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## Intergranular corrosion in 350-grade maraging steel

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### Abstract

Maraging steel was synthesised by austenitising and mechanical conditions with arc-shaping for magnetic pieces. The steel samples were exposed in a corrosive environment in Nital 2% solution, and then characterised by SEM, EDX and TEM techniques. Arc-shaped steel (2.0 mm in thickness) has shown a pure martensite nanostructure, composed of nano-precipitates obtained upon effects of a severe plastic deformation. However, intergranular corrosion and crack propagation derived from etching was observed. The results suggest that the  $\alpha'$ -martensite matrix can be slightly modified by the intergranular corrosion when exposed in corrosive environments.

**Keywords:** maraging steel, martensite, electron microscopy, intergranular, and corrosion.

### Introduction

Maraging steel is a promising nuclear material for key applications on the Brazilian nuclear program previewed for the development of the first national nuclear submarine, as well as on nuclear reactors and fuel enrichment centrifuges (1). The advantage in using them consist in combining an ultrahigh strength with soft-ferromagnetism, and maintaining their final properties up to at least 623 K temperature by operating (2).

These uses are possible due to their crystalline structure of body-centred cubic (BCC) iron matrix (ferrite) unity cells of ( $\alpha'$ ) lath-martensite (2-6). The metastable iron-nickel (Fe-Ni) martensite is formed by isothermal martensitic reactions derived from the parent face-centred cubic (FCC) austenite ( $\gamma$ ) structure. Alloying composition of maraging steels comprises high levels of nickel, cobalt and molybdenum, and little (but important) titanium. In a cobalt-free steel (which increases greatly product cost), the practice in increasing the content of Ti and to decrease the content of Mo is currently used to improve its final properties (4-6).

These metals are strengthened by the precipitation of intermetallic compounds (e.g.  $\text{Fe}_2\text{Mo}$  and  $\text{Ni}_3\text{Mo}$ ) at temperatures of about 753 K by aging thermal treatment (4,5,7). It is understood as ultra-high strength materials which have a yield strength ( $\sigma$ ) greater than 1380 MPa. The maraging steels have this parameter typically greater than specific levels from 1030 to 2420 MPa (150 to 350 ksi) (4-5). Precipitation strengthening is generally produced by a

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sequence of phase transformations that lead to a uniform dispersion of nano-sized, coherent precipitates in a soft matrix (7).

Furthermore, excellent weldability, reproducibility, fatigue and high corrosion resistances are achieved in maraging steels having fracture toughness higher than most alloys, at a relative low cost (4,7). Most recent studies of maraging steel, which result a wide investigation related to the topics about the concentration/modification of alloying elements, processing conditions and ageing hardened to monitoring their final properties, have been undertaken. However, there is a vacancy related to a better understanding about the corrosion effects in specific mechanically treated maraging steel by Nital etching.

For this purpose, this study is focused on the formation of iron-based products and their characterization upon Nital 2% exposition in arc-shaped 350-grade steel matrix. The manuscript aims to describe observations on the micro and nano structure modifications resulted on the martensite in maraging steel. Specimens were characterised by scanning electron microscopy (SEM), transmission electron microscopy (TEM), in combination with energy dispersive X-ray (EDX) spectroscopy. It is expected that this type of investigation can be useful to future experimental in producing controlled nuclear materials.

