Structural characterization of iron oxide grown on 18% Ni-Co-Mo-Ti ferrous base alloy aged under superheated steam atmosphere

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Abstract
18% Ni-Co-Mo-Ti ferrous base alloys are special materials, widely used in the industry of isotopic enrichment after specific annealing and aging thermal treatment. The desirable high mechanical properties can then be attained by adequate aging heat treatment, answering the structural materials specifications required by defense applications in aerospace and nuclear engineering. For instance, the isotopic enrichment, in rocket engine envelope application, when associated with high temperature and chemical residues like acidic solutions, can induce corrosion and hydrogen embrittlement in martensitic microstructure. In order to limit these corrosion and hydrogen embrittlement phenomena, adherent and protective layers of iron oxides can be grown on the material’s surface by performing aging treatment in an adequate atmosphere. Due to its application in strategic areas, the characterization of these oxide layers in maraging steels is of importance as well as the understanding of their growth kinetics. For this purpose, several techniques, such as optical microscopy (OM), scanning electron microscopy (SEM), glow discharge optical emission spectroscopy (GDOES), microabrasive wear testing, hardness, grazing incidence X-ray diffraction (GIXRD), and X-ray photoelectron spectroscopy (XPS), have been performed for chemical and structural characterization of the oxide films formed after vapor exposed thermal aging at 510°C. The oxide layer consists of two sub-layers composed by magnetite (Fe₃O₄) and an external layer of hematite (Fe₂O₃). A thick interface between the oxide layer and the bulk is enriched in Ti and Mo, whereas the analyses of deep bulk material show an enriched area with Ni and Co.

Keywords 18% Ni-Co-Mo-Ti ferrous base alloys · Maraging steel · Hydrogen embrittlement · Characterization oxide layers

1 Introduction

Maraging steels, basically Fe–Ni-Co-Ti alloys with low carbon content, are often used in the ultracentrifuge envelope. Thus, their microstructural matrix consists of a relatively soft martensitic structure (BCC, body-centered cubic) [1, 2], and some research compare this structure with a body-centered tetragonal (BCT) martensite with low tetragonality [3]. Nonetheless, these materials exhibit excellent mechanical properties at the aged condition due to precipitation hardening of intermetallic phases such as Ni₃(Ti, Mo) and Fe₂Mo [2, 4]. Besides, some previous works have shown that the nickel atoms in the Ni₃Ti unit cell can be replaced by cobalt and iron atoms, while titanium atoms can be replaced by molybdenum atoms [3]. It is important to note that distortions could have been observed while performing high-temperature aging due to the formation of reverse austenite (Fe,Ni). Therefore, the general formula for these precipitates would be (Ni, Fe, Co)₃(Ti, Mo), and their fraction of Mo
and Ti would depend on the alloy composition. However, when adding cobalt to these alloys family, it is also possible to find Laves phase (Fe₂Mo), which are responsible for the high hardness peak and softening resistance during thermal aging [5].

As depicted before, the great advantage of this steel family is the excellent formability in the solution annealed condition and the possibility to achieve a combination of good toughness with a high mechanical strength after aging. But despite these good properties, when subjected to a hydrogen-containing environment, the maraging steels are prone to embrittlement phenomenon, altering its mechanical behavior and ultimately leading to brittle fracture [6–8]. The general mechanism of hydrogen embrittlement involves the adsorption and subsequent diffusion of atomic hydrogen into the bulk metal, reducing its ductility and fracture resistance [9]. The formation of atomic hydrogen on the surface of the steel, when exposed to a gaseous hydrogen environment, first requires the dissociation of molecular hydrogen, and further explanations of these mechanisms are not in the scope of this work, but can be found in the literature [9, 10].

