

Impact of Analytical Electron Microscopy in Advancing Materials Technology in the Refining and Petrochemical Industry

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Structural materials used in the refining and petrochemical industry are constantly subjected to a range of hostile environments during service [1]. Based on years of experience, there are extensive industry guidelines for the safe operational limits for the structural components. However, due to lack of a detailed knowledge of the damage mechanisms, these guidelines tend to be conservative, offering the potential for extending component life and/or expanding the operation envelope. Recent efforts at SK Innovation have been directed at exploring such opportunities through a better understanding of the damage mechanisms. These efforts require detailed analytical electron microscopy studies aided by computational work. This paper highlights results from one of the ongoing studies.

One of the chronic issues in the petroleum industry has been the degradation of austenitic stainless steels of by sensitization which consists of the formation of chromium carbides at the grain boundaries. It well known that titanium or niobium is added to “stabilize” the steels through the formation of TiC or NbC with the intent to decrease the carbon solubility in the austenite prior to service. However, industry experience shows that both these steels do sensitize in service. Therefore, the question arises if these elements are inherently incapable of reducing the carbon solubility in the austenite to prevent chromium carbide precipitation or if there are other factors (e.g. composition, heat treatment) that influence their performance. If it is the latter, it would be helpful to understand those in an attempt to improve the sensitization resistance of these steels and extend their service life.

One of the key factors in understanding the performance of the stabilized steels is the role of nitrogen [3]. Although sensitization is caused by chromium carbide precipitation, nitrogen would have strong influence on the carbide precipitation by indirectly affecting the carbon solubility in the austenite. Therefore, distribution of nitrogen in the steels would be of special interest. It is also known that the addition of titanium or niobium affect the creep rupture strengths of these steels – the titanium modified steel (AISI 321) has lower creep strength compared to the niobium modified steel (AISI 347). Therefore, an understanding of the origin of the better creep resistance of steel 347 was also a purpose of the study.

Samples of steels 321 (Fe-17.5Cr, 9.3Ni, 0.03C, 0.03N, 0.35Ti) and 347 (Fe-17.5Cr, 9.4Ni, 0.02C, 0.06N, 0.6Nb), wt%, in the virgin and service exposed conditions were examined by analytical electron microscopy. CBED, WDS, EDS and EELS techniques were used to determine the crystal structure and chemistry of the precipitates. In addition, solubilities of carbon and nitrogen in the austenite phase were calculated by Thermocalc. The following were the key findings to date [4]:

1. Neither steel showed extensive precipitation of grain boundary chromium carbides.
2. Both the steels contained coarse particles in the size range of 2 to 5 μ m. These particles were determined to be $Ti_{0.35}N_{0.65}$ in steel 321 and $Nb_{0.60}(C_{0.15}N_{0.25})$ in steel 347 by WDS.
3. Thermocalc analysis showed that the carbon solubility in austenite is reduced with increasing ratios of Ti/C in 321 or Nb/C in 347. The reduction was higher in 321 compared to 347, Figures 1 and 2.

4. The austenite solubilities of nitrogen and carbon at 900°C were calculated by Thermocalc:

Steel	Composition for Calculation	Austenite Nitrogen, wt.%	Austenite Carbon, wt%
321	0.025C, 0.025N, 0.5Ti(wt%)	1×10^{-7}	5×10^{-5}
347	0.03C, 0.03N, 0.9Nb (wt%)	1.5×10^{-3}	9×10^{-4}

5. Steels 347 and 321 contained a higher density of secondary particles, Figures 3 and 4. These particles were identified to be Nb_{0.50}(C_{0.35}N_{0.15}) while work is in progress to identify their chemistry in steel 321.