## **Methodology**

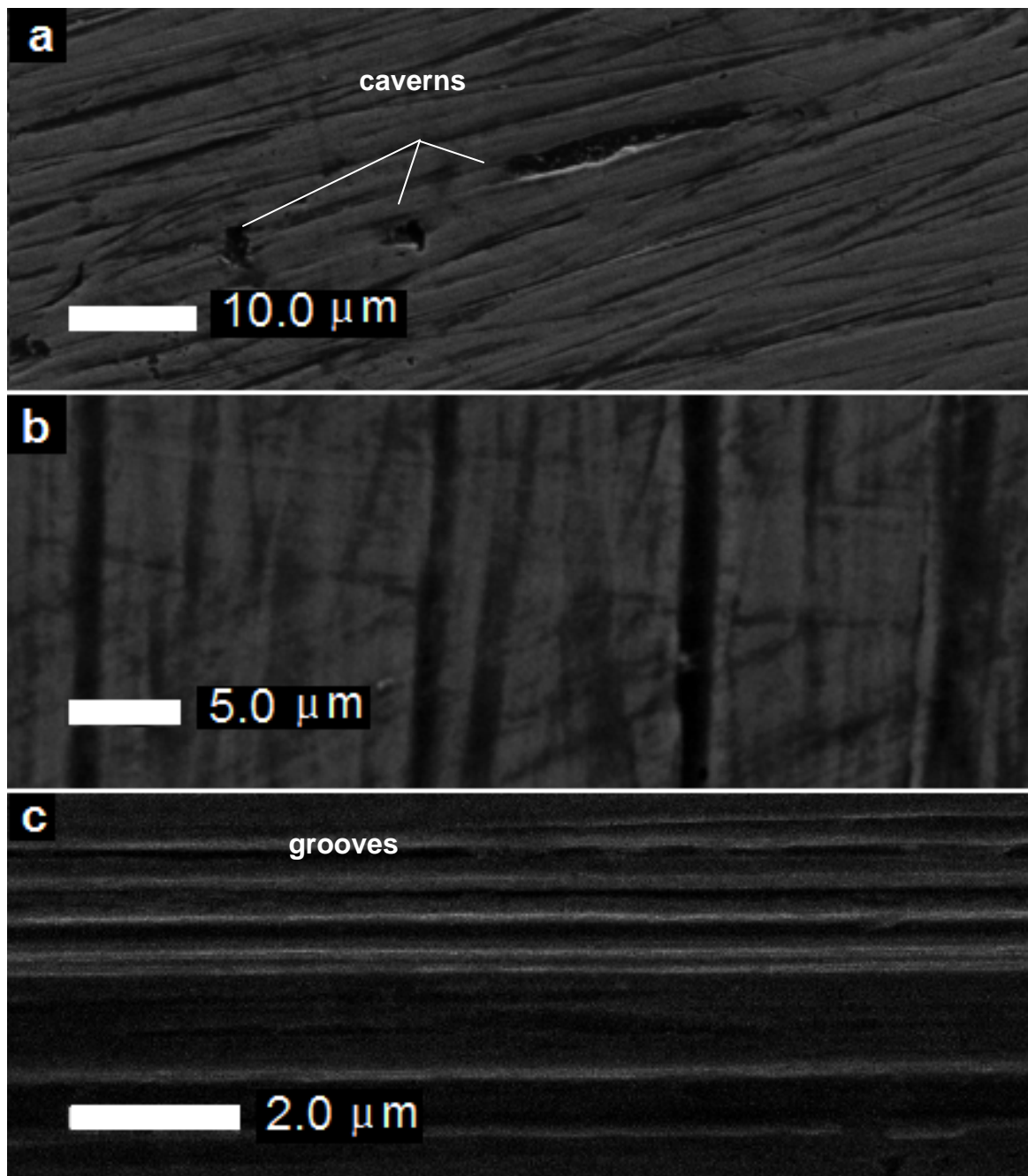
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The 350-grade maraging steel sample containing 18.0 wt.% Ni was manufactured at Nuclear Technology Centre Program Navy (CTM), in Brazil. The steel was enriched with Co, Mo and Ti alloying elements, and Fe-balanced. The manufacturing parameters from baseline material were combined to obtain optimal magnetic and/or mechanical properties by forming of arc-shaped pieces for radial magnetic rings with wall thickness of #2.0 mm. Samples were prepared from maraging steels sheets, in the martensitic condition plus aged condition (deformed) followed of the chemical etching with Nital (2.0% solution HNO<sub>3</sub> in ethyl alcohol). Samples were conveniently prepared and characterized by electron microscopy and EDX techniques at Research & Analysis Support Centre (UEM). SEM analysis was made using a Shimadzu Superscan SS-550 microscope. A JEOL JEM-1400 120 keV transmission electron microscope was used with bright field detector. Chemical analysis and alloying element maps were carried out using a Bruker microanalysis system with an EDX detector coupled to the electron microscope.