An oxide layer can be used as a protective barrier against hydrogen diffusion and uptake and can withstand stress and corrosion phenomena commonly associated with nuclear fission environments [9, 10]. Such an oxide layer can be formed during thermal aging while being exposed to a superheated water vapor atmosphere. So, studying the oxidation kinetics involving the alloying elements and estimating the layer composition is of major importance. Various studies pointing out the Gibbs free energies of oxide formation [11, 12] lead to the conclusion that the oxide layer formation could be approximated by 3 different kinetic models: linear, parabolic, and logarithmic. The model which will better describe a particular case will depend on the temperature and on the alloy chemical composition. In this study, the mathematical model which better represents the oxidation process is logarithmic, with a rapid initial oxide growth rate, which then decreased as its thickness increased, indicating the protective effect [5].

Malafaia and Oliveira [13] and Shreir et al. [14] proposed the formation of three overlapping layers: the outermost, composed by hematite or iron oxide II (Fe₂O₃) hexagonal compact is considered the highest state of iron oxidation, with almost 70 at.% iron in its composition, while oxygen occupies the other 30 at.%); an intermediate layer, corresponding to the magnetite oxide (Fe₃O₄) layer; and finally, the inner wustite (FeO) layer [13, 14]. These three layers act together as a barrier to the progress of oxidation and also hinder the hydrogen uptake, thus playing a vital role in reducing hydrogen damage [15].

The growth mechanism of the oxide film was earlier studied by Klein et al. [10, 16] which, in this case, has been described as an outward migration of iron cations during the thermal oxidation of Fe–Ni-Co alloys, which might take place in the air, water steam, and also carbon dioxide environment. Experimental results obtained by Auger electron spectroscopy [16, 17] and depth profile determination, SEM-XES analysis, and X-ray diffraction [18] supported these assumptions, but besides the fact that the oxide formation and cation migration were proven measuring their binding energies, they did not quantify the oxide layer thicknesses.

On the other hand, Rezek et al. [10] studied the microstructure and mechanical behavior changes when producing an oxide layer in a 250 maraging steel by high-temperature heating in a water-steam-containing environment. The coating consisted of an innermost layer of the austenitic phase and a magnetite Fe₃O₄ external layer. The results showed lower elongation and only a small reduction in the measured hydrogen diffusion coefficient for the coated maraging when compared with the bare steel. Despite that fact, the threshold stress in stress corrosion cracking (SCC) evaluation was significantly higher for the coated steel. This benefit is attributed to the presence of the austenitic sub-layer.

Another interesting study, promoted by Greyling et al. [17], investigated the oxidation kinetics of a grade 300 maraging steel heated in air at temperatures ranging from 300 to 600°C. The authors used Auger electron spectroscopy in conjunction with argon ion sputtering and noted that an thin gold layer sputtered onto the surface, before oxidation, changed the kinetics from a limited-thickness model to an approximately parabolic growth at temperatures below 480°C. The limited-thickness oxide growth is described in terms of space-charge effects, as outlined by the theory of Formhold. The insulating properties of a thin mixed spinel oxide present at the metal/oxide interface are critical in bringing about the space charge in the oxide.

Recently, Florez et al. [19] showed that the characterization of the oxide layer is important when considering hydrogen embrittlement environments because surface treatments induce the formation of a superficial layer that, in some cases, could be protective. In this work, an oxide layer was generated under different atmospheres during thermal aging treatment in different maraging steel grades. Afterward, this layer was microstructural and mechanically characterized by advanced characterization techniques, and the results showed that the oxide layer was made up of several compounds like TiO₂, MoO₃, α-Fe₂O₃, and CoFe₂O₄. Furthermore, it detected a nickel-rich austenitic phase at the interphase, mainly made up of cobalt ions (Co²⁺) instead of iron ions (Fe²⁺) within the spinel lattice [19].

So, the purpose of the present study is to perform a thorough characterization of the structure and composition of the iron oxide layer grown on a maraging steel 350 class after thermal aging in a superheated steam media. In this sense, the characterization methods employed in this study consisted of optical microscopy (OM), scanning electron microscopy
Profiler®, using a Pure Argon (800 Pa) R.F. plasma with
[21, 22].

Next, ten samples were aged (ST 910 °C by precision cutting. Then, they were all annealed (ST) at
possible to study the most superficial oxide layer (~ 1000 Å) by Rupetsov and Minchev [23].

