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Microstructural evolution of a modified HP alloy: experimental and complementary computational study

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ABSTRACT

We present results of the microstructural characterization of austenitic stainless steel (HP series) modified with Nb, aged at temperatures of 750, 800, 850, 900 and 950oC in air at different times. Microstructural changes were analyzed using optical microscopy, scanning electron microscopy (SEM) equipped with (EDS), x-ray diffraction and Vickers hardness. In the as-cast condition, the microstructure consists of an austenitic matrix and eutectic carbides network, rich carbides and other Cr, Nb-rich. The Cr-rich carbides are M7C3 type, whereas, those rich in Nb are NbC. During aging, there is a second precipitation in very fine needle form in the matrix of M23C6 carbides, which leads to an increase in hardness. Computational study shows that M23C6 is the lesser stable carbide presenting the biggest changes in the orbitals atomic populations.

Keywords

austenitic steel, microstructure, carbides, secondary precipitation, Vickers hardness

Academic Discipline And Sub-Disciplines

Material Science

SUBJECT CLASSIFICATION

Corrosion

TYPE (METHOD/APPROACH)

Experimental and Computational

INTRODUCTION

In the chemical and petrochemical industry, furnaces are used to satisfy various hydrocarbon processes such as pyrolysis and reformation. The most important part of these processes takes place in the bundle of tubes located in the radiation zone, where reactions of an endothermic nature occur. These tubes are designed to reach a life of 100,000 hours, operating at constant pressure (between 5 and 30 MPa), depending on the type of furnace. The operating temperature is often between 600 °C and 1040 °C. The dimensions of the tubes are usually between 100 and 150 mm in diameter and between 10 and 20 mm in wall thickness. The service life they reach is between 30000 and 150000 h. Due to these extreme working conditions, high-alloy steels with high strength and limited ductility, such as stainless steels of the Ni- Cr-Fe type, are used. These alloys consist of an austenitic matrix strengthened through a fine dispersion of hard carbide particles. In the condition as the plaster of the microstructure is composed of a network of dendritic type of primary carbides along the edges of grain. During the service at high temperatures, a fine dispersion of secondary carbides is formed in the matrix, responsible for the strengthening of the alloy. The mechanical resistance to high temperatures depends on the distribution, hardness and stability of these particles. At high temperatures, these particles tend to decrease their surface energy following a coarsening mechanism, increasing in size, assisted by the mechanism of diffusion and causing a worsening of their mechanical properties. Thus, there is a need to stabilize the fine dispersion of particles [1-4]. In this work, we present experimental data of hardness obtained on samples aged by heat treatment of aging at 750, 800, 850, 900 and 950 ºC in modified HP steels. From the observations obtained in this work, a characterization of the microstructural evolution of the phases and their transformations is obtained. Based on these results, the consequences on the mechanical properties are analyzed.

EXPERIMENTAL PROCEDURE / METHODOLOGY

In this study, samples extracted from tubes with 110 mm diameter and 11 mm wall thickness were used. The analysis of the chemical composition of the material was carried out, whose results are shown in Table 1.

Table 1. Nominal chemical composition of HP material (% by weight)

Material	C	Si	Mn	Cr	Ni	Nb	Fe	Others
Modified HP	0.60	1.8	2.0	25	35	1.34	Bal.	Mo

The thermal treatments of aging were carried out in the air in resistive furnaces where the samples were extracted in different times and later cooled to the air. For the subsequent observation, the samples were prepared by mechanical polishing and electrolytic etching using a solution of 10% oxalic acid in water (3v for 60 s).

For the study of its microstructure these samples were observed by optical microscopy using a Leyca microscope equipped with a digital camera. They were also analyzed by a scanning electron microscope JEOL Model JSM 35 CF (SEM).

The hardness determination was also performed on the aged samples, using a Vickers durometer OSHMA, applying a load of 1 kgf for 15 seconds.

