# Effect of Hot Deformation on Microstructure, Hardness and Precipitation Kinetics in a C350 Maraging Steel Modified by Titanium Addition

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Maraging steels are alloys with a good balance between strength and fracture toughness. These properties are obtained by quenching and aging treatments, where the precipitation of intermetallic compounds is promoted in a martensitic matrix. In this context, this paper aims to evaluate the effect of hot deformation on microstructure, kinetics and formation of reverted austenite in a C350 maraging steel modified by titanium addition, in order to improve the mechanical properties without addition of alloying elements. The following characterization techniques were used: optical microscopy (OM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Vickers microhardness and Dilatometry. The results showed that the deformation promoted a refinement of martensitic packages and blocks, proportional to the reduction of height and a preferred alignment towards the center of the sample. In the aging treatment, the deformation accelerated the kinetics of precipitation and formation of reverted austenite. It was also verified a reduction of the volumetric variation produced by reactions and a reduction of precipitation temperature and formation of reverted austenite in the greater deformation.

**Keywords:** *Maraging, hot deformation, precipitation, reverted austenite, precipitation kinetics.*

## 1. Introduction

Maraging steels present high strength and good fracture toughness, allowing its use in a wide range of applications. Other important characteristics to be considered are: good conformability, good machinability and resistance to corrosion[1]. Despite their excellent properties, their applications are justified when the cost of the alloys is less important than their mechanical properties. The mechanical properties of these materials are obtained by the precipitation of intermetallic compounds in the matrix during the aging treatment. However, for long aging times, the formation of reverted austenite occurs, resulting in a reduction of hardness, characterizing the overaging process[1-4].

The plastic deformation of austenite before the martensitic transformation in maraging steels promotes a change in the microstructural units of the martensite, a fact that is related to the dynamic or static recrystallization of the austenite. As the deformation increases, the sizes of the packages increase while the width of the blocks decreases[5]. Blanter, Kovaleva and Tiskovich[6] studied a maraging steel and showed that either cold or warm deformation improve the tensile strength. In a maraging C300, Güiza[7] showed that the hot deformation produced a significant refinement of the microstructure and accelerated the precipitation kinetics. He also reported that the deformation promoted changes more intensely when the martensitic transformation occurs from the non-recrystallized austenite. The following changes were

described: refinement of the martensitic microstructure and acceleration of the formation of precipitates and formation of reverted austenite during aging. Güiza observed that the deformation promoted an increase in hardness that decreases gradually during aging, what was justified by the recovery mechanism. Also, studying maraging steels, Jha *et al*.[8] showed that hot working can be used to improve the fracture toughness by redistributing the carbonitrides formed during solidification and prevents the formation of new inclusions during solution treatments.

Thus, deformation has been shown to be a promising process to improve the maraging steel properties by accelerating the obtained of the peak hardness during the aging and consequently reducing the time of the heat treatment. As reported by many authors[5,9], the thermomechanical process promoted good improvements on maraging steel, therefore, it should be considered, taking into account that in a large scale is more advantageous than increasing the addition of alloying element.

In this context, in order to improve the mechanical strength of these steels without increasing their manufacturing cost with the addition of alloying elements, an alternative that has been studied is the hot deformation, a process that may be able to modify the microstructure, accelerate the precipitation kinetics and improve the mechanical properties. This paper describes the effect of hot deformation in the microstructure, hardness and precipitation kinetics in a C350 maraging steel modified by titanium addition.

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## 2. Materials and Methods

Prismatic test samples made from a disc of 18Ni C350 maraging steel manufactured by vacuum induction melting and vacuum arc remelting (Table 1), subsequently being sectioned in a cut-off machine and machined to the dimensions showed on Fig. 1. Then, they were deformed by uniaxial compression without lubrication in a 150 Ton friction drive screw press following the conditions shown in Table 2. Right after the deformation, samples were quenched in water, after that all samples were cut in small pieces, which were characterized in either the as deformed state, or after aging for 1, 5, 7,5, 10, 25 and 40 hours at 500 ºC and for 10, 30 min, 1, 5 and 10 hours at 550 ºC. For characterization, the samples were metallographically prepared following the procedures of the ASTM E3 standard, and chemically etched following the guidelines of the ASTM E407 standard, with modified fry etchant (50 ml of HCl, 25 ml of $HNO_3$, 1 g of $CuCl_2$ and 150 ml of $H_2O$) to the optical microscopy and microhardness measure, marble (4g $CuSO_2$, 20 ml HCl, 20 ml $H_2O$) to TEM analysis and chromic acid (10 gr $CrO_3$, 90 ml $H_2O$) to measure the grain size by linear intercept method. The characterization methods used are described in Table 3.

## 3. Results and Discussion

### 3.1 Dilatometry

The dilatometric curves showed a typical behavior of the maraging steels with two inflections during heating, the first one between 480 ºC and 600 ºC corresponding to the precipitation of intermetallics, and the second one between 640 ºC and 750 ºC corresponding to the austenitic transformation[11]. During cooling, a variation was observed at approximately 200 ºC equivalent to the martensitic transformation (Fig. 2).