Cross-section samples were prepared by low-speed cutting to be characterized by several techniques described beforehand. To perform the optical microscopy (OM) characterization, the ST and STA cross-section-treated samples were carefully embedded, grindable, and polished by metallographic conventional procedure, followed by a chemical attack with both potassium metabisulfite and marble regents. OM was then performed in a model Axioscope 2 Carl Zeissin, whereas the scanning electron microscopy (SEM) took place in a model Vega 3 Tescan, operated at 20 kV in a secondary electron (SE) mode in both chemical attacks. Microelemental analyses by EDS (energy dispersive spectroscopy) were performed along with the sample’s depth, starting from the oxide layer, going to the bulk. Finally, Mössbauer spectroscopy was performed using “converting electron” (CEMS) geometry. Thus, it was possible to study the most superficial oxide layer (~ 1000 Å) [21, 22].

GDOES test was performed in a Horiba Jobin–Yvon GDProfiler®, using a Pure Argon (800 Pa) R.F. plasma with an applied power of 20 W on a 2-mm diameter electrode. Light intensities emitted by deexcitation of sputtered atoms/ions were separated in a polychromator enabling simultaneous analysis of the most relevant chemical elements. The elemental fraction quantification was performed using previously obtained calibrations curves, based on references samples. The sputtering rate was determined on each sample by measuring the produced crater, which led to the determination of the concentration profile. Each sample was analyzed several times, stopping at different depths to determine the sputtering rate of each layer.

The ST and STA samples were also characterized by microabrasive wear tests, which were performed on a small-scale abrasive wear test instrument from Anton Paar®. The test was conducted on an oxidized sample with a flat surface, whose dimensions are 25 × 15 mm2, using a 25.4-mm diameter steel sphere with a normal force N of 0.2 N, applied for 5 s. The peripheral speed of the sphere was 6.65 mm/s, and the abrasive solution consisted of diamond paste with ¼ μm average particle size. The results obtained were corroborated by Rupetsov and Minchev [23].

The analyzed thicknesses were calculated by $h = xy/D$ [23–25], where $x$ is the width of the halo, $d$ is the inner diameter of the groove ($y = d - x$), and $D$ is the diameter of the ball. After the wear testing, a Vickers hardness profile was raised along the layers of the hubcap, from the oxidized layer to the substrate, using nanohardness measurements. Two penetrators were used: first a square-based pyramidal penetrator and then the Berkovich penetrator, consisting of a regular triangular base pyramidal geometry. Eighteen measurements in cross-section from surface to the bulk were obtained with a 2.5 gf load maintained for 10 s, while on the surface, it used 0.01 gf for 15 s. Micro-hardness HV tests were also carried out with a load of 25 gf for 10 s in triplicate at the cross-section and on the surface. The complementary ultrasonic contact impedance test was conducted on the sample’s surface, in triplicate, using a 5 kgf load with the MIC®-205 31,991–7747 and the MIC® 10 digital display.

The GIXRD technique was used to access the structural characterization of the most superficial oxide layer [15, 17, 20]. This technique was performed with the Rigaku® equipment, model Ultima IV, equipped with CuKα source ($\lambda = 1.5406$ Å). The equipment operated with an angular step of 0.02°, under voltage of 40 kV and 30 mA current. The critical angle for this case, to avoid the total external reflection of the X-ray beam, was 0.32° [26]. Consequently, the grazing incidences were chosen as follows 0.5°, 1°, 1.5°, 2°, 3°, and 5°, in continuous scan mode from 20 to 90°, leading

| Table 1 Chemical composition (wt.%) of the maraging steel grade 350 | Ni | Co | Mo | Ti | C | S | P | Al | Cr | Mn | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17.65 | 11.65 | 4.69 | 1.44 | ˂0.1 | ˂0.1 | ˂0.1 | ˂0.1 | ˂0.1 | ˂0.1 | Balance |

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to 0.09 µm until 8.7 µm probed depths [24]. Rigaku® PDXL was used for the identification and quantification of the volumetric fraction of the present phases [23]. The computational calculation of the mass attenuation coefficient of the mixture was based on NIST Standard, NBSIR 87–3597 [27], with the relative weights for each compound quantified by GIXRD.

