



# Effects of working temperature and carbon diffusion on the microstructure of high pressure heat-resistant stainless steel tubes used in pyrolysis furnaces during service condition

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## ABSTRACT

In the present study, high pressure heat-resistant cast stainless steels (HP steels) modified with niobium and titanium were investigated in as-cast conditions and after being used in pyrolysis furnaces. Life span of the studied specimens obtained from pyrolysis furnace was 5 years. Microstructural changes were studied via scanning electron microscopy (SEM) equipped with energy dispersive spectrum (EDS), optical microscopy (OM), and X-ray diffraction (XRD). The effect of temperature and carbon diffusion on the microstructure, chromium-rich carbides, the NbC transformation to G-phase and other precipitates formed during service condition were discussed. The results showed that two major phases, namely chromium and niobium carbides, existed in the as-cast specimens. Temperature and carbon diffusion influenced the composition and volume fraction of secondary precipitates. Chromium and niobium carbides were transformed to  $M_{23}C_6$  and G-phase respectively during service. Higher working temperatures do not always cause coarsening of precipitates. However, factors such as decarburization and carbon diffusion have important roles, too.

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## 1. Introduction

The pyrolysis furnaces are heavily used in the chemical industry. These furnaces are composed of several vertical tubes. There are gas torches in the furnace chamber and the lower parts of furnace which act as the heat sources. Therefore, the lower parts of the furnace have a higher temperature. In pyrolysis furnaces, heavy hydrocarbons are broken to light hydrocarbons at temperatures beyond 850 °C. Therefore, the presence of atomic carbon and hydrogen is inevitable in the fluid flowing through the tubes. High heat transfer coefficient, mechanical strength at elevated temperatures, creep resistance, microstructural stability, carburization resistance, oxidation resistance, and economic considerations are various criteria that should be considered for the appropriate selection of materials for tubes. The use of HP steels in pyrolysis furnaces has been started since 1960s. This class of steels has high-temperature strength and corrosion resistance. To access the best properties, HP tubes are produced via centrifugal casting. Coarse dendritic grains, segregation of alloying elements during casting, and precipitation of primary eutectic in dendritic boundaries lead to an increased creep properties in these alloys [1]. In 1970s, niobium was added to HP alloys in order to improve their

high-temperature properties. This trend was followed by adding titanium, zirconium, and rare-earth elements [2,3].

One of the main problems with pyrolysis furnaces is carbon deposition on inner wall of the tubes and creation of a porous layer of coke. This phenomenon reduces the heat transfer and increases the heat transfer coefficient. On the other hand, fluid velocity increases with a reduction in internal diameter of the furnace. This results in a decrease in the contact time of fluid with the high heat areas. This layer reduces heat transfer and leads to an increase in the temperature of the external scale of the tubes. The presence of carbon in inner wall of the furnace at high temperatures provides appropriate conditions for the carbon diffusion into the alloy [4,5].

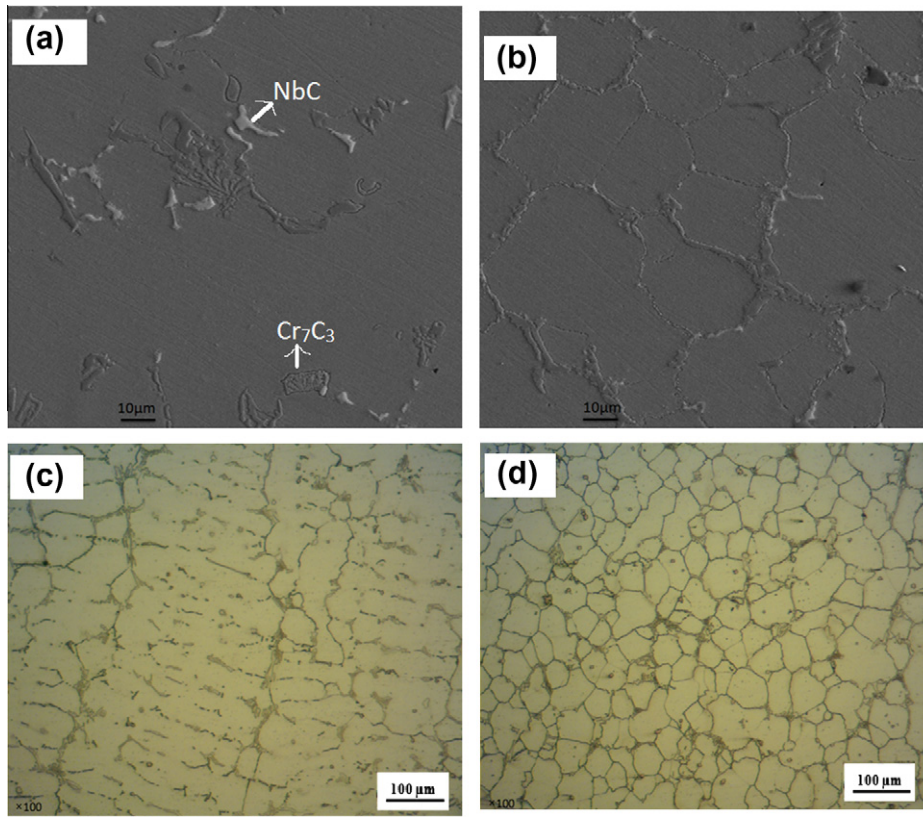
During the service condition, interstitial carbon atoms react with carbide-forming elements and precipitate in the grain boundaries [6]. In the present research, the effect of temperature and carbon diffusion on the microstructure of HP tubes during service condition was studied. Selection of specimens studied in this research was accomplished according to the works of Gong et al. [7] and Mucek [8]. Gong et al. claimed that tube damage was particularly significant in the lower part of the furnace [7]. Tube condition has a significant effect on the microstructure and also on the property changes. Mucek [8] indicated that the carburization near the torch was higher than elsewhere. Central regions of the furnace have the highest temperature (about 1100 °C). This is because of the fluid flow from the marginal zones toward the center of the furnace. Thus, two central