In order to obtain the maximum reaction rate temperatures, the derivatives of dilatometrics curves were calculated (Fig. 3). These curves showed two well defined peaks, the first one at 524 ºC related to the precipitation of intermetallics, and the second one at 664 ºC related to the formation of austenite. A third region that was observed is an irregularity between 700 ºC and 750 ºC, which decreases with the deformation. Others authors found in this region well defined peaks and related to the adifusional stage of austenite formation[10,11].

In deformed samples, two changes were observed, the first one, a reduction of the volumetric variation produced by reactions, and second one, in the 60% deformed samples,
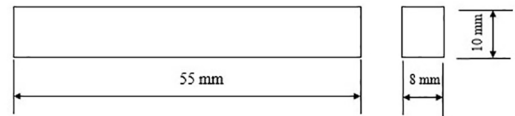


**Figure 1.** Dimensions (mm) of the samples used in this study.

**Table 2.** Experimental conditions and number of samples used.

| Temperature (ºC) | Deformation (%) | | |
|---|---|---|---|
| | 0 | 30 | 60 |
| 950 | 2 | 2 | 2 |
| 1050 | 2 | 2 | 2 |

a reduction of temperature of maximum rate of precipitation and austenite transformation. The reduction of contraction was also reported by others authors, on cold-deformed C350 maraging steel samples[12] and in a hot-deformed C300 maraging steel[13]. This alteration was justified by them to the anomalies of expansion as a consequence of the texture induced by deformation.

### 3.2 Microstructural analysis

The non-deformed samples showed a homogeneous martensitic microstructure with the morphology of laths, blocks and packets (Fig. 4), a typical characteristic of maraging steels[14].

Furthermore, the blocks and packet sizes in the samples solutionized at 1050 ºC were larger than the ones solutionized at 950 ºC. The results of linear intercept measuring of previous austenite (Fig. 5) showed that the samples solutionized at 1050 ºC previous austenite grain size significantly larger than the ones solutionized at 950 ºC, 130 µm against 54 µm.

About the effect of deformation, it produced several changes on the microstructure. First of all, due to the friction between matrix and samples was observed a profile in the microstructure as described by Dieter[10], with non-deformed regions in the top and bottom, moderate deformation zones on the sides and a central concentrated shear. The deformation promoted a refinement of the size blocks of the martensite and a preferred alignment of the microstructure towards the center of the samples, this were observed more intensely in the greater deformation (Fig. 6).

**Table 1.** Chemical composition of the material.

| % Wt. | Ni | Co | Mo | Ti | C | S | Fe + impurities |
|---|---|---|---|---|---|---|---|
| Sample | 17.76 | 11.61 | 4.89 | 2.03 | 0.016 | 0.013 | Balance |
| 18Ni C350 | 18 - 19 | 11.5 – 12.5 | 4.5 – 5.2 | 1.3 – 1.6 | Máx. 0.03 | Máx. 0.010 | Balance |

**Table 3.** Characterization techniques employed.

| Technique | Description |
|---|---|
| Dilatometry | A Netzsch DIL 402C dilatometer was used to evaluate the effect of deformation in the temperatures of phase transformation, precipitation and formation of reverted austenite in samples solutionized at 1050 °C. Was heating rates used was 10 °C/min. |
| Optical microscopy | The microstructure was observed by a Olympus BX60 optical microscope with a Leica EC3 camera, the images were processed using the ImageJ software. |
| Scanning electron microscopy (SEM) | A Jeol JSM-6390LV microscope was employed in order to complement the analysis of the martensite morphology. |
| Transmission electron microscopy (TEM) | A JEM-1011 TEM microscope was used to identify crystallographically and morphologically the precipitates present in the samples solutionized at 950 °C, non-deformed and 60% deformed, aged for 7.5 and 40 hours at 500 °C. |
| X-ray Diffraction (XRD) | A Philips X´Pert Pro diffractometer, with Cu kα radiation ($\lambda = 1.5406$ Å) was employed, with intensity measurements taken every 0.02° in the range between $30° < 2\theta < 120°$. Was used in the identification and quantification of the reverted austenite in non-deformed samples and 60% deformed aged for 1 and 10 hours at 550 °C. After the measurements were made, the diffraction patterns were refined by the structural Rietveld method using the GSAS with EXPGUI software and the angular positions and intensities of the peaks were compared with those given in the ICSD 632934 and 632930 for the martensite and austenite phases. |
| Hardness Testing | A Shimadzu HMV2 microhardness tester with a load of 1kgf, according to ASTM standard. In the deformed samples, the measurements were made in concentrated shear regions formed by the compression as shows in Dieter[10] and in the non-deformed samples were taken randomly. |
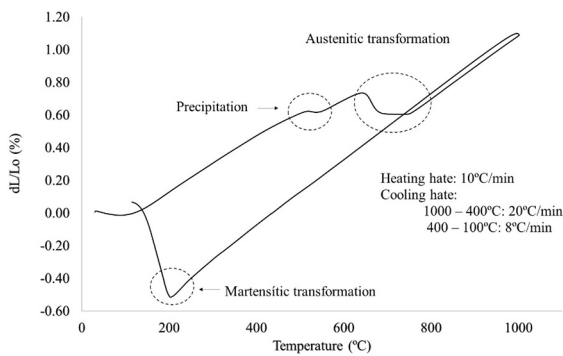