COMPUTATIONAL STUDY

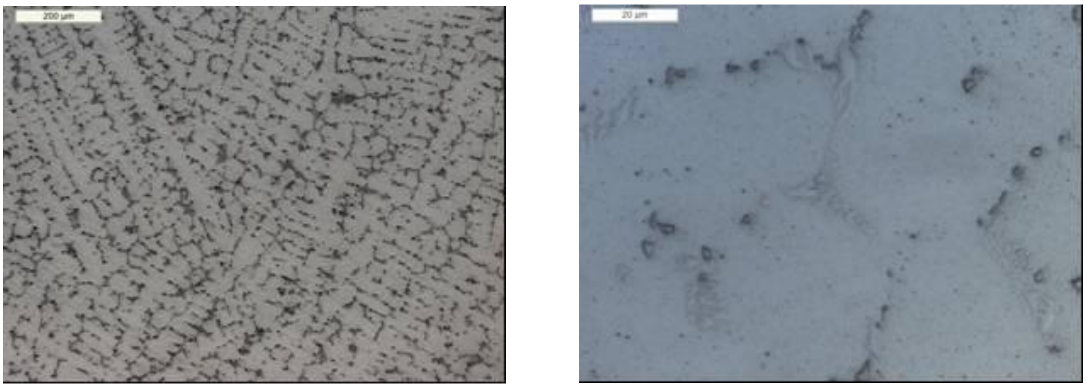
A complementary theoretical study was performed to analyze the electronic structure changes during carbides formation. By simulation using the Viena Abinitio Simulation Package (VASP) [5], we have performed calculations to compare the alloy structure before and after carburization and their potential relation with carbides stability.

RESULTS AND DISCUSION

In this work an analysis by optical microscopy, scanning electron microscopy (SEM) and X-ray diffraction, first under the as cast conditions, and then, under aging condition were carried out in order to characterize the different microstructures and their evolution with temperature and aging time.

As cast microestructure

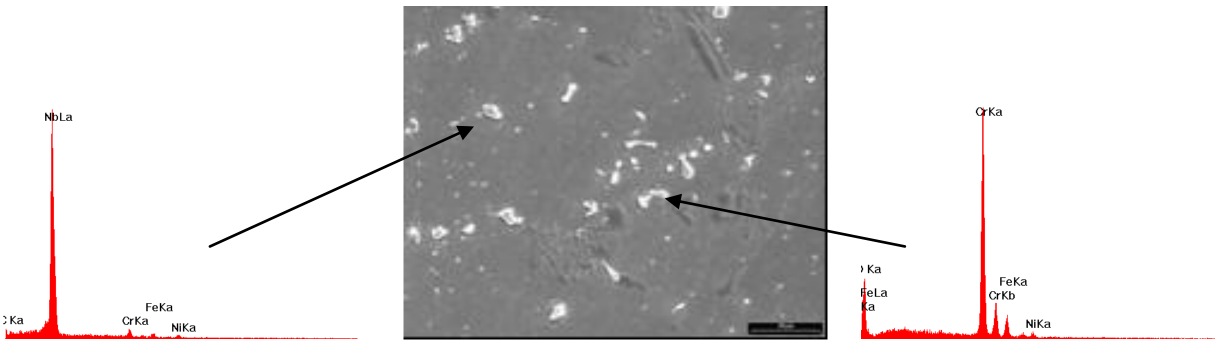
In Fig. 1a, a dendritic type microstructure is observed (100X) and in Fig. 1b the same microstructure is presented but at the greatest magnification (1000x).



(a) (b)

Figure 1. As cat microestructura of modified HP

Figure 2 shows the as-cast microstructure obtained by SEM scanning electron microscopy and two microcomposition spectra taken on a Nb-rich carbide (bright particles in Figure 2a) and another spectrum taken on a carbide rich in Cr (dark particles in Figure 2.b)



(a) (b) (c)

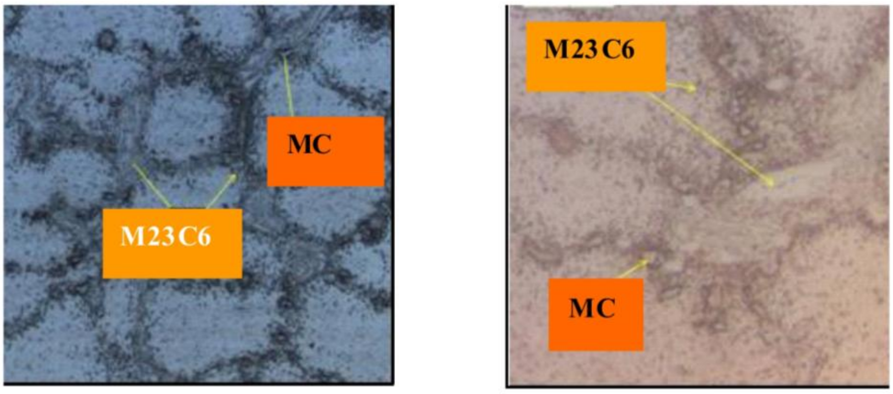
Figure 2. As cast microstructure observed by scanning electron microscopy (SEM) and EDAX spectra, corresponding to two types of carbides.