## **Results and Discussion**

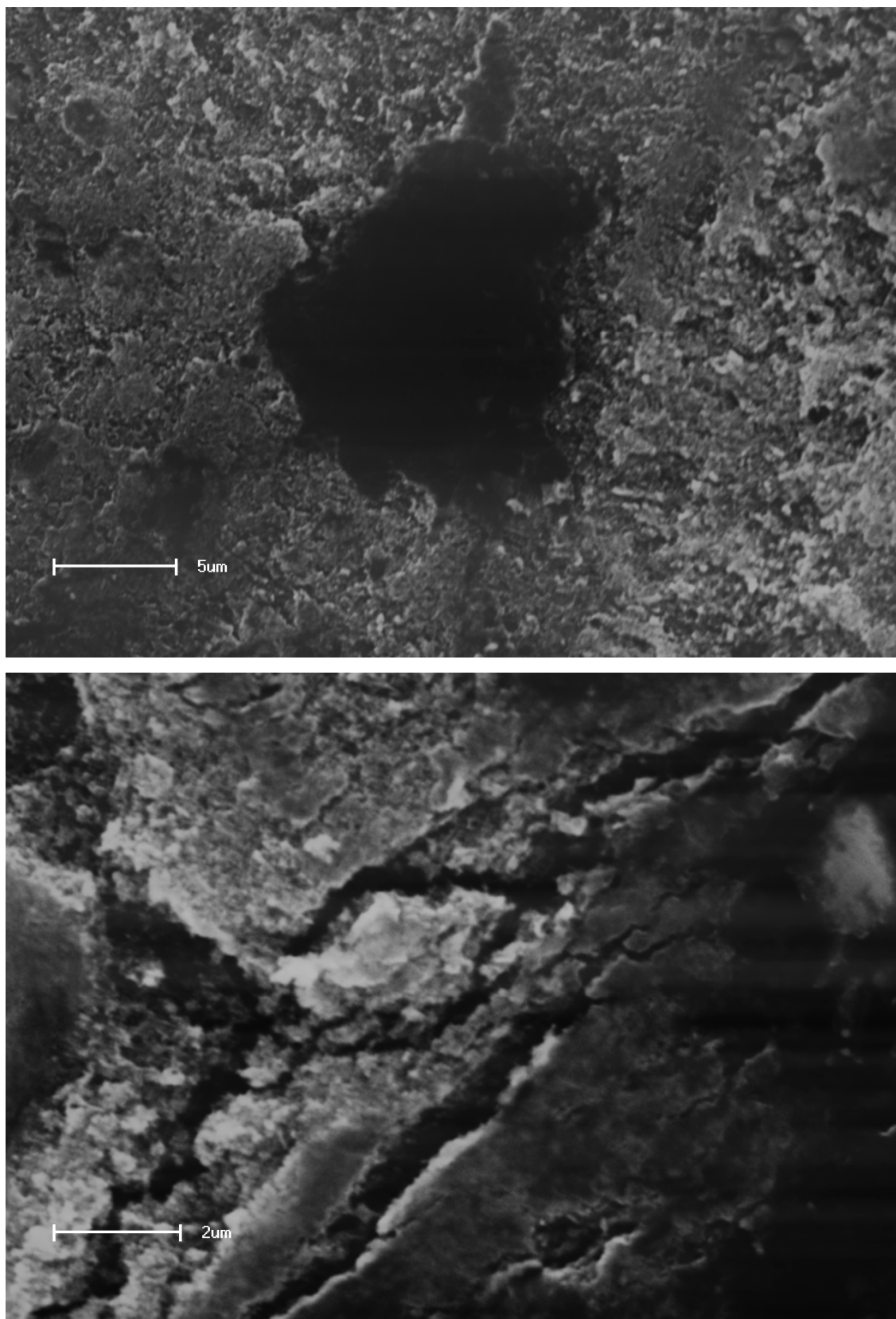
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SEM analysis of as-prepared maraging steels samples are showed in **Figure 1**. The formation of a flat surface and risks and a region with macro roughness are observed. These regions constitute both open areas, which heterogeneities were observed as caverns (or "valleys") in the segregated surface; localized open porosity with pore diameter ranging between 150 nm and 1.2 µm was also identified (**Figure 1a**). The formation of a linear texture was formed, consistently with the directional rolling process. A homogeneous surface with a linear texture, absent of defects, was characterized in arc-shaped steel by having relief groove distances of about 250-313 nm up to ~2 µm (**Figure 1c**).