**Figure 2.** Dilatometric curve of non-deformed sample solutionized at 1050 °C.
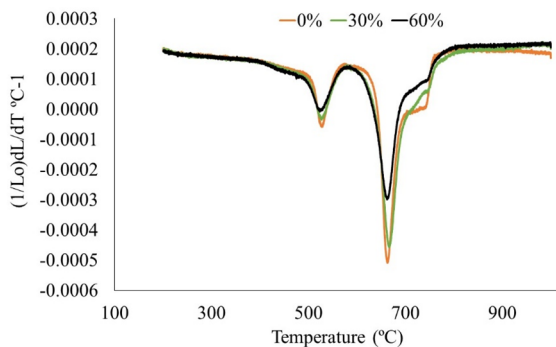


**Figure 3.** Derivatives of the dilatometric curves.

In 30 % deformed samples a microstructure composed of blocks with refined width in the specimens deformed both at 950 °C and 1050 °C (fig. 7) was found. In the 60% deformed samples, were observed microstructures with larger shear bands on the sides and narrower ones in the central region (Fig. 8), this was similar to that found by Güiza in a C300 maraging steel[7]. It was noticed that even after the deformation, the blocks and packets of the samples deformed at 1050 °C kept larger than ones deformed at 950 °C.

## 3.3 Precipitates

After aging for 7.5 h at 500 °C, TEM dark field images show the reflection of the crystallographic planes (201) and (112), characteristic of spheroidal precipitates and in the dark field of reflection of crystallographic planes (107) and (201) needle-like precipitates (Fig. 9). The results of measurements of the interplanar spacing of the spherical particles were similar to $Fe_2Mo$, with lattice parameters a = 0.473 nm and c = 0.772 nm, and the needle-like to the $Ni_3Ti$ with a = 0.5101 nm and c = 0.83067 nm, both phases with hexagonal structures. These precipitates were also founded and studied by others authors at many aging temperatures[15-19].

Increasing the aging time to 40 hours, were found precipitates with dense dispersion through the matrix. Qualitatively, it was possible to observe that the fraction of these intermetallics increased significantly, what was already expected, since the kinetics is strongly influenced by treatment time. About the morphologies, as well as in early condition, precipitates were also found in needle-like and spheroidal, the spheroidal ones were found in the reflection of crystallographic planes (220) and (201), and continued to be indexed as $Fe_2Mo$ (Fig. 10 - a, b and c), and, the needle-like ones were found in the reflection of crystallographic planes (107) and (300) as $Ni_3Ti$. The $Ni_3Ti$ precipitates observed in the dark field of crystallographic plane (300) were found segregated and aligned, as shown in Fig 10 - d.
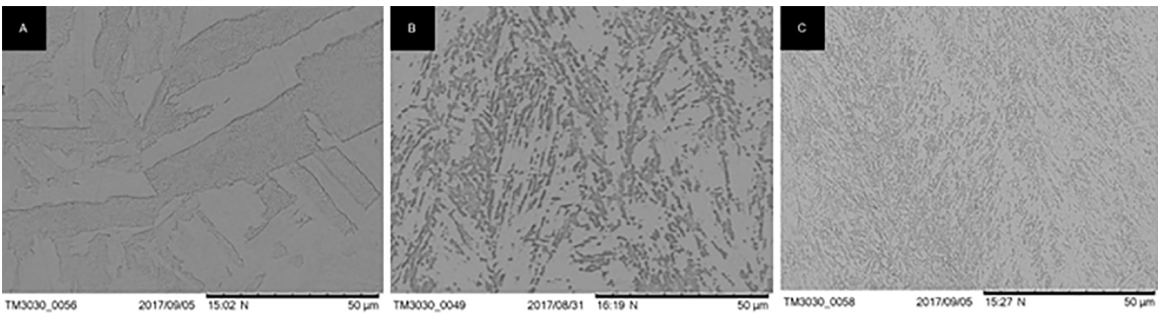
## 3.4 Reverted austenite

