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Aging of a cast 35Cr–45Ni heat resistant alloy

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The microstructural evolution during aging and its effect on the mechanical properties of a centrifugally cast 35Cr–45Ni heat resistant alloy was studied by means of optical and electron microscopy, and by mechanical testing in samples aged in air at 750 °C for a period of time of up to 1000 h. The as-cast microstructure consisted of an austenitic matrix and a network of two types of primary carbides that were identified as NbC and M₇C₃ by their light and dark tones when viewed in backscattered electron mode in a scanning electron microscope. Aging promoted the occurrence of different phenomena such as the transformation of primary M₇C₃ to M₂₃C₆ carbides, precipitation of secondary M₂₃C₆ carbides and the transformation of NbC to Nb₃Ni₂Si. It was found that aging promoted an increase in Vickers microhardness of more than 50%, the increment in tensile strength of around 20% and the reduction in ductility of close to 70%.

1. Introduction

Heat resistant alloys are materials designed to withstand oxidizing and corrosive environments in sustained operations at temperatures in excess of 650 °C; most of these materials are cast from melts rich in nickel and chromium. Elements such as niobium, titanium, vanadium and zirconium are commonly added to impart higher creep resistance, as they form stable precipitates at the operating temperatures. Silicon and manganese are added to increase their resistance to different degrading environments. These alloys are used as tubes, flanges, cones, headers and coils in furnaces, transfer lines, heaters, and others appliances, for direct reduction of iron ore plants, as well as in petrochemical, chemical and commercial heat treating industries [1–7].

These alloys have been produced by centrifugal casting for more than 50 years and are used in conditions that involve high

pressures and temperatures. Early work involved alloys of the HK type (25Cr–20Ni), being followed later on by the HP type (25Cr–35Ni). Demands for the reduction in fuel and emissions impose harsher operating conditions in many industrial sectors, and so the development of a new generation of heat resistant alloys with contents of 35% Cr and 45% Ni, as well as and many other elements [1–7].

The high content in chromium and nickel promotes an as-cast microstructure composed of a network of primary carbides within an austenitic matrix. Exposure at high service temperatures promotes the occurrence of different metallurgical phenomena that affect the mechanical properties of the alloy [1–4]. Niobium and titanium are added to these alloys to provide stability of the structure while being under severe service conditions. Niobium promotes the formation of MC carbides, which are more resistant to coarsening than chromium-rich carbides. The stoichiometry of chromium carbides changes from M₇C₃ to M₂₃C₆ as niobium takes carbon to form more stable MC carbides. Microstructural refinement and precipitation of fine carbides at high temperature exposure are one of the positive aspects of niobium addition as has been reported by several authors [5–7].

The present work focuses on the microstructural evolution, on and its effects on mechanical properties of a centrifugally cast 35Cr–45Ni alloy aged at 750 °C for up to 1000 h under laboratory conditions, as these alloys are used for long times at high temperature due to their resistance to carburization and oxidation.

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Table 1

Chemical composition of experimental alloy (wt.%).

C	Ni	Cr	Si	Nb	Mn	Ti	P	S	Fe
0.49	46.9	34.45	1.83	0.883	0.764	0.1009	<0.001	<0.001	Bal.

2. Experimental procedures

Samples from a heat resistant 35Cr–45Ni alloy, Table 1, were cut from centrifugal cast pipes of 224 mm in length and of internal and external diameters of 86 and 97 mm, respectively. The samples were held at 750 °C for up to 1000 h in air in an electric resistance furnace. The samples were prepared for their metallographic examination following standard polishing procedures and were etched with an electrolytic solution of 10 g of oxalic acid in 100 ml of water. A potential of 6 V was applied for 3–5 s using a stainless steel cathode; the temperature was kept at 26 °C.

The microstructure of specimens in the as-cast conditions and aged for 500 and 1000 h were examined in an inverted optical microscope. A scanning electron microscope (SEM) was used to evaluate the microstructure of selected samples using secondary (SE) and backscattered electron (BE) detectors; X-ray analyses of selected areas were also obtained (EDX).

