

EFFECT OF MODIFYING ELEMENTS IN YTTRIUM-BEARING HP STEELS. Frederico de Carvalho Nunes(1), Luiz Henrique de Almeida(1). (1)Materials Science and Engineering Department, COPPE, Federal University at Rio de Janeiro (UFRJ), Ilha do Fundão, 21945-970, P.O. Box: 68505, Rio de Janeiro, Brazil. Email: fcnunes@metalmat.ufrj.br

HP-type stainless are the material of choice for the fabrication of radiant tubes to be used in reformer furnaces, where hydrogen production takes place. Being heat-resistant, these steels present high mechanical strength under elevated temperatures as well as good resistance to oxidizing and reducing atmospheres. Its microstructure in the basic composition (0.4%C, 35.0%Ni, 25.0%Cr, 1.6%Si) consists of a fully austenitic matrix and chromium carbides at the interdendritic spaces. Service conditions comprise high temperatures and a carburizing environment. Due to these conditions the steel shall have a very stable microstructure in order to avoid excessive coarsening. The demand for better service performance has motivated developments in these steels, specially concerning their chemical composition. The addition of niobium have proved successful, resulting in better creep properties, through microstructural refinement and substitution of part of the chromium carbides with niobium carbides, more stable to coarsening[1]. However, under exposition at high temperatures, niobium carbides undergo an *in situ* transformation to a deleterious phase, caused G phase. The combined addition of niobium and titanium presents improvements such as a higher level of refinement and also the inhibition of the G phase transformation[2]. This is important, since creep cracks tend to nucleate and develop at the G phase/matrix boundaries [2]. More recently, yttrium was considered to be added to these steels because of its desulfuring and deoxidizing effects, and because of its stabilizing effect on the passive oxide layer of these steels, thus improving carburization resistance[3]. Nunes [4] has centrifugally cast two HP-NbTi tubes modified with yttrium (called YA and YB), whose additions were (in wt%): YA – 0.87%Nb, 0.05%Ti, 0.07%Y, 1.76%Si and YB – 0.89%Nb, 0.002%Ti, 0.012%Y, 1.30%Si. These alloys have displayed better creep properties than commercially available alloys with similar composition without yttrium, because of the higher level of fragmentation exhibited by the yttrium-bearing alloys, since it prevents the formation of continuous paths for creep crack growth, as quantified by Nunes[4]. Small yttrium-rich particles were observed associated to primary chromium carbides and mixed niobium-titanium carbides in both alloys. Electron diffraction analyses were carried out and it was detected that yttrium forms carbides (Y_3C) – mostly – and sulfides before the solidification of the matrix, which serve as heterogeneous nucleation sites for the primary carbides, thus developing composite precipitates. These particles can be directly or indirectly associated to chromium carbides – that means they can serve as nucleation sites for mixed niobium-titanium carbides, which are associated to primary chromium carbides. This is the reason for the fragmentation of the primary chromium carbides observed in the yttrium-modified HP steels[4]. Tensile tests run at room temperature presented no considerable difference between the alloys YA and YB, but the latter presented an average creep rupture time 42% longer. The main objective of this work is to understand the role of variable additions of modifying elements in yttrium-bearing HP steels under service conditions (high temperature). The data for this work was gathered from TEM observations, X-ray mappings and phase identification by EDS and electron diffraction analyses. Thin foils were obtained in the aged condition, that is, 980°C for 100h. Significant differences between the microstructures of alloy YA and YB after aging heat treatment were observed. Figure 1 shows that exposition to high temperature results in the formation of G phase in alloy YA, which was identified by the Ni, Nb and Si peaks in the EDS spectrum presented in figure 1c. Alloy YB presented a much smaller volume fraction of G phase. The reason for this is explained by Ibañez [5], who detected that in alloys with higher silicon content the transformation NbC \rightarrow G phase is favored, whereas this transformation is delayed in alloys having lower silicon contents. Furthermore it was observed a significant amount of nanometrically-sized niobium-rich particles in the alloy YB. An example is shown in figure 2, where small niobium-rich particles surround a mixed niobium-titanium carbide/yttrium carbide composite precipitate. These particles are smaller and more round than secondary chromium carbide particles. These two aspects are the responsible the better creep performance detected in alloy YB.