By SEM analysis rich regions of reverted austenite in non-deformed samples aged for 10 hours were found (Fig. 11),
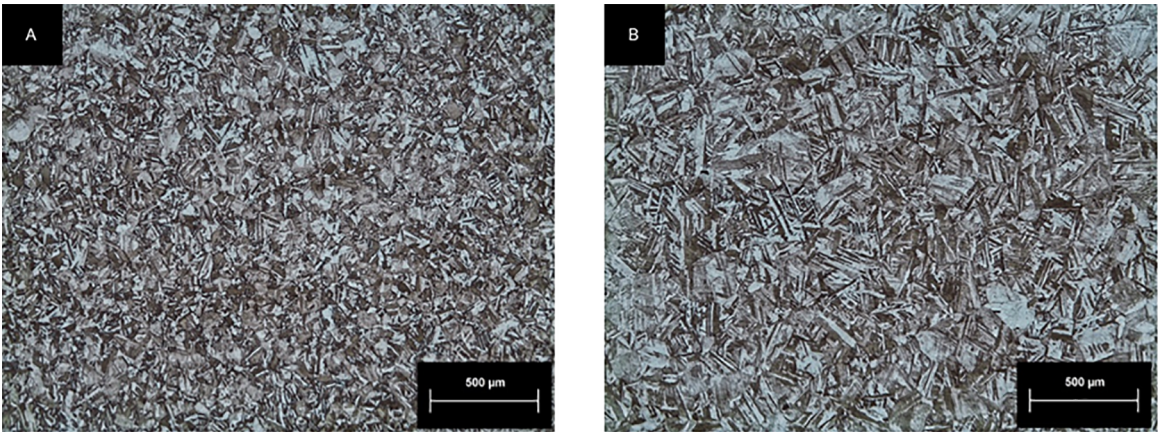
**Figure 4.** Blocks and packets morphology found in the non deformed samples. Solutionized at: a) 950 ºC and b) 1050 ºC.
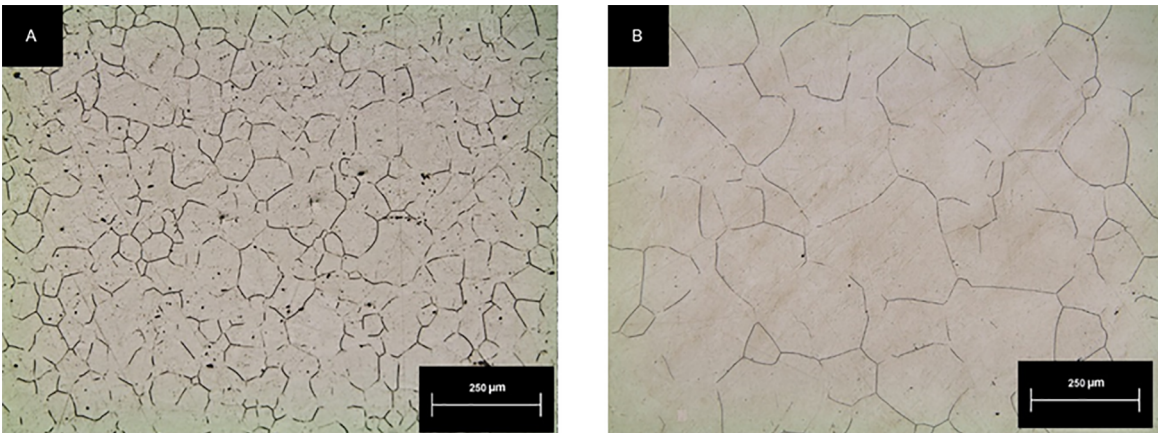


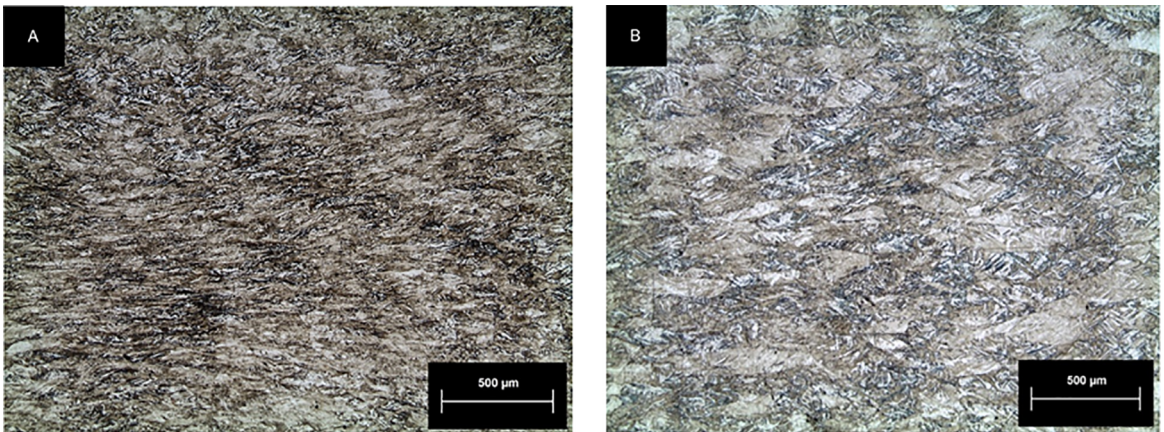**Figure 5.** Grain size of the non deformed samples. Solutionized at: a) 950 ºC and b) 1050 ºC.



**Figure 6.** Effect of hot deformation on microstructure of samples solutionized at 1050 ºC. Condition: a) non-deformed samples, b) 30 % deformed and c) 60 % deformed.

that wasn't found in the Rietveld refinement. The refinement of the diffraction pattern just showed reverted austenite in 60 % deformed samples aged at 550 °C for 10h, 8.2 %, the other conditions showed only the martensite (Fig. 12), this shows that the deformation had an important role in the formation of reverted austenite found in the steel. The angular positions and intensities of the peaks were compared with those given in the ICSD 632934 and 632930 for the martensite and austenite phases, respectively, and an excellent agreement was observed (Table 4). Regarding the morphology,

reverted austenite was observed in ribbons between blocks and packets. At this temperature, Li[20] also found in a C350 maraging steel, a greater amount of reverted austenite, the less quantity found in this paper may be due to the higher content of titanium, which affect the enrichment of nickel in the matrix retarding the formation of reverted austenite.

