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Microstructural analysis of a HP 40Nb alloy aged

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ABSTRACT

In this paper, the change in the microstructure of the centrifugally cast heat-resistant alloys of HP40 Nb after exposure to 0.5h and 2h of ageing times at 1123K and 1323K were investigated. The microstructures of the as-received alloy and aged conditions were examined using light microscopy (LM) and scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS). The chemical composition of various phases and precipitates observed in the aged sample microstructure was characterized by the means of scanning electron microscopy SEM via back-scattered electron (BSE). The present results indicate that ageing enhanced the occurrence of different phenomena such as the transformation of primary M_7C_3 to $M_{23}C_6$ carbides and precipitation of secondary $M_{23}C_6$ carbides. It can be summarized that the present phases and the morphology of secondary carbides in the microstructure of aging results in higher values of hardness.

KEYWORDS

Heat resisting cast alloys, Aging, Microstructure, Carbides

1. INTRODUCTION

Thanks to the unique properties of centrifugally cast heat-resistant alloys of HP series, such as: high mechanical properties, corrosion resistance and stability of mechanical properties under service at temperatures below 1323K; these alloys are found in application in many industries such as petrochemical, chemical and commercial heat treating industries [1-8]. The centrifugally cast heat–resistant austenitic stainless steels are mostly used in petrochemical plants as alloys for production reformer tubes for hydrogen production by steam reforming [9-10].

The creep resistance of these alloys is high, thanks to the main alloying elements chromium and nickel, as well as other alloying elements (Ti, Zr, W and Cs) which in new generations of alloys have proven to be important for improving the required properties. Most heat-resistant alloys contain elements such as niobium, titanium, vanadium, and zirconium are commonly added to give higher creep resistance, as they form stable precipitates at the operating temperatures. In recent years, there has been growing interest in the application of the centrifugally cast HP40Nb alloy, which has been developed by adding a small amount of niobium element into HP40 alloy [11]. It should be mentioned that the addition of niobium in the HP alloy hinders the precipitation of chromium carbides and improves the mechanical properties (increase creep strength and creep ductility, as well as carburization resistance) [12].

The normal designed service life of reformer furnace tubes is defined by the API standard and is 100,000h [6, 7]. However, the actual working life varies from 30,000 to 180,000 h, because it is correlated with the damage mechanisms (corrosion, fatigue, creep and erosion). In addition, the designed service life is not expected to be the same as the actual service life, because the actual operating conditions or the actual performance of the materials and components are not precisely known at the time of design.

It is known that the characteristic microstructure of as-cast HP alloys consists of an austenitic matrix strengthened by a network of intergranular eutectic-like primary chromium-rich carbides (M_7C_3 and/or $M_{23}C_6$ types (M= Cr, Ni, Fe) and niobium carbides of MC type (M= Nb) [13]. However, the microstructure of HP-modified steel of the catalyst tubes changes during service at elevated temperatures. It was reported in [14,15] that the microstructure of centrifugally cast Fe-Cr-Ni heat resistant alloys would change relatively rapidly during service at high temperatures, in a process known as microstructural steel ageing. During ageing, the primary chromium carbides eventually transform into $M_{23}C_6$; while intragranular secondary $M_{23}C_6$ carbides precipitate, also. As a result of this process, the original niobium carbides undergo an in situ phase transformation to a nickel-niobium silicate, $Ni_{16}Nb_7Si_6$ as reported by [16].

The purpose of the present study, due to the mentioned facts, is to examine the microstructural stability of the as cast tube made of HP 40Nb alloy after short-term exposure to temperatures of 1123K and 1323K for 0.5h and 2h, and to identify the types of phases and carbides in this alloy during ageing treatment.