Another technique used to evaluate the chemical composition on the surface of the oxidized samples was the X-ray photoelectron spectroscopy (XPS) [28–30], using Kratos Analytical® model AXIS ULTRA DLD. XPS uses monochromatic Al-Kα radiation and a fixed transmission mode analyzer (80 eV and 40 eV). The spectra were referenced from line C 1s (binding energy, BE = 284.5 eV) of the hydrocarbon. Samples were analyzed with 400 µm diameter beams with 300 W. Survey spectra and high-resolution spectra were acquired using pass energies of 300 eV and 50 eV, respectively. The power step size is 0.100 eV, and the number of power steps is 401. The acquisition and quantification of the data were performed with the Kratos Analytical® software, while the spectra were analyzed by peak adjustment, followed by Gaussian second order and second derivative, taking into account the baseline according to the Shirley method [28] in the origin software.

### 3 Results and discussion

Figures 1 and 2 present the microstructure of class 350 maraging steel obtained by OM analyses for the ST and STA samples, respectively. These figures show the surface characteristics in the ST condition and the presence of lath martensite. The STA condition leads to an oxide microlayer with 2 ± 0.3 µm formed at the samples surface.

The SEM–EDS analysis presented in Fig. 3 and Table 2 indicates the segregation of Ni, Co, Mo, and Ti from the base steel to the external sub-layer, causing local enrichment near the layer boundary [31]. However, the semi-quantitative analysis by EDS presented in Table 2 indicates that the chemical composition of the bulk material was not affected by the heat treatment. In this sense, Klein et al. [16] stipulated that elemental oxidation in steam oxidized Fe–Ni-Co alloys can be explained by the iron diffusion mechanism. Since Ni and Co cannot be oxidized in the process, they serve as inert markers and their position indicates the interface between the base material and oxidized layer (Fig. 4).

The SEM images also allowed the measurement of the oxidized layer thickness, as observed in Fig. 3. It is important to note the existence of two distinct regions, one external and one internal sub-layer, with an approximate total...
thickness of 2 μm. The innermost layer is marked by the diffusional behavior of the different alloying elements added to 350-grade maraging steel. These elements were involved in the formation of the protective oxide layer during thermal aging under a superheated water vapor atmosphere [15]. In Fig. 5 and Table 2, it can be noted that an intermediate layer is formed at the bulk material region, near the boundary with the oxide layer, which is rich in Ni and Co at points 3 to 5, while the increased Ni enrichment at points 6 and 7 led to austenite stabilization [21, 22, 32].

However, still, regarding Fig. 5 and Table 2, the outermost layer presents a semi-quantitative stoichiometry of approximately 66 wt.% Fe and 32 wt.% O, with traces of Mo, Ni, and Co, indicating that it is composed basically of hematite (Fe₂O₃) [14, 33]. This result was corroborated by Mössbauer spectroscopy on CEMS, corroborating the presence of the sextet that refers to the hematite oxide formation, as presented in Fig. 6.

On the other hand, the microabrasive wear testing characterization results shown in Fig. 7 presented the formation of two layers formed on the substrate. Following the V RUPETSOV and R MINCHEV method, after 5 s of microabrasive wear testing, the outermost layer thickness measured approximately 1.5 ± 0.2 μm, and the innermost layer about 0.7 ± 0.1 μm [34].