Based on the above observations, it appears that the partitioning of nitrogen between the primary (coarse) particles and austenite is different for the steels. In steel 321, most of the nitrogen in the steel is tied up as primary TiN leaving little nitrogen in the austenite. In steel 347, however, there is significant amount of nitrogen in the austenite resulting in the formation of fine niobium carbo-nitrides during service. Also, the higher creep rupture strength for the 347 steel could be the result of solid solution strengthening of niobium in addition to precipitation strengthening by fine carbides or carbo-nitrides. Details of other experimental results and discussion of their impact will be presented.

References:

[1] R. Viswanathan in “Damage Mechanisms and Life Assessment of High-Temperature Components”, (ASM International)
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 [3] J. Oh, J.H. Yoon and J.H. Hong, Corrosion vol. **56** (2000) p.289
 [4] I. Park, Y. Ro, J. Shim, J. Nam and J. Kim, Unpublished work, SK Innovation, Daejeon (2016).

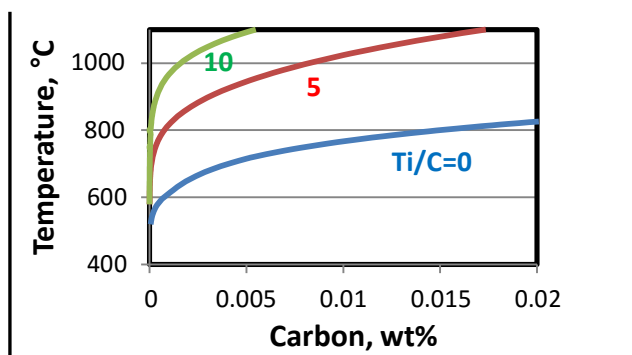


Figure 1. Austenite carbon solubility in steel 321 for Ti/C= 0, 5,and 10 (Thermocalc)

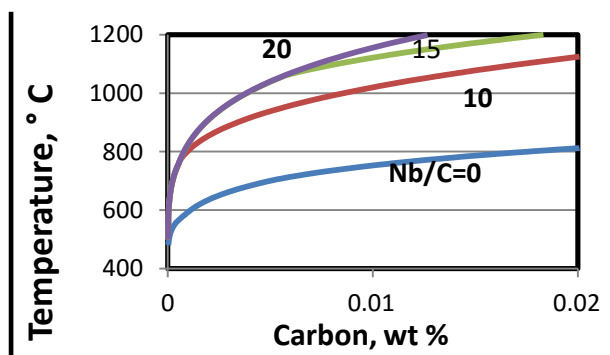


Figure 2. Austenite carbon solubility in steel 347 for Nb/C= 0, 10, 15,and 20 (Thermocalc)

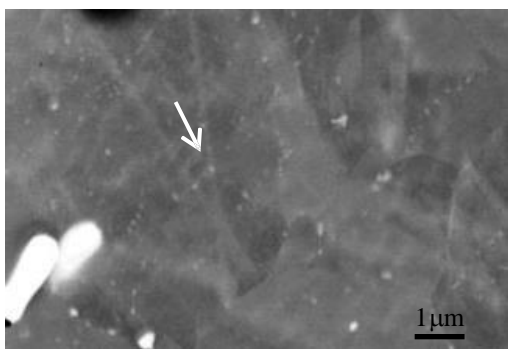


Figure 3. SEM image of steel 347 after 1 year at 460°C service showing coarse and fine precipitates (arrow)

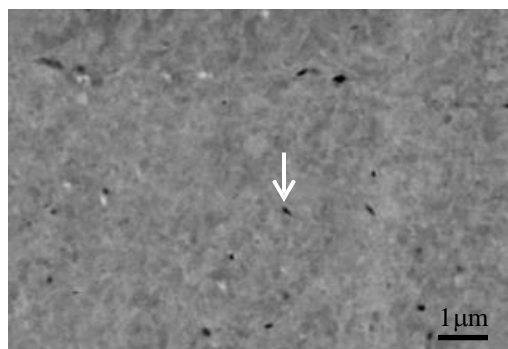


Figure 4. SEM image of steel 321 after 7 years at 650°C showing fine secondary precipitates (arrow).