### 3.5 Hardness

Before aging, the deformation promoted a gradual increase in hardness proportional to the reduction of height,

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**Figure 7.** Effect of 30 % hot deformation in the microstructure. Solutionized at: a) 950 ºC and b) 1050 ºC.
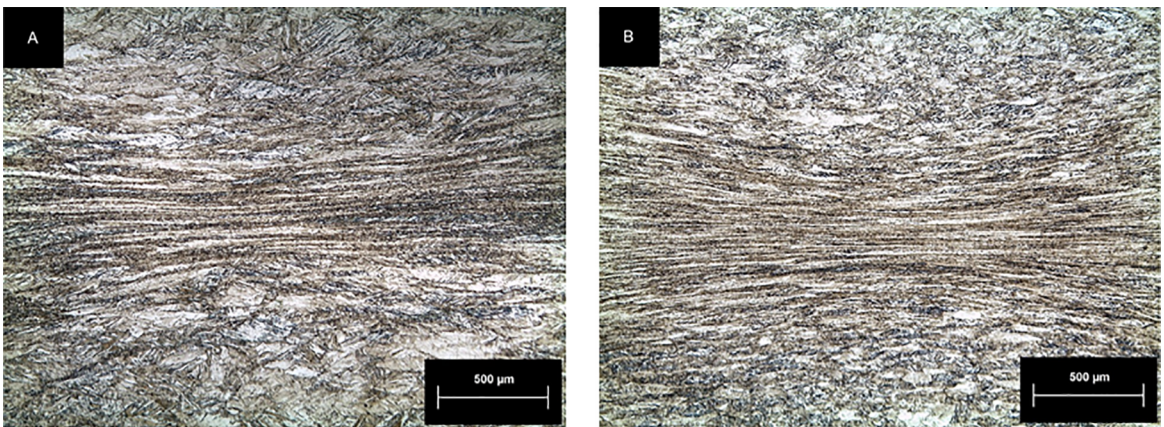


**Figure 8.** Effect of 60 % hot deformation in the microstructure. Solutionized at: a) 950 ºC and b) 1050 ºC.

as greater the deformation, greater was the increase in hardness. (Fig 13). The hardness increase in the samples deformed at 950 ºC was approximately 13% and in the 1050 °C, 8%. This difference is justified by the larger grain size of the 1050 ºC solutionized samples.

It is noted in the Fig. 13 that there wasn't difference of hardness between the non deformed samples solutionized at 950 and 1050 ºC, it can be related to the competition between the mechanisms of solid solution hardening and grain boundaries hardening.

As reported by others authors[7,15,16,17], the behavior of maraging steel during the aging is a hardness increase until reaching a peak followed by an overaging. In this paper, the non-deformed samples solutionized at 950 ºC, aged at 500 ºC presented a hardness increase up to 5 hours, followed by a plateau up to 25 hours. In the deformed samples, the hardness increase was verified up to 1 hour, also followed by a plateau up to 25 hours (Fig. 14 - a), so it wasn't found an overaging at this temperature. To see if rising the time of aging an overaging would occur, one more sample was tested and it was observed that up to 40 hours there wasn't an overaging. In this condition, it was observed that the deformed specimens had superior hardness in the initial

periods and similar in the posterior regions, this is related to the continuous recovery of the substructure of dislocations during aging[7]. In the samples deformed at 1050 ºC, it wasn't observed a significant effect between the conditions related to deformation up to 10 hours, this can be explained by the recrystallization at this temperature. The behavior of all conditions was a hardness increase up to 7.5 hours, followed by a plateau up to 40 hours. Just in the 60% deformed samples was observed a significant decrease of hardness from 10 hours, which indicates that the deformation accelerates the kinetic of formation of reverted austenite (Fig. 14 - b).

Increasing the aging temperature to 550 ºC, samples deformed at both temperatures, 950 ºC and 1050 ºC, had the same behavior. In non-deformed samples, there was a hardness increase up to 1 hour, followed by an overaging, and, in the deformed samples, there was a quick hardness increase until reaching the peak at 17 minutes, a plateau up to 1 hour and finally the hardness fall characterizing the overaging (Fig. 14 - c and d).