Nanohardness measurements were carried out at the spherical cap at different depths, producing the profile plotted in Fig. 8. In the referred figure, there can be distinguished three different layers: the first starting at the surface, with 0.8 μm thickness, with a 1600 HV hardness at the surface, which increases up to approximately 2000 HV at 0.8 μm depth, coinciding with the boundary with the next layer; this second layer remains up to a thickness of 1.5 μm, presenting a maximum hardness of 2000 HV that gradually decreases to 1500 HV at 1.8 μm; then, the third layers consists of the iron-depleted bulk, which is also enriched in nickel, ranging from depths of 2.0 to 2.6 μm, with hardness approximately of 900 HV, whereas the bulk presented an average of 750 HV, at a depths greater than the 2.6 μm. The analysis of the mean hardness values at these regions, ranging from the surface to the bulk, presented a high standard deviation. The growth kinetics of oxide layers were nonlinear since the atomic diffusion is not a unidirectional phenomenon, resulting in a non-planar boundary surface between substrate–magnetite and magnetite–hematite. This fact was the main cause for the high deviations observed. So, the initial measurements on the sample’s surface might be represented both by a hardness peak or valley, depending on the characteristics of the iron oxide layer under study. The presence of a high standard deviation points out the existence of sub-layer interfaces, corroborating that the material presents a double layer formation, originated from the growth of the protective oxide during the heat treatment in a steam furnace.

| Table 2 | Cross-section and surface top semi-quantitative point chemical analyses of EDS in wt.% |
|---------|---------------------------------|----------------|----------------|-----------|-----------|-----------|-----------|
| Point analyses | Fe | O | Ni | Co | Mo | Ti |
| Cross-section analyses | 68.0 | 27.0 | 0.0 | 2.5 | 2.4 | 0.0 |
| 1 | 60.6 | 27.4 | 4.0 | 3.4 | 3.5 | 1.1 |
| 2 | 50.5 | 25.6 | 7.8 | 6.8 | 7.5 | 1.8 |
| 3 | 49.8 | 23.3 | 8.7 | 8.0 | 8.1 | 2.2 |
| 4 | 49.8 | 23.3 | 8.7 | 8.0 | 8.1 | 2.2 |
| 5 | 35.7 | 6.0 | 31.7 | 19.2 | 5.5 | 1.8 |
| 6 | 32.2 | 7.1 | 32.2 | 20.7 | 6.1 | 1.8 |
| 7 | 48.3 | 3.2 | 26.0 | 15.8 | 5.3 | 1.4 |
| 8 | 58.5 | 1.9 | 19.7 | 13.0 | 5.5 | 1.4 |
| Surface analyses | 65.6 | 31.7 | 0.9 | 1.1 | 0.5 | 0.1 |

Fig. 3 Metallographic section with an indication of microanalysis points
Furthermore, the hardness measurements accessed by nanoindentation in the cap region presented average values for each separate layer: The white layer next to the substrate presented 900 ± 200 HV; the intermediate layer 2090 ± 380 HV, the region near the boundary 1640 ± 250 HV, and the substrate, or bulk material, 785 ± 120 HV. The nano-, micro-, and impedance hardness results obtained on the surface and in bulk are gathered in Table 3. It is clear that the surface measurements with nano and impedance techniques have a higher deviation due to the porous characteristic of the outermost layer, and these are techniques sensitive to heterogeneous surface formation [1, 5].

The elemental at.% profiles, determined by GDOES, are presented in Fig. 9. An oxide layer of about 1 µm is clearly visible, with oxygen content decreasing from 80 at.% to about 60 at.% and iron content increasing between 20 at.% and 40 at.%. Ni, Co, and Mo were not observed in this layer for depths lower than ~0.7 µm, presumably due to the rough interface between the top iron oxide and the underneath oxide. Below this iron oxide layer, the at.% O character.
values are decreasing quickly until depths of about 2 µm, whereas the at.% Fe still increases toward its bulk value. Within this intermediary layer located between 1 µm and 2 µm depth, Ni, Co, and Mo are increasing till a maximum at 1.5 µm before decreasing back to their bulk value. These profiles confirm the growth mechanism of the oxide, based on iron diffusion from the bulk toward the surface, in order to build the Fe₂O₃ oxide, and also some inward diffusion of oxygen and resultant enrichment in alloying elements (Ni, Co, Mo) at the intermediate oxidized depth, due to the lower Fe content [17, 35].

To obtain structural information about the surface layers, grazing incidence X-ray diffraction (GIXRD) was operated with different incidence angles, allowing different penetration depths of the radiation. Figure 10 shows the diffractograms generated for incidence angles of 0.5°, 1°, 1.5°, 2°, 3°, and 5° [5, 36–38], and Table 4 presents the quantification data acquired by the Rietveld method.