This technique demonstrates that the microstructure of this alloy in the as cast condition is dendritic, with an austenitic matrix and a network of primary eutectic carbides of two types; one rich in Nb and one rich in Cr. The structure observed is in agreement with that reported by several authors [6-8], the compound rich in Nb is a precipitate of type MC (M = Nb); while the other would be M_7C_3 (M = Cr, Ni, Fe).

Aging microstructure

During the heat aging treatment of the samples, the secondary precipitation of very fine carbides is produced from the interior of the austenitic matrix (as cast condition), which results in an increase in Vickers hardness values.

In Fig. 3a and 3b, microstructures corresponding to the samples can be observed, before and after reaching the maximum hardness value. Primary eutectic carbides ($M_{23}C_6$ and MC) and secondary $M_{23}C_6$ are indicated.



(a) (b)

Figure 3. Microstructures of two aged samples (a) before reaching the maximum hardness value and (b) after the maximum.

In Fig. 4, Vickers hardness values determined in samples that have been subjected to the aging heat treatment, at five temperature values and at different aging times are presented.

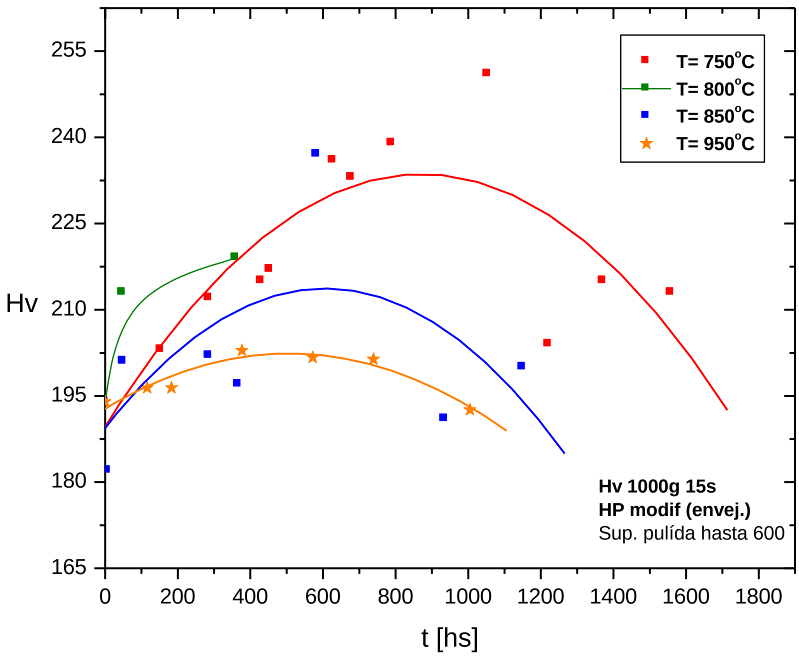


Figure 4. Vickers hardness for four aging temperatures and different times.

Fig. 4 shows that the hardness of the samples has increased from the value in the as-cast condition to a maximum value and then, hardness decreases as the aging heat treatment is prolonged.

It is interesting to note, in particular, the evolution of hardness values, experimentally determined for the temperature of 750°C, where the phenomenon is verified at a slower speed and its evolution can be seen in greater detail.

The increase in hardness to the maximum value is associated with the increase in the volume fraction of the precipitation of secondary carbides, which occurs as very fine particles in the matrix.

In order to deep in our microstructure analysis, several samples were characterized using various techniques such as MO, SEM and X-ray diffraction.

In Fig. 5, the microstructure analyzed by SEM, corresponding to an over-aged sample with a time of 1371 h is shown. The coalescence between precipitated particles in the matrix can be observed.