Comparing the hardening response of the material in this study with the literature[21], it was clear that the higher titanium content promoted a faster hardening due to the precipitation of $Ni_3Ti$ earlier. At 500 ºC, the authors found
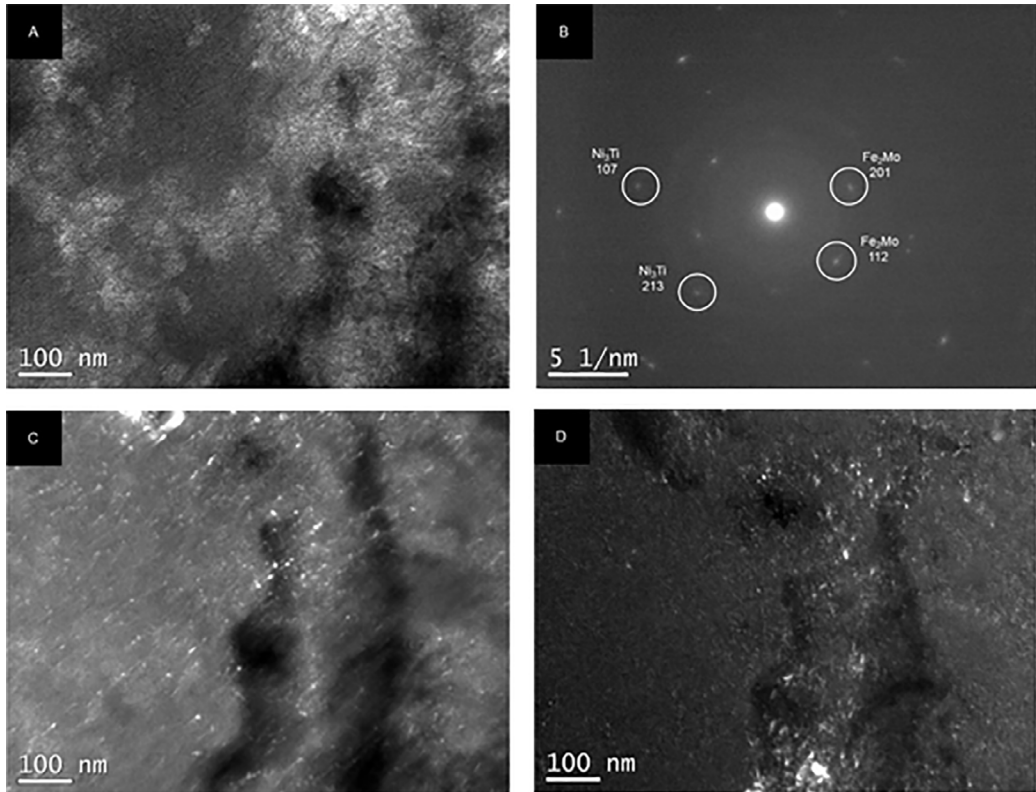
**Figure 9.** Precipitates found in non-deformed samples solutionized at 950 ºC aged at 500ºC for 7,5 hrs. a) Bright field, b) Diffraction pattern, c) Fe$_2$Mo precipitates in the dark field of the reflection of crystallographic plane (201) and, d) Ni$_3$Ti precipitates in the dark field of the reflection of crystallographic plane (213).
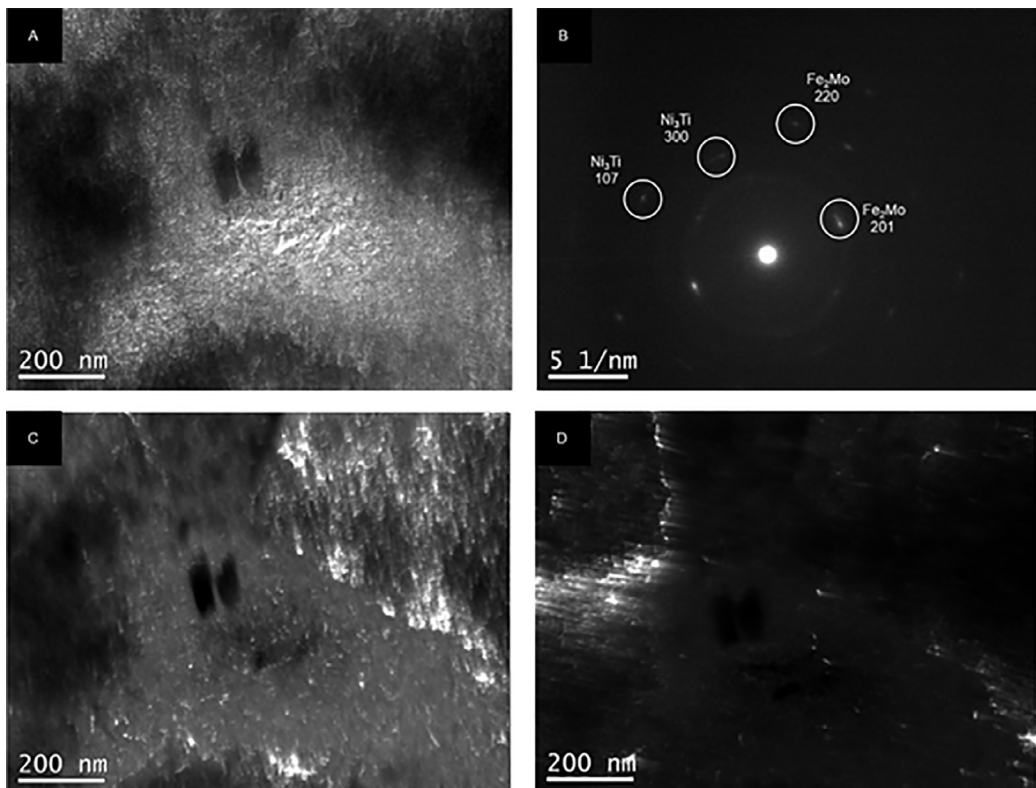


**Figure 10.** Precipitates found in non-deformed samples solutionized at 950 ºC aging at 500ºC for 40 hrs. Forming conditions: a) Bright field, b) Diffraction pattern, c) Fe2Mo precipitates in the dark field of the crystallographic plane (201), d) Ni3Ti precipitates in the dark field of the crystallographic plane (300).