Using incident angles typically lower than 1.5°, the signal from the substrate can be minimized, increasing the intensity of the diffraction peaks associated with the crystalline structures next to the surface. Some researchers [24] argue that it is possible to obtain a more reliable quantification for the oxide layer using the relationship of photon interaction with the substrate thickness at some angles, especially in the case of phases with lower volumetric fractions. As for example, one can refer to the intermetallic, binary, and inorganic compounds formed at the substrate interface [2].
At the studied layer, the main crystalline phase is hematite, followed by magnetite. For the incident angles between 0.5° and 1.5°, an average hematite/magnetite ratio of 60% per 40% is maintained, which was also reported by other studies [13, 14]. However, for angles higher than 2°, the magnetite fraction increased, and at 3°, the results also presented martensite peaks (characteristic peaks of α’ Fe (110), (200), and (211)). From these results, it could be presumed that there was formed an external hematite layer and an internal magnetite sub-layer. According to Rezek et al. [10], X-ray diffraction results indicate a higher percentage of hematite, inferring that a third oxide layer could be formed [2].

In an approach to calculate the penetration depth, it used the method described by Birkholz [39], considering a sample with infinite total thickness, and the thickness of the upper layer that accounts for \((1 - 1/e) = 63\%\) of the measured intensity. With the thickness and phase quantification of each GIXRD diffractogram, an estimative of phase quantification for each thickness was carried out. Considering that only the depth penetration of the incident beam changes with the increase of \(α\), Eq. (1) was proposed to perform the layer phase quantification:

\[
q_n = \left( \frac{Q_n}{(t_n - t_{n-1})b} \right) \left( \frac{t_n}{t_n - t_{n-1}} \right)
\]

where \(Q\) is the phase quantification measured in all volume by GIXRD, \(t\) is the analyzed film thickness, \(b\) is the surface area of analysis, \(q\) is the layer quantification, and \(n = 0.5° \rightarrow 5°\).

Figure 11 shows the estimated results for the layer thickness on the material based on Eq. (1). The result with a 5° incidence angle shows a penetration depth of 3.5 µm and the highest quantity of α and γ phases. This is in good correlation with the previously observed 2-µm-thick oxide layer. Regarding the oxide layer, the results for the first 1-µm layer point out a predominance of hematite. For a deeper thickness, at the interface with the bulk, the magnetite presents a significant peak.

Graat et al. [40] made the analysis through the Fe 2p spectrum for a sample of pure Fe and obtained the peaks with a binding energy of 706.8 eV for Fe⁰ and 709.8 eV and 711.2 eV for the Fe²⁺ and Fe³⁺ cations (Table 5). Satellite peaks were also present, with a higher energy level, less intensity, and always to the left of the main peaks, with energies of 722.8 eV and 724.3 eV for Fe²⁺ and Fe³⁺ cations [32], respectively. The doublets or multiplets reveal the formation of satellite peaks in the spectrum of the main ions (Fe²⁺ and Fe³⁺). These peaks are due to the movement of electrons from the 3d orbital to the empty 4s orbital during

| G. A ° | Fe₂O₃ | Fe₃O₄ | γ | α |
|-------|-------|-------|---|---|
| 0.5°  | 65.5% | 25.0% | 8.8% | 0.7% |
| 1°    | 58.7% | 29.1% | 7.3% | 4.9% |
| 1.5°  | 57.6% | 27.3% | 12.5% | 2.6% |
| 2°    | 48.8% | 34.8% | 11.7% | 4.6% |
| 3°    | 45.8% | 31.8% | 15.2% | 7.2% |
| 5°    | 41.0% | 22.6% | 20.5% | 15.9% |

**Table 4 Phases proportions obtained by Rietveld quantification method**
the ejection of the electron-photon from the 2p nucleus [35]. In analyses performed in Table 5, the peaks summarize those binding energies used for the XPS technique.