2. EXPERIMENTAL PROCEDURE

2.1. Material

The material investigated in this work was machined out of one tube and manufactured of the centrifugally cast alloy HP-40Nb. The chemical composition of the studied material is shown in Table 1. The specimens were aged at 1123K and 1323K for 0.5h and 2 hours in the electric furnace in an air atmosphere and then each aged sample was cooled in air. The temperature was controlled by the thermocouple Pt-Pt13%Rh placed just above the sample. Microstructural observations were performed on samples of the as-cast tube before and after heat treatment. The chemical composition of various phases and precipitates observed was characterized by the means of scanning electron microscopy via back-scattered electron (BSE) imaging and EDS analyses.

2.2. Methods

Chemical composition

The chemical composition of the service reformer tube was analyzed through standard analytical spectrometry method, using the Optical Energy Spectrometer (OES) type I Spark 8860, Thermo Scientific, USA.

Metallurgical evaluation

Standard metallographic preparation techniques (mechanical grinding and polishing, followed by etching in Nital) were applied before light microscopy (LM) examinations on an Orthoplan microscope (Leitz, Germany).

Metallographic specimens were prepared in accordance with standard metallographic preparation technique: grinding (with SiC papers, from 180 to 2400), polishing (diamond suspensions with 6, 3, 1 and 1/4 µm particle size) and etched with a solution of 15 ml HCl, 10 ml Glycerol and 5 ml HNO_3.

The microstructure was examined using a scanning electron microscope JOEL JSM 6460 LV. The phases observed were analysed using an energy dispersive x-ray analyser system (EDS) INCA Oxford Instruments in conjunction with an SEM.

Hardness measurement

The Vickers hardness HV10 (ISO 6507) was determined with a test load of 98.07 N (10 kg) and a dwell time of 15 s. The testing machine was an HPO 250 (WPM, Germany).

3. ANALYSIS RESULTS AND DISCUSSION

3.1. Microstructure of as–cast material

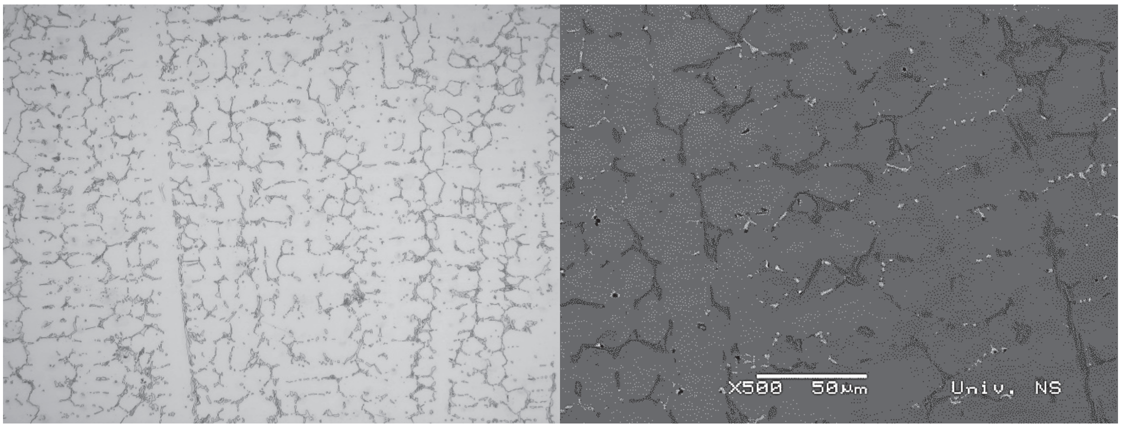
The results of the chemical analysis of the investigated alloy are shown in Table 1. The results correspond to centrifugally cast alloy HP-40Nb.

Table 1: Chemical composition of the investigated alloy (in wt%)

	C	Si	Mn	Cr	Ni	Nb	Ti	Cu	Fe
Wt%	0.44	1.81	1.11	26.99	34.04	0.63	0.03	0.01	Bal.

3.2. Microstructural analysis (Light microscopy)

The microstructure of the as-cast samples consists of an austenite dendrite matrix, a cellular structure containing a network of skeleton shape eutectic primary carbides located at grain boundaries and between dendrites (Fig. 1a-b). At higher magnification observation, based on light contrast, the presence of two types of second phase particles of different morphology may be seen at the grain boundaries (Fig.1b). As can be seen in Fig.1b, one is a niobium-rich phase (white phase) having laminar type (or skeleton form) features, whereas the other is a chromium-rich phase (dark grey phase) having fine particle-like features [17, 18].