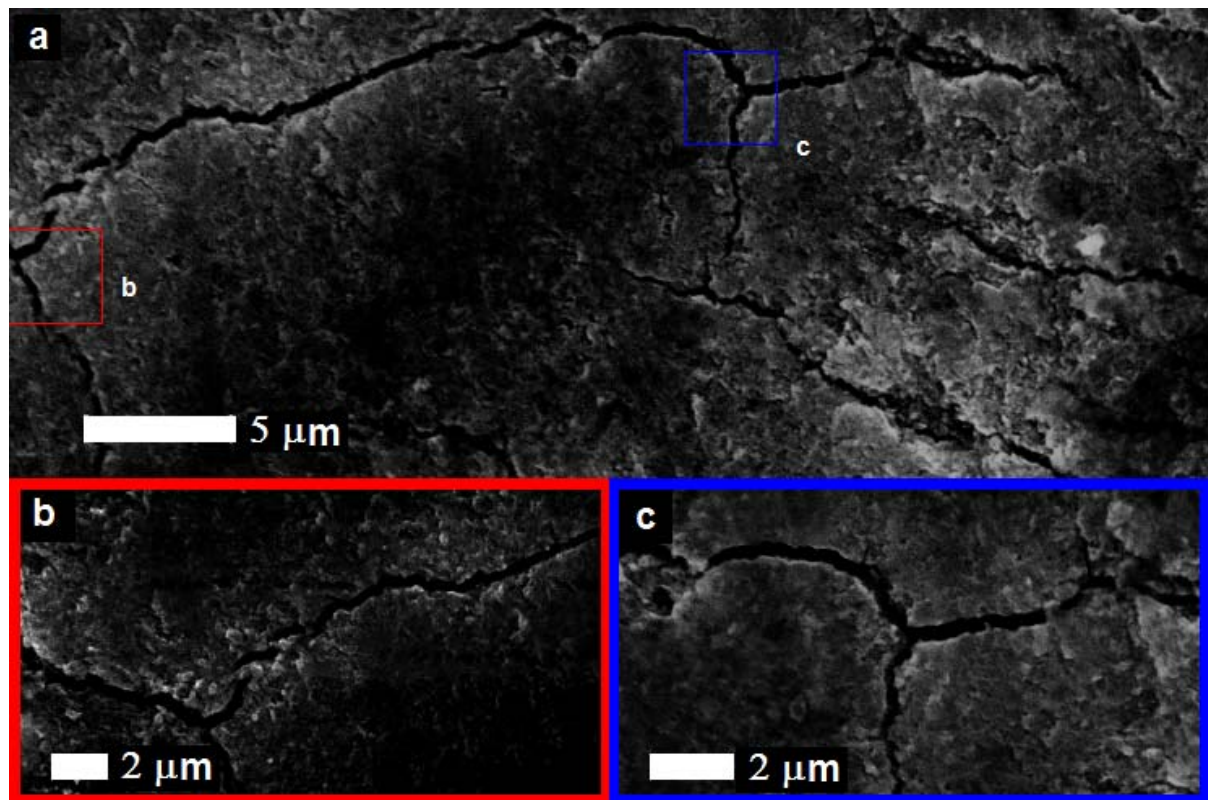
**Figure 1 – SEM images of samples with amplifications of (a)  $\times 1000$ , (b)  $\times 5000$  and (c)  $\times 3000$ .**

Since precipitates are formed along the grain boundaries of primary austenite on the microstructure of maraging steel, the intergranular corrosion type (sensitization) is favoured as the natural course for crack propagation (8), in agreement with shown in **Figure 2**. This factor occurs by decohesion of grain boundaries after the precipitates have been dissolved. Moreover, it is possible to detect that no austenite phase (retained and/or reverse) was observed in arc-shaped steel by electron microscopy techniques. Accordingly, it was the particular sample that revealed intergranular corrosion by etching — since the total absence of austenite does not offer any kind of protective behaviour against corrosive environments by hydrogen embrittlement, as shown in **Figure 3**.