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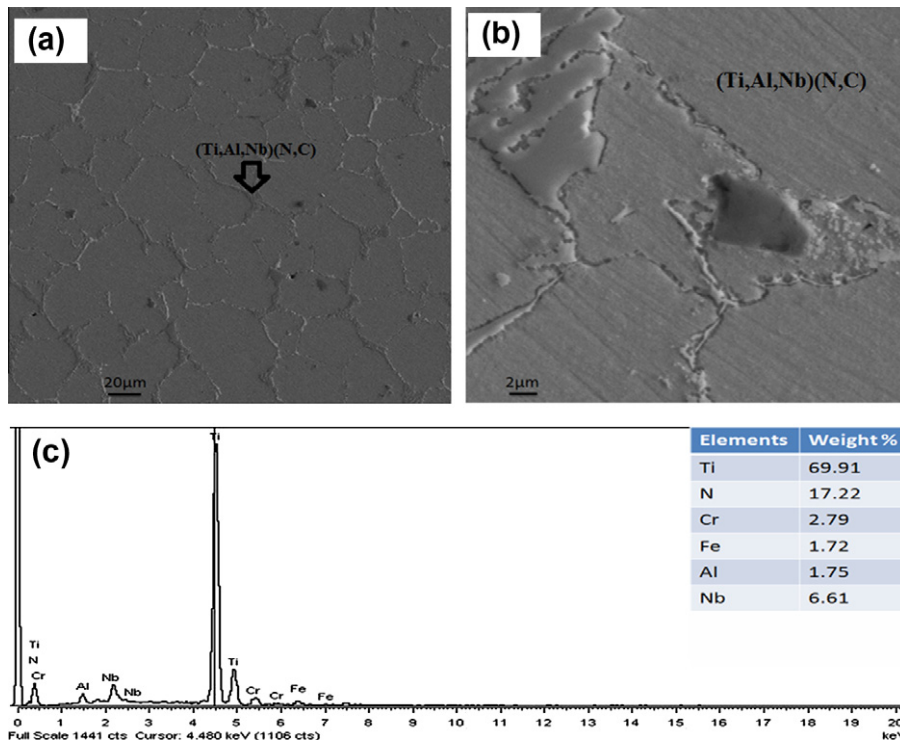
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**Table 1**  
The chemical composition (wt.%) of as-cast specimen.

C	Si	Mo	Mn	Ni	Cr	Nb	W	Ti	Al	V
0.450	2.000	0.090	1.000	33.000	24.000	0.700	0.400	0.200	0.050	0.026



**Fig. 1.** Microstructure of as-cast specimen (a) SEM image of outer regions of tube, (b) SEM image of inner regions of tube, (c) OM micrograph of outer regions of tube and (d) OM micrograph of inner regions of tube.



**Fig. 2.** (a) SEM image of inner regions of as-cast specimen, (b) SEM image of dark precipitates and (c) EDS pattern from dark precipitates.

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