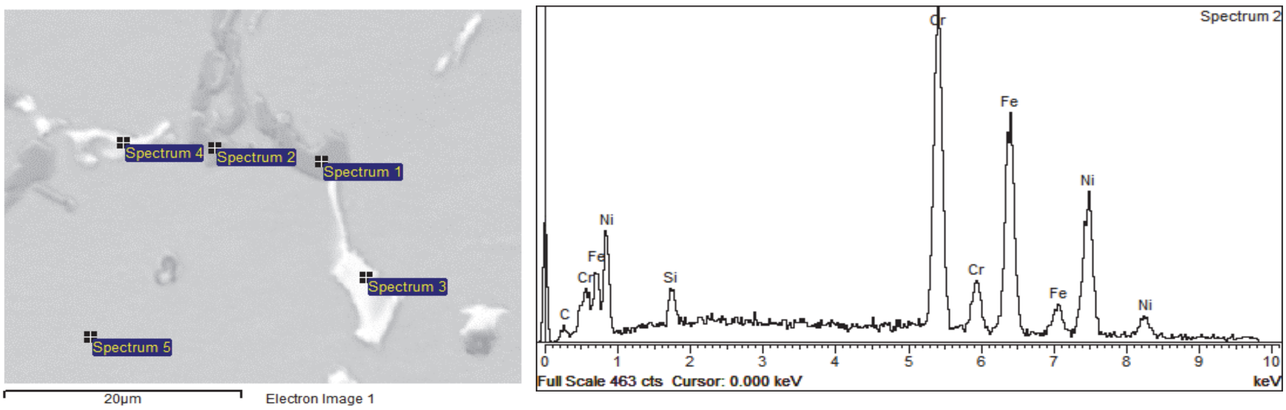


a) 100× b) 500×

Figure 1 Microstructure of HP40 Nb alloy as cast a) LM (Light microscopy) at low magnification (100×); b) SEM image at high magnification (500×).

3.3. Scanning Electron Microscopy (SEM) and X-ray Energy Dispersive Spectroscopy (EDS)

Figure 2a shows an SEM micrograph of the HP -40 Nb alloy in the as-cast condition. As seen in this Figure 2, the microstructure consists of an austenitic matrix and a network of primary carbides of two types: MC carbides (M = Nb, Ti) mainly NbC in white), and M_7C_3 carbides (M = Cr, Ni, Fe), in dark grey. One rich in Nb (bright particles in Fig.2a, Spec 3 and 4) and one rich in Cr (dark particles in Fig.2a, Spec 1, 2). Carbides in the inter-dendritic boundaries appear as lamellar or skeleton forms. The niobium-rich carbides are more stable at high temperatures compared to the secondary chromium carbides [12].



a) b)

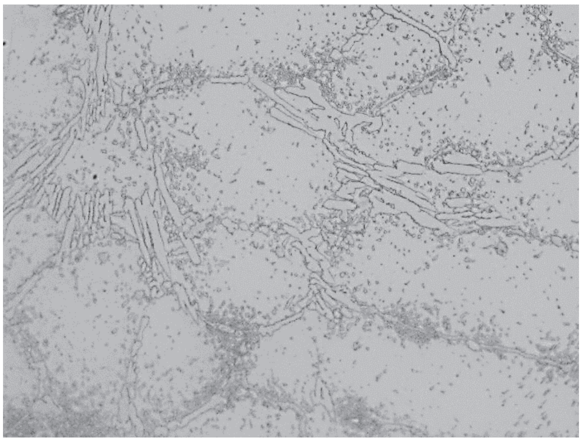
Figure 2 Micrograph of present phases in as-cast HP40 Nb alloy: a) SEM micrographs (BSE), b) EDS spectrum of M_7C_3 carbide (M = Cr, Ni, Fe) in examination point 2 (Spectrum 2)