**Figure 2 – SEM images of sample with amplifications of (a)×1000, (b) ×5000 and (c) ×3000.**





**Figure 3 - SEM images of arc-shaped steel showing (a) intergranular corrosion by cracking propagation at grains boundaries of prior austenite after severe plastic mechanical deformation and etching, which (b-c) are the corresponding vertices indicated in (a).**

The combination of alloying elements Ni, Fe, Co, Mo, Mn, Al, Ti, Nb and W (6), in presence of atoms of impurities Si and S (**Figure 4**), allow the formation of diverse secondary phases as inclusions and precipitates. Apparently, the atomic ratio of Ni/Fe/Mo/Al demonstrates that the maraging steel is rich in Mo and Al atoms.

Note that crystalline particles and irregular inclusions such as rod-like shaped particles of  $Ti_2S$  and  $(Ti,Ni)S$  are also seen by TEM images (**Figure 5**). This lath-martensite comprises the magnetic domains of ferromagnetic steel. Moreover, the steel matrix in this sample is homogeneously decorated with nano-precipitates of about 100-200 nm diameter.

A schematic image of ferromagnetic ordering in maraging steel is drawn in **Figure 6**, resulted from the microstructural transformation of (a) paramagnetic  $\gamma$ -austenite to (b)  $\alpha'$ -martensite, as referred in literature (2); since the growth of laths within the prior austenite (mother) grains. In this representation, the grains have been characterised by (c) magnetic domains randomly ordered along the steel matrix, for which (d) maximum alignment of the ferromagnetic moments occurs upon an applied field.

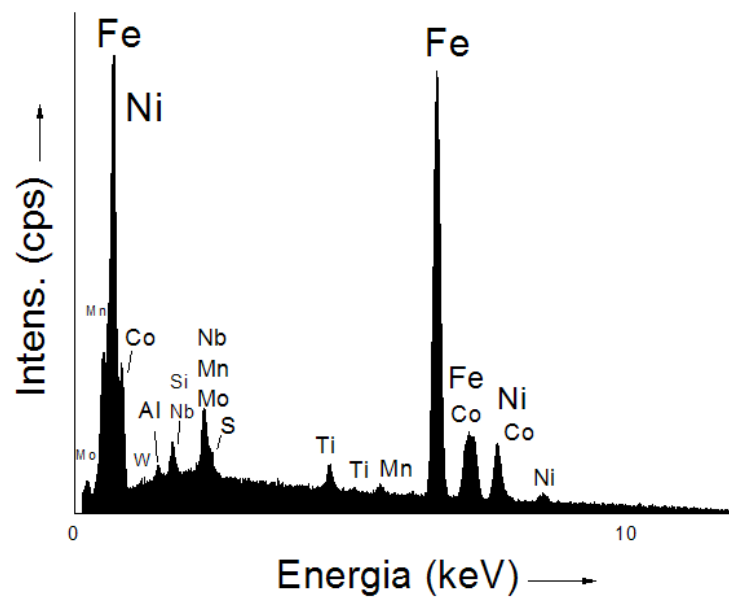
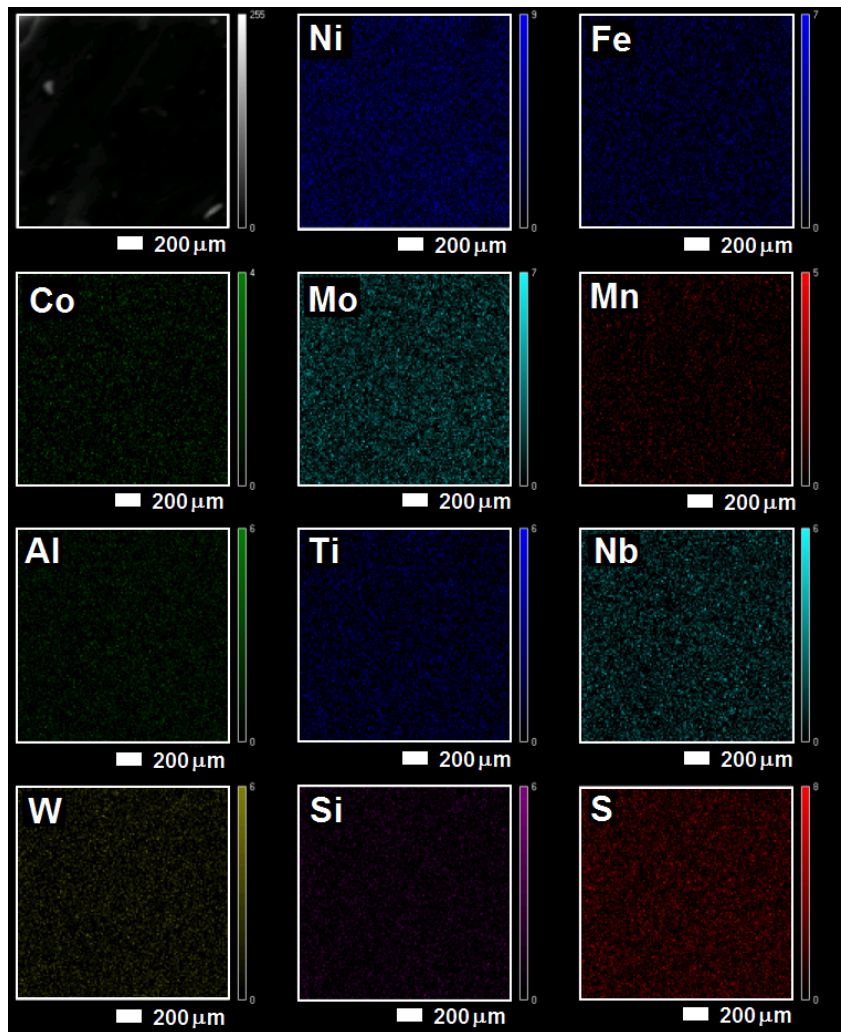