The presence of different phases was identified by X-ray diffraction (XRD). The study was complemented by Vickers microhardness tests (200 g for 15 s). Cylindrical tensile specimens of 25 mm in length and 6.4 mm in diameter were machined and tested at room temperature following ASTM E8 standard [8]. Fracture surface of tensile specimens in the as-cast and aged condition were observed by SEM to evaluate the fracture mode.

3. Results

Optical examination of an as-cast sample indicates that the microstructure of the alloy is made of an austenite matrix and a network of primary carbides present in the interdendritic areas, Fig. 1a. The SE image, Fig. 1b, does not distinguish between the different types of carbides present, but the image by BE, Fig. 1c, reveals that the carbides have different chemical composition, as heavier elements appear in lighter tones. Selected EDX analyses carried out on the matrix and on either type of carbide, Fig. 2, show that the bright particles contain Nb, whereas the dark carbides are rich in chromium. Aging promote changes in the microstructure of the alloy. Fig. 3 shows the optical and SEM images from a sample held for 1000 h at 750 °C. The most remarkable features in the aged sample are the precipitation of small secondary needleshape particles and the rounding of primary carbides. The EDX spectra corresponding to a dark globular carbide and a fine needleshape one are shown in Fig. 4; the spectra are very similar, except for the higher amount of Ni in the spectrum for the needleshape particle, but this may be due to the small size of the particle so the nickel that is detected may be present in the surrounding matrix.

A series of semiquantitative chemical analyses were carried out on the matrix to evaluate the changes in composition as a function of aging, this was done by conducting three EDX readings in different zones of the matrix, care was taken to avoid the needleshape particles in the aged samples. Fig. 5 plots the values for nickel, chromium and iron in the matrix; it is clear that the amount of iron does not change with aging, but those for nickel and chromium do. The change in nickel content in the matrix is only detected in the sample being aged for the longer time, whereas depletion of chromium was observed after aging for 500 and 1000 h.

Figs. 6 and 7 plot representative EDX spectra from the bright, Fig. 6, and dark, Fig. 7, particles at different aging times at 750 °C. Fig. 6 shows that the amount of niobium of the bright particles