Table 2. Chemical composition (mass. %) of participate phases in HP40 Nb alloy, corresponding to Fig.2b

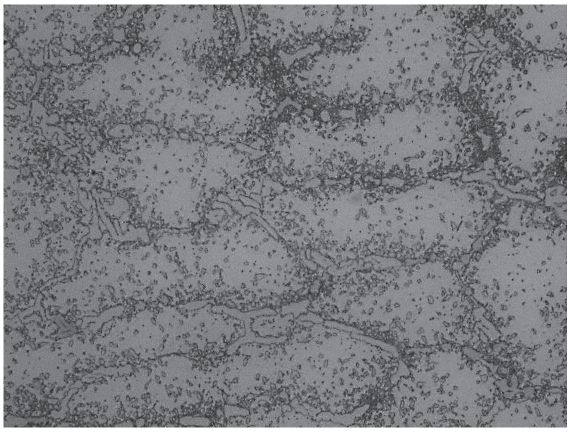
	C	Si	Cr	Mn	Ti	Fe	Ni	Nb
Spectrum 1	36.97		54.39			6.92	1.72	
Spectrum 2	15.83	3.41	28.73			27.11	24.93	
Spectrum 3	44.98		4.62		4.30	2.56	1.8	41.73
Spectrum 4	38.99	1.52	11.78		1.02	10.03	8.49	28.16

3.4. After ageing treatment

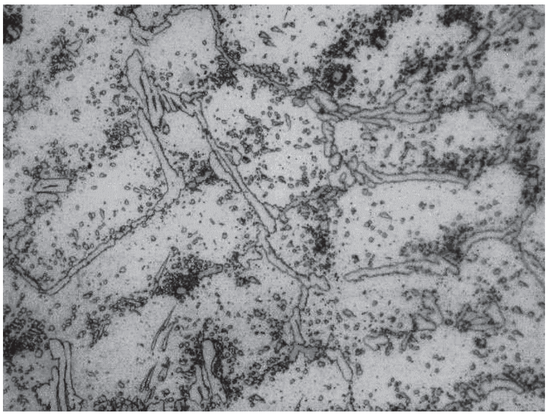
The change of microstructure during ageing at 1173K and 1323K after 0.5h and 2h is shown in Figure 3. The microstructures of HP-40 Nb alloy obtained by light microscopy (LM) after 0.5 h and 2h of ageing treatments performed at 1173K are given in Fig. 3a) and Fig. 3b), respectively. After short–term heat treatment (0.5h) at 1173K, the very fine precipitates of secondary carbides were found in the austenitic matrix, in zones close to primary carbides (Fig. 3a). The number of secondary carbide particles increases with ageing time (2 hours), as shown in Figure 3b. From Figure 3b it can be noticed clearly, that more fine secondary carbide particles precipitated in the matrix and agglomerated along the grain boundaries. Results of the EDS analysis of phases in the aged specimen at 1173K for 2h observed at SEM micrograph in Figure 4, are given in Table 3. The microstructure consists of an austenitic matrix (Spec.1) and two types of precipitates: one rich in Nb (white phase) - Spec.4, and one rich in Cr (dark gray phase) - Spec. 2, 3.