Figure 4 – Chemical analysis and alloying element maps of maraging steel.

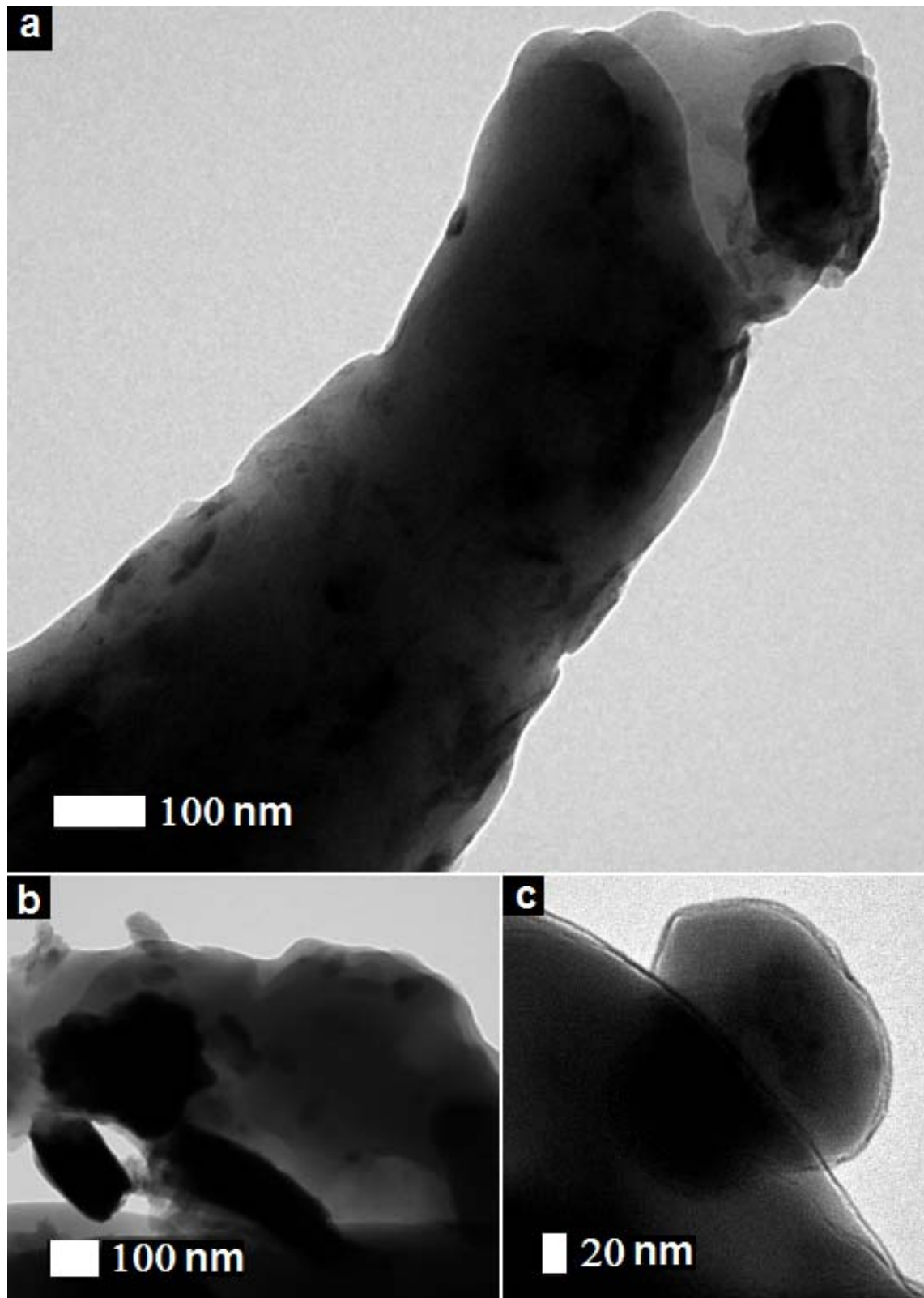


Figure 5 – Bright-field TEM images of maraging steel.