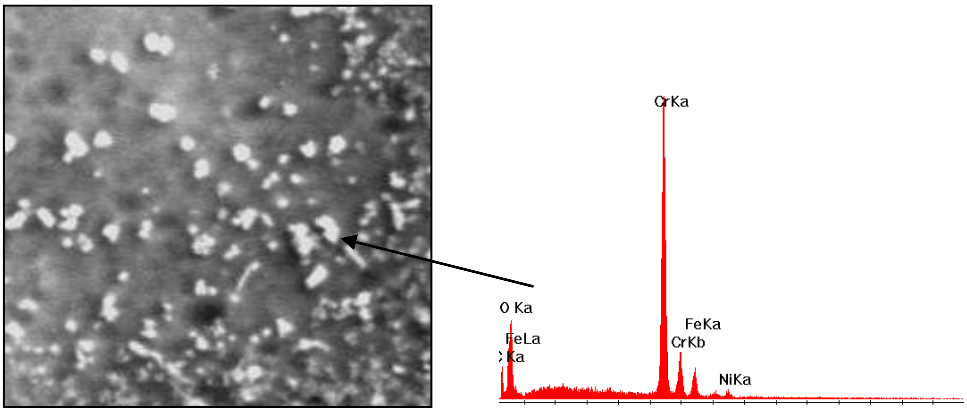
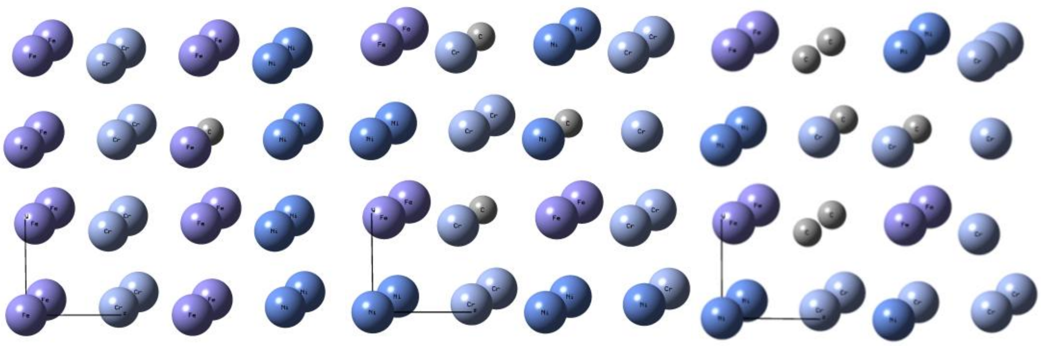


Figure 5. Secondary precipitation of carbides in an over-aged sample.

The semi-quantitative analysis by EDAX shown in Fig. 2 indicates a high Cr presence in the secondary precipitates and is in agreement with those advanced by some authors [9-11], the precipitated compound would be of type M23C6, with M = Cr , Ni, Fe. In this way, we can conjecture that the loss in hardness values, after reaching the maximum value, is associated with the coalescence phenomenon that occurs in the secondary precipitation. Similar case can be observed for the other temperatures, although in those cases the phenomenon is verified more quickly.

Carbides models

In order to analyze the changes in the electronic structure after carburization, we have modeled a cell of the HP alloy and the same size cell simulating M7C3 and M23C6 carbide formation. After relaxation by VASP program, the models (a schematic view) are shown as presented in Fig. 6. The atomic orbital occupations of neighbor metallic atoms are modified due to the present of the C atoms. These changes are responsible of the carbide formation as the new C-metal and C-C interactions are formed in the alloy. The carbides are less stable than the original matrix (see Table 2), as we can see the M23C6 carbide is lesser stable than M7C3. On the other hand, M23C6 presents the bigger changes on spd orbitals (see Table 3). In general, a bonding between C and the metals can arise because of the nearness of the C valence levels to the s–d band of metallic atomic levels and because of the availability of C 2p orbitals for better bonding interactions with d metal orbitals. The resulting orbitals population redistribution during C bonding with surrounding metallic atoms could have influence on the relative embrittling or cohesion enhancing behavior of M23C6 or M7C3 carbide, respectively.



(a) **(b)** **(c)**

Figure 6. Schematic view of (a) HP, (b) M7C3 and (c) M23C6 models.

Table 2. Relative energies

Carbide	Energy (eV)
M23C6	4.22
M7C3	3.24

Table 3. Orbital population changes (%) after carbide formation

Carbide	Orbital population		
	s	p	d
M23C6	+ 9	+14	-22
M7C3	+4	+8	-9

CONCLUSIONS

In this work, it was determined experimentally that the modified HP alloy in as-cast state presents a microstructure formed by an austenitic matrix and a network of eutectic primary carbides formed by MC type niobium carbides and chromium rich carbides of type M7C3. (M = Cr, Ni, Fe). The kinetic evolution of the microstructure in this alloy that has been aged at temperatures between 750 and 950oC at different times demonstrates the precipitation of secondary carbides which are of type M23C6 and MC. Simulation shows that M23C6 is lesser stable and presents the bigger changes in the orbitals populations than M7C3 carbide. The behavior observed during the heat treatment is increasing the hardness from the as-cast condition to a maximum value and then decreasing is associated with a coalescence phenomenon of the secondary precipitates.

ACKNOWLEDGMENTS

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