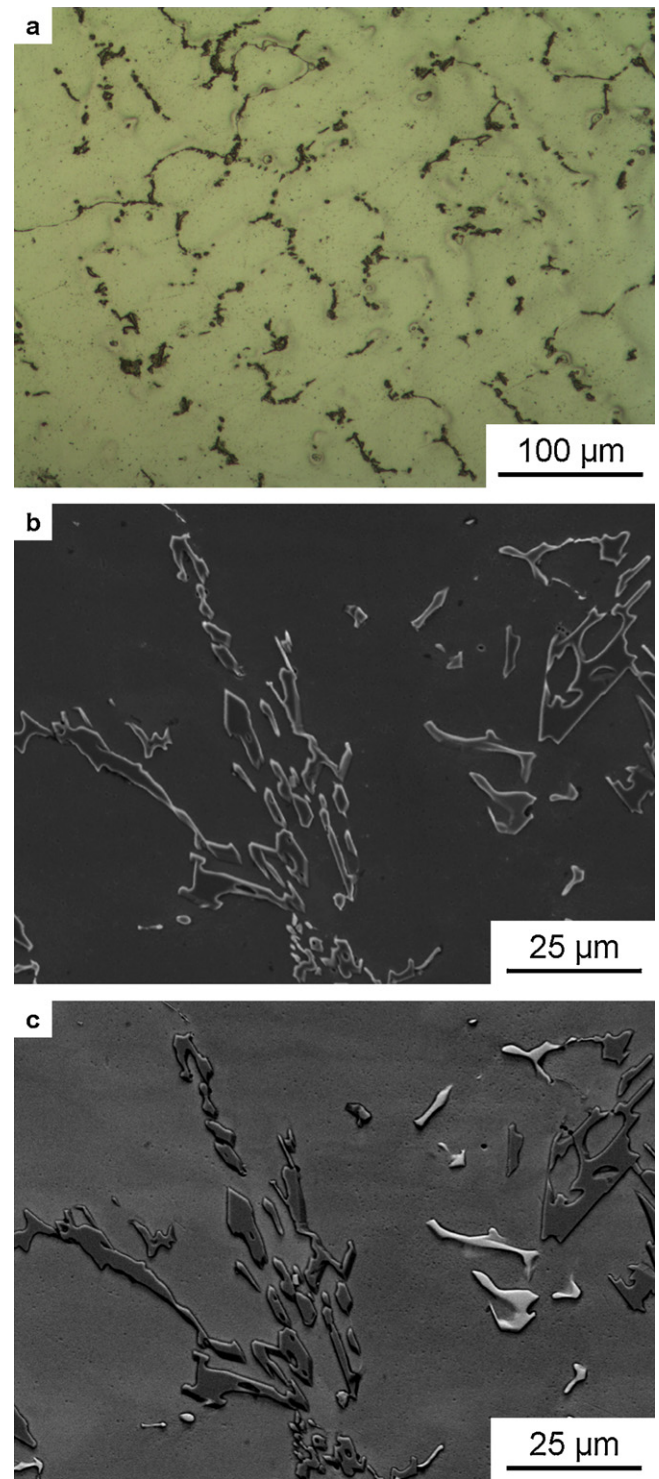


Fig. 1. Light optical microscopy micrograph (a) and scanning electron microscopy micrographs in secondary (b) and backscattered modes (c) of an as-cast sample.

diminishes as the contents of silicon and nickel increase with time. These changes are more notorious in the spectrum taken on the sample aged for 1000 h. The spectra from the dark particles, Fig. 7, show that the amount of chromium increases while that of carbon decreases with aging. X-ray diffraction analyses were carried out on samples in their as-cast and aged conditions, Fig. 8. The as-cast alloy showed diffraction peaks of austenite, NbC and M_7C_3 . Whereas the charts from the samples aged for 500 and 1000 h at 750 °C showed peaks corresponding to austenite, Nb_3Ni_2Si , NbC, M_7C_3 and $M_{23}C_6$.

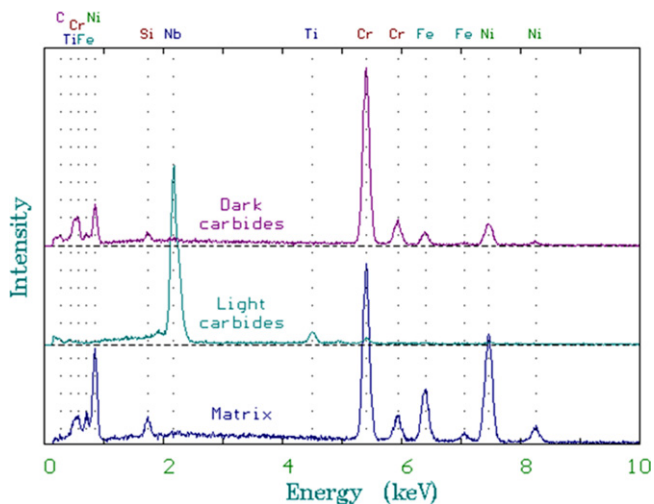


Fig. 2. EDX spectra from the matrix and from the bright and dark primary carbides observed in Fig. 1c.

Fig. 9 shows the increase in microhardness in the samples as a function of the aging time at 750 °C. It can be speculated that precipitation ends after 500 h, as the increment in hardness is marginal beyond this time. Another point to notice in Fig. 9 is that a considerable amount of precipitation takes place at shorter times than 200 h as the increment in Vickers microhardness is of around 50 HVN. Aging results in an increment in hardness higher than 50%. Table 2 shows that aging affects the mechanical properties as the ultimate tensile strength of the alloy is increased by secondary precipitation, but at expenses of ductility. The aging treatment promoted an increase in the tensile strength of the alloy of around 20% at the cost of reducing the ductility to close to a 70%.