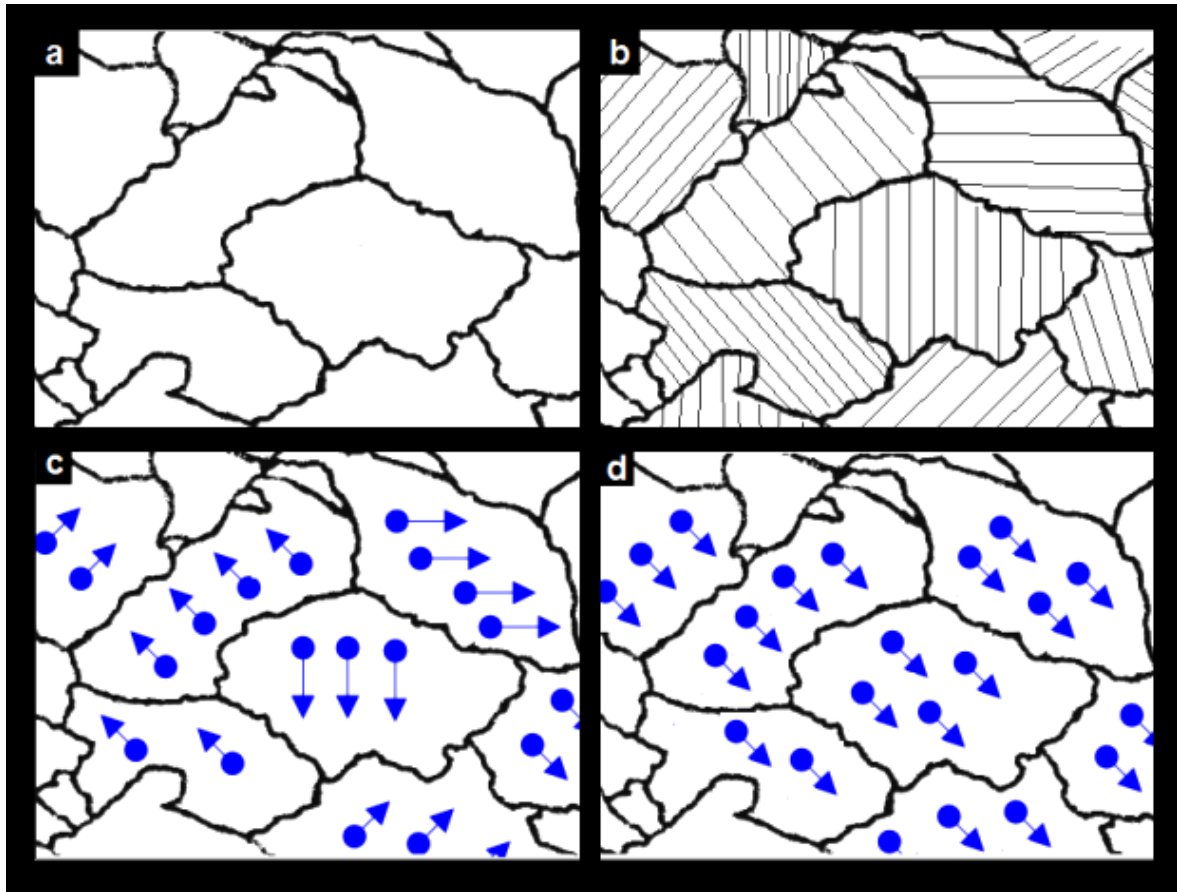


Figure 6 – Magnetic phase transformation from (a) austenite to (b) martensite; the arrows denote the ordered magnetic moments inside grains in (c) or fully aligned on the microstructure (d).

## Conclusion

Mechanically and corrosive treated maraging steel upon Nital 2% etching was investigated.

The most significant results obtained allow concluding that:

- after the corrosive treatment, the observations on the martensite microstructure have shown evidences of intergranular corrosion (sensitization) and grain decohesion (embrittlement) in arc-shaped 350-grade steel matrix by cracking;
- since that alloying elements and impurities were detected by chemical analysis, as well as inclusions and precipitates were observed by electron microscopy, some of these secondary particles around grains possibly can have been dissolved in response to the chemical reagent;
- the combination of arc-shaping and Nital etching through intergranular corrosion has been revealed an effective technique to characterize the obtaining martensitic microstructure in maraging steels.



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## References

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- (1) **Brazilian Navy Nuclear Program**, Nuclear Technology Centre Program Navy — CTMSP, São Paulo, 2013. in: <http://www.mar.mil.br/pnm/pnm.htm>; and Indústrias Nucleares do Brasil S.A. — INB, **Nuclear Fuel Cycle**, 2013. in: <http://www.inb.gov.br>.