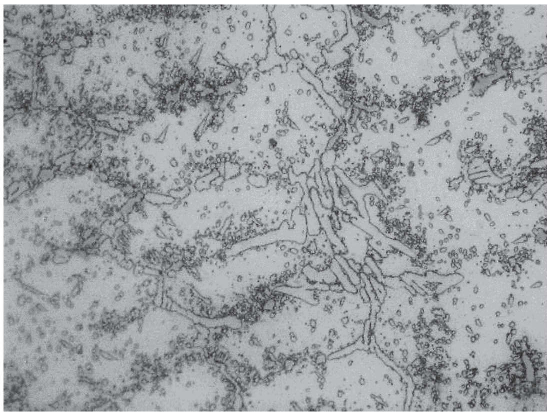
a) 500×



b) 500×

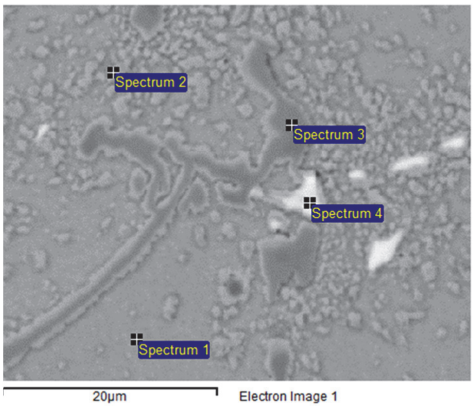


c) 500×

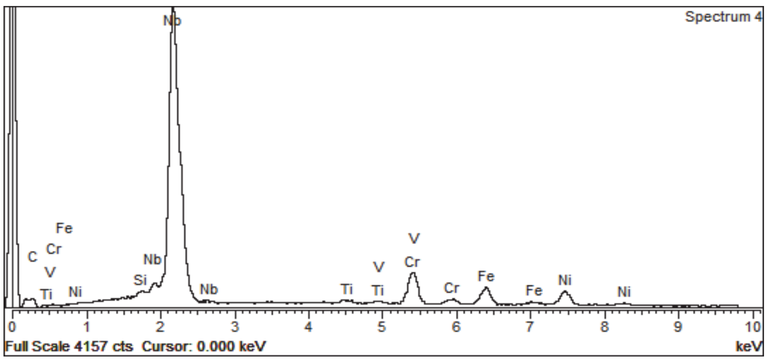


d) 500×

Figure 3: Light microscopy micrographs of a samples aged at: a) 1173K for 0.5h; 1173K for 2h; c) 1323K for 0.5h; d) 1323K for 2h



a)

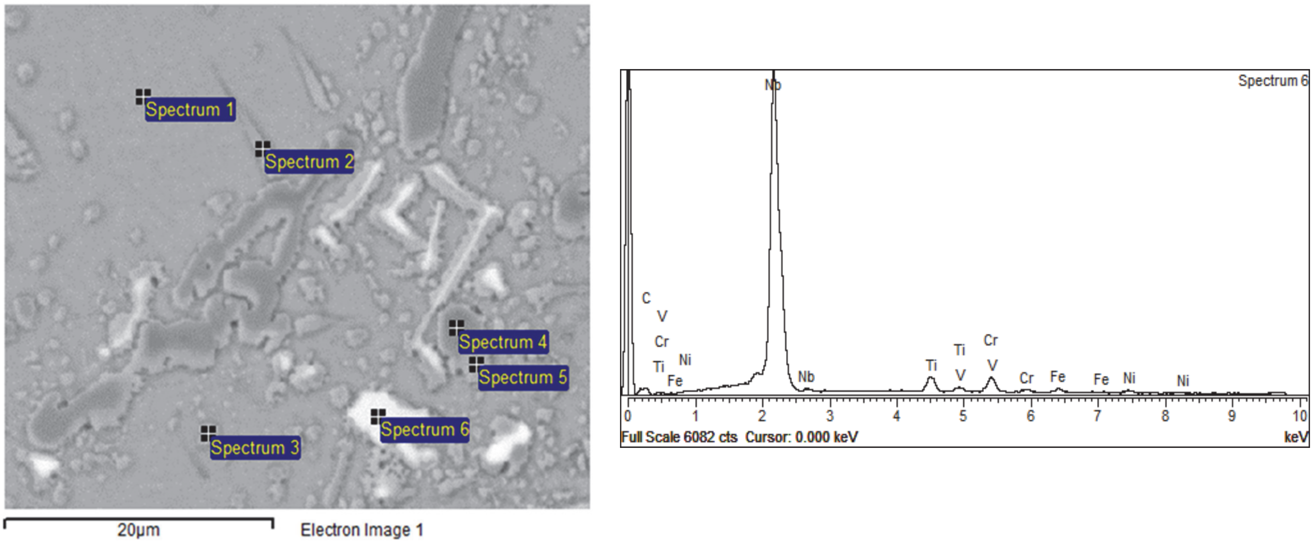


b)