4. Discussion

It is observed that the secondary carbides have the tendency to grow along well defined directions, Fig. 3; the angles between different needleshape particles were measured, and it was found that they grow following directions that were inclined either 60 or 90° to each other, indicating that the particles align to $\langle 110 \rangle$ directions (it can be deduced by crystallographic means that any two different $[110]$ directions are inclined either 60 or 90° with respect to each other). One characteristic of the cubic system is that planes and directions normal to each other have the same index, therefore, it can be deduced that the growing particles are of the $Cr_{23}C_6$ type, as these carbides nucleate and grow on $\{110\}$ planes [9].

The spectra shown in Fig. 7 and the diffraction analyses shown in Fig. 8 can be taken as an indication of the transformation of the primary M_7C_3 carbides into $M_{23}C_6$. Studies on similar alloys have reported that NbC transforms to a silicide referred as G-phase [5,10–14], in this work Fig. 6 shows evidence for the formation of a silicide from a carbide (evidence also supported by the XRD analyses, Fig. 8). Transformation from NbC to G-phase takes place by diffusion [15], and is not complete even after 1000 h of aging. It has been suggested that carbon is released into solution, producing a local increase in solute to promote the precipitation of $M_{23}C_6$

Table 2
Mechanical properties in the as-cast and aged conditions.

Property	As cast	Aged for 1000 h at 750 °C
Vickers microhardness (200 g)	205.6	302.9
Tensile strength (MPa)	488	593
Elongation to fracture (%)	6.23	1.97

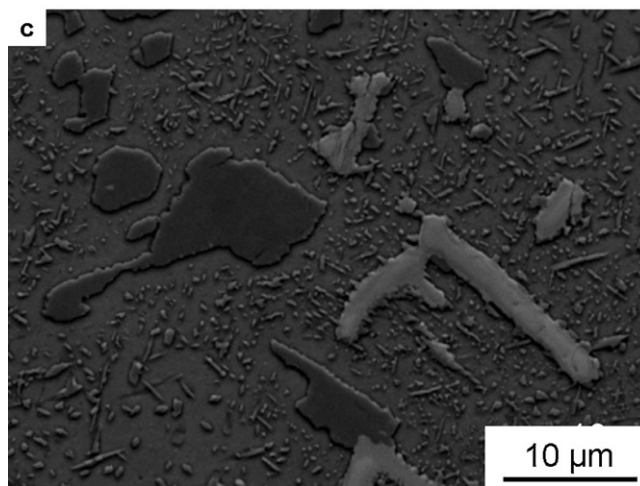
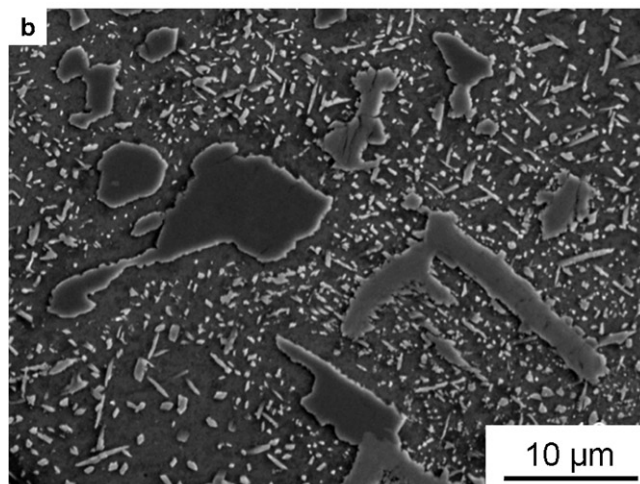
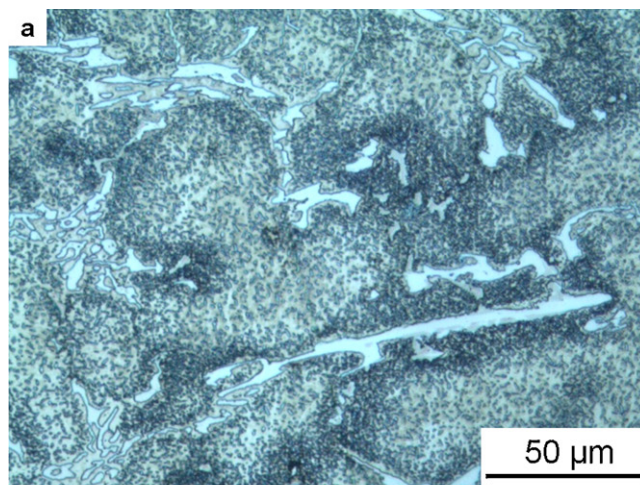