In Fig. 12, the XPS spectrum on the surface of the ST sample can be interpreted as the sum of the following iron components: \( \text{Fe}^0 \), \( \text{Fe}^{2+} \), \( \text{Fe}^{3+} \), and \( \text{Fe}_2 \text{O}_3 \), in the 2p spectrum and their respective satellite peaks. For the STA condition, Fe in hematite was identified at 709 to 710 eV at 2p\(_{3/2}\) and 722 to 724 eV at 2p\(_{1/2}\); Fe in magnetite is found at 728 eV for the 2p\(_{1/2}\) peak and in the range of approximately 713 to 718 eV for the 2p\(_{3/2}\) peak. It also observed the formation of satellite peaks to 2p\(_{3/2}\) \( \text{Fe}^{3+} \) at 714.5 eV, to 2p\(_{1/2}\) \( \text{Fe}^{2+} \) at 725 eV, and to 2p\(_{3/2}\) \( \text{Fe}^{2+} \) at 716 eV. The 2p\(_{3/2}\) \( \text{Fe}^+ \) in FeO is also found at 709.5 eV. In Fig. 10, it can be seen that the analysis of the zero point, near the bulk-STA at approximately 715 eV and 730 eV, shows the minor presence of magnetite in the STA condition. The peaks at 706.5 eV and 720 eV show a high presence of metallic Fe for the ST condition [21, 37].

The ST-top in XPS analysis showed 41% of oxide composed of Fe\(_2\)O\(_3\) in 709.96 eV and 723.27 eV, 27% Fe metal formation in 706.78 eV and 720.14 eV, 7% FeO in 707.65 eV, and 16% other components. The top of STA formation of oxide composed of 63% Fe\(_2\)O\(_3\) in 709.96 eV and 723.27 eV and 37% of the mixture of Fe\(_2\)O\(_3\), FeO, FeOOH, Fe\(^{2+}\), Fe\(^{3+}\), and others is observed in 715.21 eV, 707.65 eV, and 711.58 eV. However, this analysis technique still needs to be improved. In Fig. 10, it presented a movement of the peaks with the layer analysis, showing that the ratio of oxides formed changes with the depth; however, the hematite and magnetite peaks divide the energy range very closely, making it difficult to analyze with great precision.

According to microabrasive wear and hardness analyses, the layers have two characteristic thicknesses of approximately 1.08 \( \mu \)m and 0.84 \( \mu \)m, resulting in a 1.92-\( \mu \)m thick oxide layer. Therefore, since the scanning of the spectra was carried out up to 1.8 \( \mu \)m, it was not possible to analyze the relative increase of magnetite and iron oxide in the deeper layers. However, it noticed a decrease in the \( \text{Fe}^{2+} \) satellites peaks, which accompany the hematite phase, even though no peaks referring to magnetite were observed. It is also important to note that hematite was the main oxide composing all analyzed layers, showing a higher mass fraction at the surface, which decreased toward the center of the analyzed layer. This behavior was corroborated by XRD and GIXRD results and by the diffusion of iron and oxygen observed by the GDOS technique. In brief, all presented techniques pointed to the formation of a triple oxide layer, composed at its surface mainly by hematite (Mössbauer), followed by

### Table 5 Binding energies used for XPS analysis for the Fe 2p spectrum [37]

| Spectrum compound | Peaks of binding energies (eV) |
|-------------------|--------------------------------|
| \( \text{Fe}_2 \text{O}_3 \) | 709.8–710.9 | 724.3 |
| \( \text{Fe}^{3+} \) satellite | \( \sim \)719.0 | \( \sim \)733.0 |
| \( \text{Fe}_3\text{O}_4 \) | 709.0–710.4 | 722.0 |
| \( \text{Fe}^{2+} \) satellite | \( \sim \)715.0 | \( \sim \)730.0 |
| FeO | 708.4–709.4 | N/A |
| \( \text{Fe}^0 \) | 706.7–707.0 | 719.8 |
| Fe 2p | 710.9 | 724.5 |
| FeOOH | 711.8 | - |

![Fig. 12 XPS Fe-2p peaks for the ST sample surface (ST-top) and for the STA sample surface (STA-top) and obtained after sputtering at different depths till the bulk](image-url)
a mixture of hematite and magnetite. Near the material’s bulk, it also presents a thin layer with wustite and cobalt-containing oxides, leading to iron depletion and cobalt and nickel enrichment, favoring austenite stabilization and diffusion hardening at the matrix next to the oxide layer.