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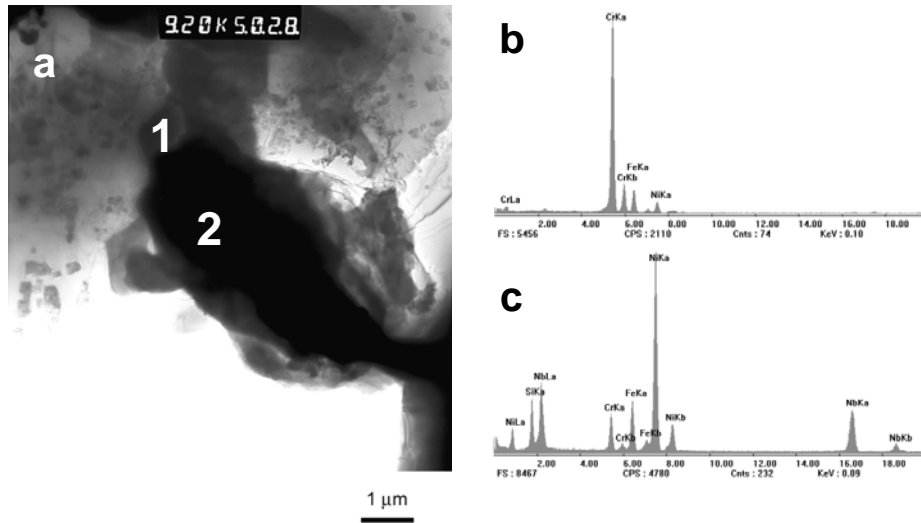


Figure 1 – a) Large G phase particle surrounded by smaller chromium carbide particles, b) EDS spectrum of the chromium carbide (particle 1), c) EDS spectrum of the G phase, identified by the strong peaks of Ni, Nb and Si (particle 2)

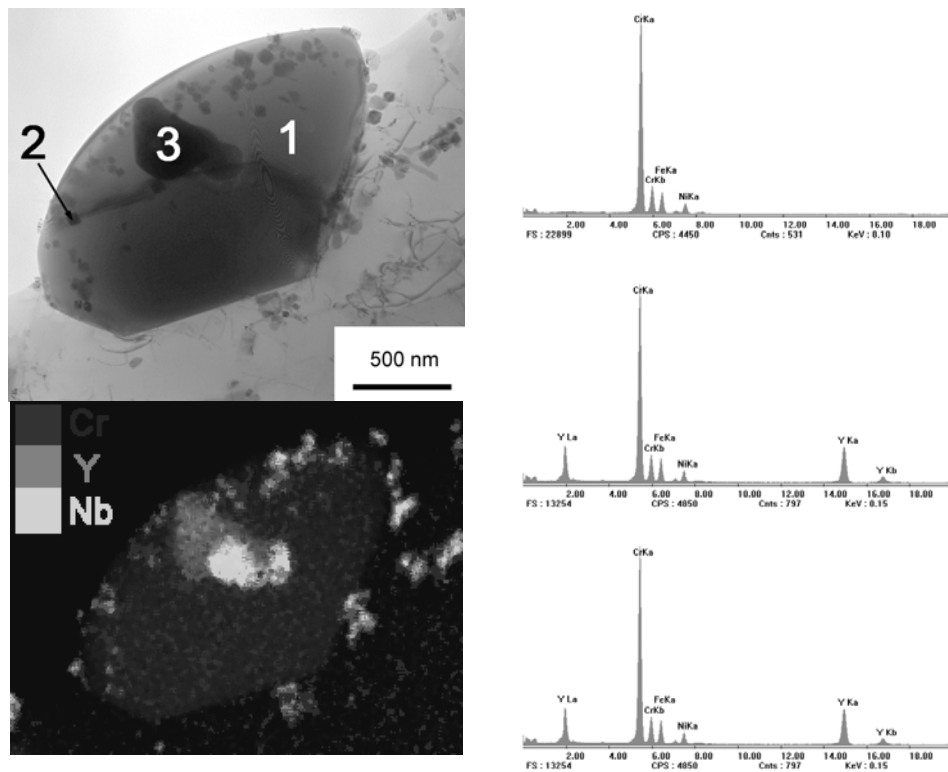


Figure 2 – a) Chromium carbide particle with an yttrium-rich nucleus and small niobium-rich particles, b) combined X-ray mapping of Cr, Y and Nb, c) EDS spectrum of the chromium carbide particle (identified as 1), d) EDS spectrum of the niobium-rich particle (identified as 2), e) EDS spectrum of the yttrium-rich nucleus (particle 3)