Fig. 3. Light optical microscopy micrograph (a) and scanning electron microscopy micrographs in secondary (b) and backscattered modes (c) of a sample aged for 1000 h at 750 °C.

[10,11]. The transformation of M_7C_3 to $M_{23}C_6$ carbides is consistent with published results [2,7,12,15–17]. Experimental results conclude that this transformation starts after aging for only a few hours [12]. The FCC lattice parameter for the $M_{23}C_6$ carbides was calculated from the XRD diffraction charts yielding to 1.075 nm, which is consistent with the values of 1.06 to 1.11 nm reported in the literature [10,11,18].

Table 3
Data related to η - and G-phase.

Phase	Stoichiometry	Lattice parameter (nm)	Structure	Alloy	Author
-	Nb_3Ni_2Si	1.13	FCC	35Cr-45Ni-0.5C-0.8Nb-0.1Ti-1.8Si	This work
η	Nb_3Ni_2Si	-	-	26Cr-35Ni-0.45C-1.26Nb-0.42Mo-0.6W	Shinozaki et al. [12]
G	Nb_3Ni_2Si	1.065	Cubic	25Cr-20Ni-0.4C-1.5Nb	Barbabela et al. [5]
				25Cr-20Ni-0.4C	
G	$Nb_6Ni_{16}Si_7$	1.11-1.12	FCC	25Cr-35Ni-0.4C-1Nb-2S	Molina [11]
G	$Nb_6Ni_{16}Si_7$	1.12	FCC	20Cr-25Ni-0.03C-0.68Nb-0.6Si	Powell et al. [10]
G	$(Nb,Ti)_6Ni_{16}Si_7$	1.12	-	18Cr-30Ni-0.03C-1.75Nb-0.83Ti	Piekarski [19]
				18Cr-30Ni-0.03C-1Ti	
				18Cr-30Ni-0.03C-1.75Nb-0.05Ti	
G	$Ni_{16}Nb_6Si_7$	1.12	FCC	25Cr-35Ni-0.43C-1.34Nb	de Almeida et al. [20,21]
				25Cr-35Ni-0.41C-0.78Nb-0-04Ti	

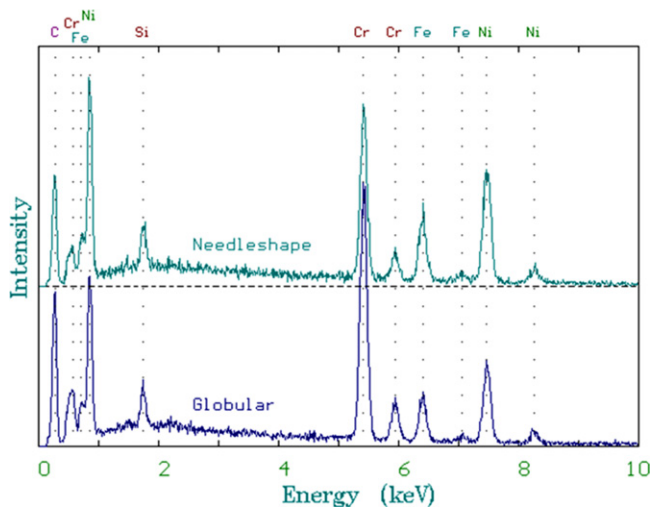


Fig. 4. EDX spectra corresponding to a dark primary carbide and a needleshape secondary carbide from Fig. 3c.