4 Conclusion

The following conclusions could be drawn from the present work on the structural characterization of the iron oxide obtained on 18% Ni (350) maraging steel treated in a superheated vapor steam furnace.

The optical microscopy and scanning electron microscopy analyses pointed out the presence of lath martensite at both conditions (ST and STA). Regardless, the STA sample treated in a water-steam environment presented a 2.0 ± 0.3 µm thick oxide microlayer on its surface.

The energy dispersive spectroscopy (EDS) evidenced distinct surface regions from the bulk toward the top surface: a nickel-rich region with iron impoverishment covered by 2 sub-layers of iron oxides. At the sample’s surface, the outermost layer presents a semi-qualitative stoichiometry of approximately 66 wt.% Fe and 32% wt.% O, with small traces of Mo, Ni, and Co, indicating that the outermost oxide is composed of hematite (Fe₂O₃). This result was confirmed by Mössbauer spectroscopy with the sextet formation.

Using microabrasive wear testing characterization, it was possible to corroborate the formation of the two layers on the substrate and to measure the thickness of the outermost layer to approximately 1.5 ± 0.2 µm, while the internal layer was 0.7 ± 0.1 µm thick.

The hardness measurements by nanoindentation into the cap region produced by microabrasive wear testing confirm the formation of a double layer, as well as an interface between these layers and the substrate. The mean nanohardness values for each region studied were of 900 ± 200 HV for the white layer next to the substrate, while 2090 ± 380 HV for the intermediate oxide layer, 1640 ± 250 HV for the region near the bulk interface, and 785 ± 120 HV for the substrate itself. Conventional hardness measurement resulted in 442 ± 6 HV for the ST matrix, 768 ± 6 HV for the STA matrix, and finally 830 ± 310HV at the oxide layer surface. These conventional results for the bulk might be compared with the ones for maraging 300, obtained at a previous work [6], which indicates ~300 HV in the ST condition and values varying from 450 up to 700 HV depending on the aging heat treatment, due to formation of different retained austenite fractions.

The grazing incidence on X-ray diffraction analysis confirmed the presence of hematite and magnetite. Angles between 0.5° and 1.5°, corresponding to the lower-probed depths, evidenced the hematite formation in the top oxide, while angles higher than 2° led to the magnetite peaks.

In the XPS peak deconvolution analysis, it detected the interaction of Fe with oxygen at the top until the nearest region of the bulk (1.8 μm), using sputtering for depth analysis. On the other hand, the outer layers presented the formation of iron oxides composed of 63% Fe₂O₃ and a mixture of Fe₂O₄, FeO, FeOOH, Fe²⁺, Fe³⁺, and other residuals. When analyzing the surface region, up to 1 µm deep, it noted the major presence of hematite (between 60 and 70%); however, this technique still needs to be improved.

All correlated techniques showed that the oxide coating consists of a double layer formed from the surface of the iron-depleted substrate by reverse diffusion and oxygen reduction. The substrate close to the layer is significantly richer in Nickel, also with a higher Co and Mo content, which leads to the formation of stable austenite. The interlayer has a mixture of oxides that consists mainly of a certain ratio of hematite and magnetite. The amount of hematite increases toward the surface, followed by a reduction in the magnetite, which may indicate hematite formation in its outermost layer.

The formations of a multi-layered oxide coating through thermal treatments in superheated vapor, as well as its mechanical properties and composition, are valuable results regarding applications that need to consider hydrogen embrittlement, hot hardiness, and abrasion resistance, such as tool steels and specialties ferrous alloys.

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Data availability Not applicable.

Code availability Not applicable.

Declarations

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Conflict of interest Not applicable.

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