.

4. CONCLUSION

Analyzes of the residues obtained in the Rietveld Method was essential to answer some questions about the structure of the martensite during aging treatments. As a result of this work, the outcome was that in initial conditions of aging – where there weren't a great amount of austenite– the martensitic phase is considered as cubic structure. As long as there were more amount of austenite and precipitates the martensite acquires the tetragonal structure. It's relevant to emphasize that the c/a ratio of martensite lattice parameter was less than the unity, denoting a retraction of the c parameter. This fact is explained by the diffusion of the alloy elements of the matrix to constitute the precipitates and the austenite phase.

Standed on these facts, the volume of austenite was quantified in each aging condition. Apparently, curves have behavior fit by exponential function as noted by Pardal et al., 2006. Nevertheless, repetition of tests is needed for larger statistical sampling, and to plot graphs with error bars and say if in prolonged aging times the volume of austenite decrease or have an asymptotic bias.

In the case of the dislocation density of the martensite, was noticed a decrease, depending on the aging time, a product of the precipitation phenomena. However, the microstrain exhibits similar behavior, except in aging at 650°C, where reversal effects of austenite on martensite may result in an intrinsic behavior for this condition.

5. ACKNOWLEDGEMENTS

The authors acknowledge the Brazilian research agencies (CAPES, FAPERJ and CNPq) for financial support.

6. REFERENCES

Cagliotti, G., Paoletti, A., Ricci, F. P., 1958. "Choice of collimators for a crystal spectrometer for neutron diffraction." Nucl. Instrum., Amsterdam, Vol.3, pp. 223-228.

Cullity, B. D. and Stock, S. R., 2013. "Elements of X-Ray Diffraction: Pearson New International Edition." 3rd ed. Pearson, p.656.

Habiby, F., Siddiqui, T. N., Hussain, H., Ulhaq, A. and Khan, A. Q., 1996. J. Mater. Sci., 31, pp. 305 – 309.

Jenkins, R.; Snyder, R. L., 1996. "Introduction to X-Ray Powder Diffractometry." Nova York: John Wiley & Sons, 432 p, Vol. 138 (Chemical Analysis).

Klug, H. P., Alexander, L. E., 1954. "X-ray diffraction procedures." Nova York: John Wiley.

Macek, K., Lukáš, P., Janovec, J., Mikula, P., Strunz, P., Vrána, M., Zaffagnini, M., 1996. "Austenite content and dislocation density in electron-beam welds of a stainless maraging steel." *Materials Science and Engineering: A,208*(1), 131-138. doi:10.1016/0921-5093(95)10047-4

Nelson, J.B., Riley, D.P., 1945. "An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals." Proceedings of the Physical Society. London, Vol. 57, n. 3, pp. 160-177.

Nunes, G. C. S., Sarvezuk, P. W. C., Biondo, V., Blanco, M. C., Nunes, M. V. S., de Andrade, A. M. H., Jr., Paesano A., 2015. "Structural and magnetic characterization of martensitic Maraging-350 steel" Journal of Alloys and Compounds, 646, pp. 321-325, ISSN: 0925-8388.

Nunes,G. C. S., Sarvezuk ,P. W. C., Alves, T. J. B., Biondo ,V., Vashita, F. F. I, Paesano Jr., A., 2017. "Maraging-350 steel: Following the aging through diffractometric, magnetic and hyperfine analysis." Journal of Magnetism and Magnetic Materials. Vol. 421, pp. 457-461.

Pardal, J. M., Tavares, S. S. M., Cindra Fonseca, M., Abreu, H. and Silva, J., 2006. "Study of the austenite quantification by X-ray diffraction in the 18Ni-Co-Mo-Ti maraging 300 steel." Journal of Materials Science, 41(8), pp.2301-2307.

Rao, M. N., 2006. "Progress in understanding the metallurgy of 18% nickel maraging steel." International Journal of Materials Research, Vol. 11, pp.1594-1607.

Rodriguez-Carvajal, J.,1998. "Short reference guide of the program FullProf®. Version 3.5." Laboratoire Léon Brillouin (CEA-CNRS), Paris, France.

Subhash, C. and Dhaka, M.S., 2016. "Impact of termal annealing on physical properties of vacuum evaporated polycrystalline CdTe thin films for solar cell application." Physica E. Vol. 80. pp. 62-68.

Tavares, S. S. M., Abreu, H. F. G., Neto, J. M., Da Silva, M. R., Popa, I., 2003. "A thermomagnetic study of the martensite and austenite phase transition in the maraging 350 steel." J Alloy Compd.

Vasudevan, V. K., Kim, S. J., Wayman, C. M., 1990. “Precipitation reactions and strengthening behavior in 18 wt pct nickel maraging steels.” Metall Trans. <https://doi.org/ 10.1007/BF02646061.>

Viswanathan, U. K., Dey, G. K., Asundi, M. K., 1993. “Precipitation hardening in 350 grade maraging steel”. Metallurgical Transactions A, Vol. .24, pp. 2429-2442.

Viswanathan U. K., Dey, G. K., Sethumadhavan V., 2005. “Effects of austenite reversion during overageing on the mechanical properties of 18 Ni (350) maraging steel.” Mater Sci Eng <https://doi.org/10.1016/j.msea.2005.03.074.>

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