The Nb_3Ni_2Si structure that was identified in the XRD charts in the aged condition has a FCC structure with a lattice parameter of 1.13 nm. Similar structures has been identified by different names, as it has been called η [12] and G-phase [5,10,11,19,20]. G-phase is referred to either a Nb_3Ni_2Si [5] or $Nb_6Ni_{16}Si_7$ [10,11,19-21] stoichiometry. The crystal structure has been reported as cubic [5] or FCC [10,11,19-21], the lattice parameter of the later has been

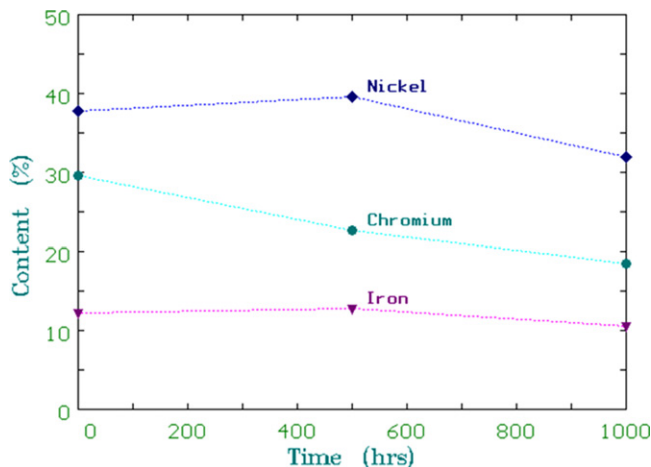


Fig. 5. Changes in the contents of Ni, Cr and Fe in the austenitic matrix obtained from EDX spectra as function of the aging time at 750°C.

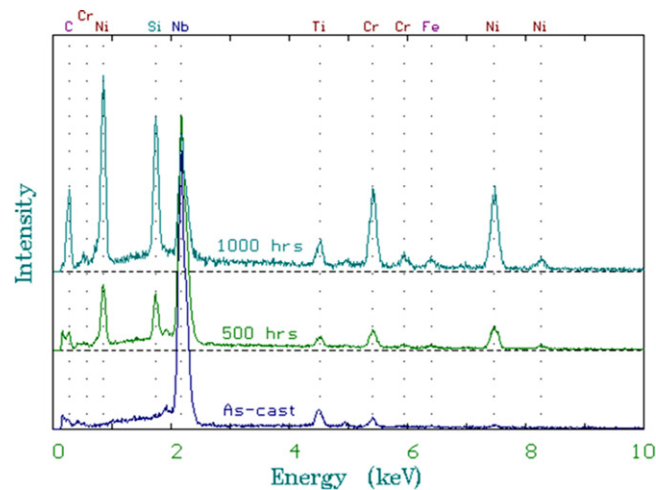


Fig. 6. EDX spectra from the bright primary particles as a function of the aging time at 750°C.

reported to vary from 1.11 to 1.12 nm [10,11,19-21]. It has been reported that silicon plays an important role because it stimulates the transformation of NbC to G-phase [7,10,22], and also that titanium inhibits the formation of G-phase [20]. The present alloy contains 1.6% of Si and 0.1% Ti. Table 3 summarizes the information related to this structure.