the peak hardness in usual C350 maraging steel within 3 hours, whereas at 550 °C, the maximum hardness was attained in 30 minutes.
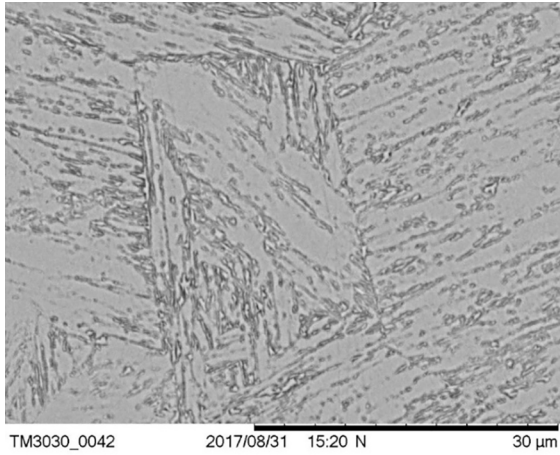


**Figure 11.** Reverted austenite around the prior grain boundaries and between blocks and packets in non-deformed samples aged at 550 ºC for 10 hours.

## 4. Conclusion

The results showed that the hot deformation promoted a refinement of martensitic packages and blocks with a preferred alignment directed towards the center of the sample. The deformation also increased the hardness proportionally to the reduction of height, with a maximum increase of approximately 13% in the material deformed at 950 ºC and 8% at 1050 ºC.

After aging, two types of precipitates were found, $Ni_3Ti$ and $Fe_2Mo$, both with hexagonal structures. It was notice that the thermomechanical processing accelerated the precipitation kinetics and the formation of reverted austenite. At 500 °C the deformed specimens showed superior hardness in the early stages, what is related to the continuous recovery of the substructure of dislocations during the treatment. Increasing the temperature of aging to 550 ºC, it was observed that the deformation accelerated the obtained of the peak hardness. By XRD diffraction, reverted austenite was just found in 60 % deformed samples aged at 550 ºC for 10 hours, 8.2 %. This shows that the deformation accelerates the formation of reverted austenite found in maraging steels.
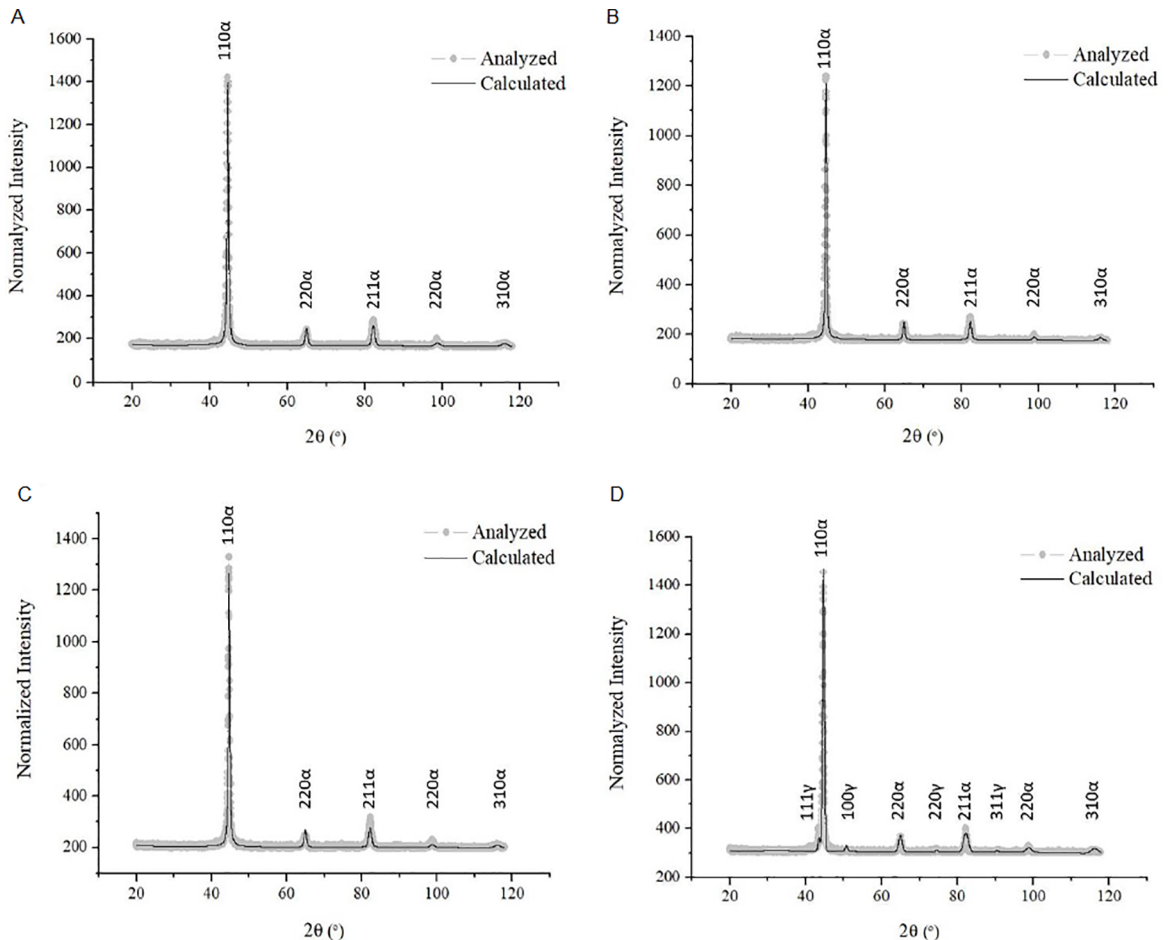


**Figure 12.** XRD patterns obtained in the samples aged at 550 °C. Conditions: non-deformed samples (a, b). 60 % deformed samples (c, d). Aging times: a, c - 1 hr.; b, d - 10 hrs.