- (2) DECKER R. F. **Source book on maraging steels** – a comprehensive collection of outstanding articles from the periodical and reference literature, American Society for Metals – ASM, 1979.
- (3) CHRISTIAN J. W. **The theory of transformations in metals and alloys** – part I: equilibrium and general kinetic theory, Pergamon Press, Oxford, 1975. 586 p.
- (4) ASM - AMERICAN SOCIETY FOR METALS. **Metals handbook: the physical metallurgy of maraging steels** by Floreen S. 13 ed. Ohio: Materials Park, 1968. p. 115-128
- (5) ASM - AMERICAN SOCIETY FOR METALS. **Metals handbook: maraging steels** by Rohrbach K. and Schmidt M. vol. 1, Ohio: Materials Park, 1991. p. 793–800
- (6) ASM - AMERICAN SOCIETY FOR METALS. **Metals handbook: alloying elements in steel** by Bain E. D. and Paxton H. W. 2 ed. Ohio: Metals Park, 1966.
- (7) JAMNIG B.; EBNER R.; STARON P.; CLEMENS H.; LEITNER H.; JEGLITSCH F. in: **Proceedings of the 6th International Tooling Conference**, Karlstadt, Sweden, September 10-13, 2002. ISBN: 91-89422, p. 549–563
- (8) DOHERTY J. E.; KEAR B. H.; GIAMEI A. F.; STEINKE C. W. **Grain Boundaries in Engineering Metals**, by Walter J. L., Westbrook J. H. and Woodford D.A. (Editors), Claitors Publishing Co., New Orleans, 1975.

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