The main effect of aging and the change in microstructure is the reduction in ductility and the increase in hardness. These results

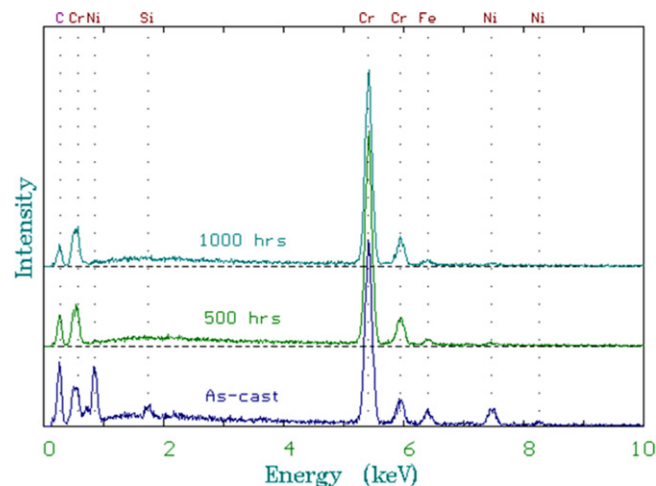


Fig. 7. EDX spectra from the dark primary carbides as a function of the aging time at 750°C.

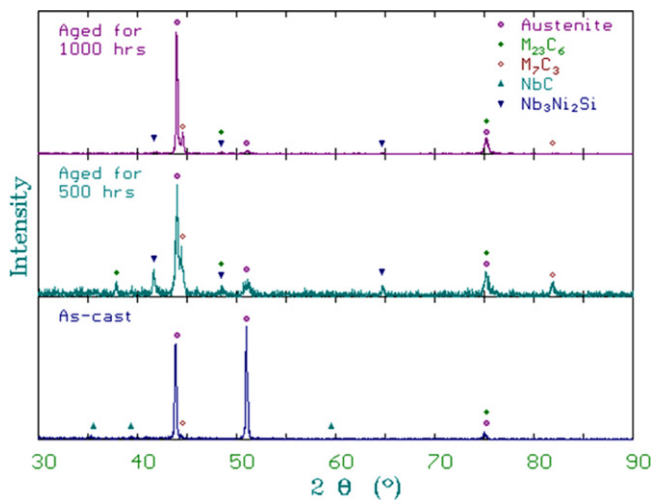


Fig. 8. X-ray diffraction charts in as-cast and aged samples to 500 and 1000 h at 750 °C.

coincide with those obtained in similar materials [1,11,23]. The loss in ductility is important when these type of alloys have to be repaired by welding after service, as the low value of ductility will no allow the repair without an adequate annealing heat treatment [24,25]. It has been claimed that heat resistant cast steels are very sensitive to weld cracking, as cracks are formed in the brittle zones created by primary carbides [26]. It is claimed that η -phase acts as nucleation point of weld cracks in aged samples that are able to grow through $M_{23}C_6$ carbides [12]. The interface between matrix and G-phase has been identified as preferential site for nucleation of cracks due to creep [20,21].

The fracture surface of the tensile sample was studied by SEM to identify the mode of fracture. Fig. 10 shows the images in backscattered mode of the samples in their as-cast and aged (1000 h at 750 °C) conditions. The image of the surface of the as-cast specimen, Fig. 10a, reveals a mixed mode of fracture. Most of the surface is of the fragile type (of faceted brittle appearance) but a series of small dimples (indicative that plastic deformation took place prior to fracture) are also appreciated. The image of the fracture surface of the aged specimen, Fig. 10b, reveals a well-faceted brittle appearance, without any plastic deformation prior to fracture, an indication that the austenitic matrix has lost its capacity to deform plastically.