**Table 4.** Convergence parameters obtained by Rietveld refinements of diffraction pattern.

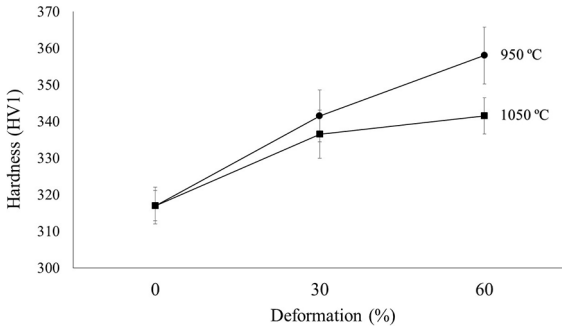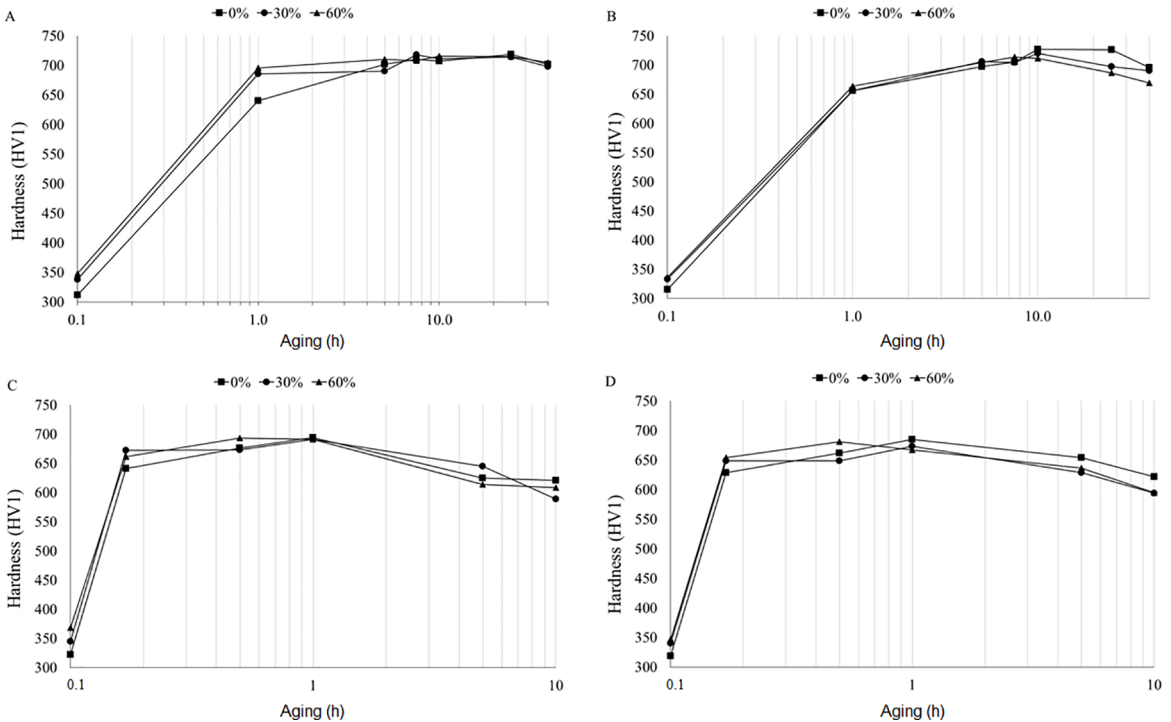| Deformation | 0 % | | 60 % | |
|---|---|---|---|---|
| Time | 1 hour | >10 hours | 1 hour | 10 hours |
| **a (Å) CIF code** | a = b = c = α=2.8707 and γ=3.5491 | | | |
| **a (Å)** | 2.8758 | 2.8724 | 2.8742 | α=2.8725 γ=3.6045 |
| **wRp** | 0.2754 | 0.3166 | 0.3019 | 0.0328 |
| **Rp** | 0.1770 | 0.2113 | 0.2002 | 0.0150 |
| **Chi**2** | 1.325 | 1.357 | 1.393 | 0.339 |

Other changes induced by deformation were: a reduction of the volumetric variation produced by reactions and a reduction of temperature of the maximum rate of precipitation and austenite transformation in 60 % deformed samples.

From the results obtained in this study it's clear that hot deformation is a process that is capable of improving the properties of maraging steels without increasing the addition of alloying elements. Since the hardness increase provided by the deformation before aging treatments and the acceleration of the reaction in the aging can help to reach the desirable properties.

# 5. Acknowledgements

**Figure 13.** Effect of hot deformation on hardness before aging.



**Figure 14.** Age hardening observed in the samples aged at 500 ºC (a, b) and 550 ºC (c, d). Solutionized at: 950 ºC - a, c; 1050 ºC - b, d.

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