Figure 4 Micrograph of present phases in 1173K aged HP40 Nb alloy: a) SEM micrographs (BSE), b) EDS spectrum of MC carbide (M= Nb) in examination point 4 (Spectrum 4)

Table 3: Chemical composition (mass%) of participate phases in HP40 Nb alloy, corresponding to Fig.4a

Spectrum	C	O	Si	Ti	V	Cr	Mn	Fe	Ni	Nb
Spectrum 1	4.12	0.89	1.25	-	-	21.22	1.32	36.35	34.85	
Spectrum 2	5.71		1.95			23.85	1.62	32.70	34.18	
Spectrum 3	7.69				0.51	75.96	2.06	10.47	3.31	
Spectrum 4	15.41		0.46	0.61	0.43	8.55		5.81	6.56	62.18



a) b)

Figure 5 Micrograph of present phases in 1323K aged HP40 Nb alloy: a) SEM micrographs (BSE), b) EDS spectrum in examination point 6 (Spectrum 6)

Table 4: Chemical composition (weight %) of participate phases in HP40 Nb alloy, corresponding to Fig.5a

Spectrum	C	Si	Ti	V	Cr	Mn	Fe	Ni	Nb
Spectrum 1	4.47	1.43			21.56	1.44	36.41	34.68	
Spectrum 2	6.33	1.41			26.91	1.45	32.02	31.88	
Spectrum 3	5.81	1.56			26.84	1.65	31.84	32.30	
Spectrum 4	9.16				70.38	1.81	12.61	5.59	0.45
Spectrum 5	6.55	1.46			27.85	1.64	30.82	31.67	
Spectrum 6	15.70		3.69	0.64	4.33		1.50	1.32	72.82

From Figure 5, it should be noted that the primary chromium carbides transform from M_7C_3 to $M_{23}C_6$. The secondary carbides were observed within the austenitic matrix close to the primary carbides. In this case, the microstructures after aging at 1323K for various aging times, are quite similar to those aged at 1173K, as can be seen in Fig.3c-d. However, it should be noted that the amount of needle-shaped $M_{23}C_6$ (M = Cr) type carbides formed in the austenitic matrix and secondary carbide film increased at this ageing condition [19].

3.5. Change of hardness during ageing

The Vickers hardness values determinations for samples aged at 1123K and 1323K and at different times are presented in Table 5. As can be seen, the different behavior in the evolution of the hardness for two temperatures of 1123K and 1323K. The hardness results after the lower temperature ageing are less than those of higher ones. The samples that have a maximum (207 HV10) and minimum hardness (197 HV10) were compared in their microstructures; for example, samples aged between 0.5h and 2 hours. The reason for this behavior can be explained by the change in the precipitate morphology and increased amounts of precipitates in the matrix.

Table 5: The results of Vickers hardness tests HV10 of the aged samples

Ageing temperature (K)	Ageing time (hours)	
	0.5	2
1123	197	207
1323	200	204

4. CONCLUSIONS

In this study, the microstructural evolution occurring in the HP 40 Nb heat-resistant stainless steel tube during the ageing was investigated. The obtained conclusions can be summarized as follows:

- After a short time of ageing (0.5h) at 1173K, the very fine precipitates of secondary carbides were found in the austenitic matrix, in zones close to primary carbides.
- The amount of the secondary carbide particles increases with ageing time (2 hours) at 1173K and more fine secondary carbide particles precipitated in the matrix and agglomerated along the grain boundaries.
- The microstructures after ageing at 1323K for various ageing times, are quite similar to those aged at 1173K. However, it should be noted that the amount of needle-shaped $M_{23}C_6$ (M = Cr) type carbides formed in the austenitic matrix and secondary carbide film increased at this ageing condition.
- The presence of these secondary carbides and change in the precipitate morphology in heat-treated specimens, resulting in higher values of hardness.

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