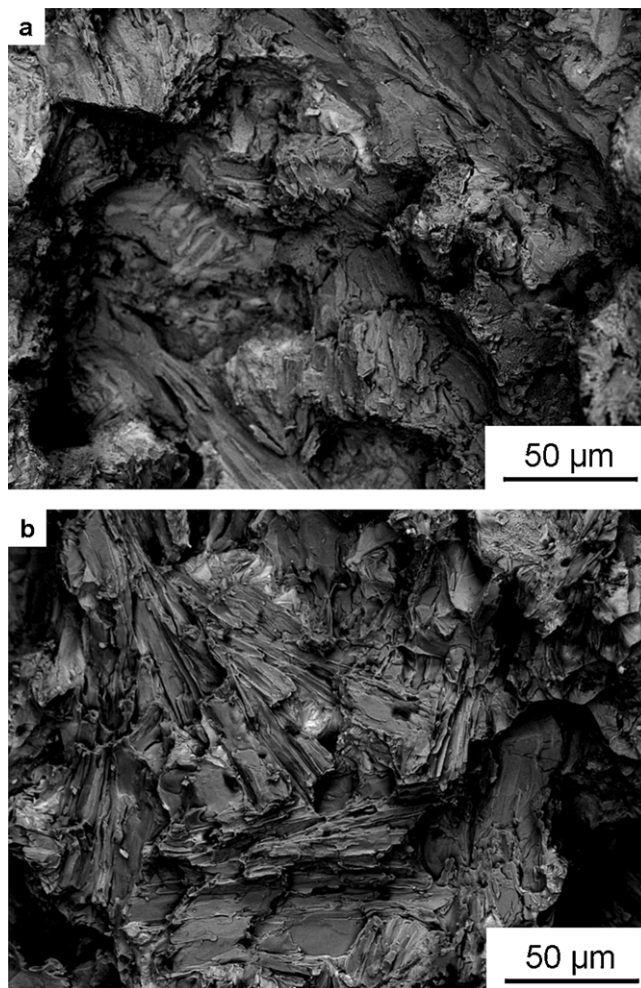


Fig. 10. Fracture surfaces of samples tested in the as-cast condition (a) and aged for 1000 h at 750 °C (b).

5. Conclusions

The microstructure of the as-cast alloy is composed by austenitic matrix and a network of primary carbides present in the interdendritic areas. The scanning electron microscopy image in backscattered electrons mode reveals that the carbides are of two different types. EDX microanalysis showed that niobium-rich carbides appear bright, whereas chromium-rich appear in darker tones. The XRD analysis revealed the presence of NbC and M_7C_3 in the as-cast condition.

Aging for 1000 h at 750 °C produced changes in the morphology and chemical composition of the primary phases and the precipitation of secondary $M_{23}C_6$ carbides. It was found that the M_7C_3 primary carbides were transformed into $M_{23}C_6$, and that the NbC transformed into Nb_3Ni_2Si . It was not possible to determine if this last structure can be identified as η - or G-phase.

Aging affected the mechanical properties of the material, the main effects were the increase in hardness of more than 50%, the increment in the tensile strength of the alloy was above 20% and the reduction in ductility of close to 70%. It was found that the surface fracture of the tensile sample in the as-cast condition was of a mixed mode fracture, although mostly fragile. The fracture surface of the aged material revealed a complete well-faceted brittle appearance.

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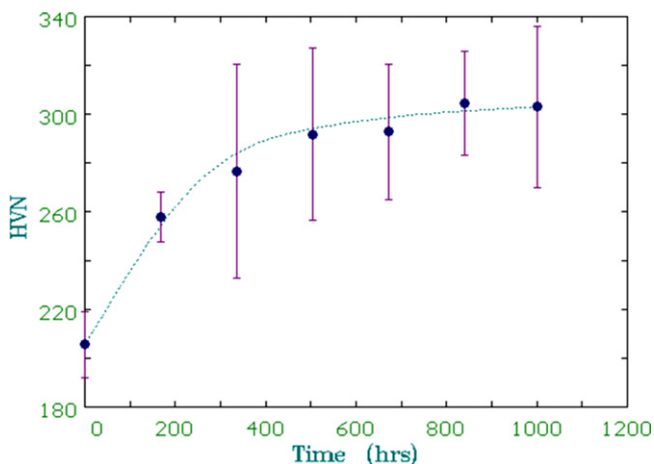


Fig. 9. Vickers microhardness as a function of aging time at 750 °C.

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