Microstructural characterisation and microanalysis of creep resistant steels

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Abstract: Steels for high temperature applications require good creep resistance which is controlled by the chemistry and microstructure of the materials. This paper focuses on the microstructural characterisation of a creep resistant steel using electron microscopy. The existence of various primary carbides, e.g. NbC, M₇C₃ and M₂₃C₆ was confirmed by electron diffraction. The primary chromium carbides transformed from M₇C₃ to M₂₃C₆ during creep while the niobium carbides were nearly unaltered. In addition, secondary precipitates (M₂₃C₆) were observed within the matrix after creep. The size and distribution of the secondary carbides were analysed by a 80 mm² windowless X-Max⁵ SDD at 3 kV on an SEM. Scanning transmission electron microscopy (STEM) observations showed the appearance of fine NbC, G phase (Ni₁₆Nb₆Si₇) and (Nb, Ti)(C, N) particles.

1. Introduction
As the service conditions in steam reforming involve a high temperature and a high pressure, the materials for this application require superior creep resistance [1]. One of the basic ways in which creep resistant steels can be strengthened is by precipitation. The precipitates, such as M₇C₃, M₂₃C₆ and MX, play an important role in the achievement of good creep properties. Traditional Si(Li) detectors, however, have a relatively poor performance in the identifications of carbides or nitrides due to limited spatial resolution. Silicon drift detectors (SDD), which were invented by Gatti and Rehak in 1984 [2], have become very powerful instrumentation tools for industrial and scientific application in X-ray spectroscopy due to their good energy resolution, high count rate capability and convenient experimental conditions [3]. Furthermore, a new generation of windowless SDD enhances the collection efficiency for low energy X-rays to improve any analyses which need to be based on low energy lines, such as Nb M lines. The present work focuses on microstructure characterisation and microanalysis of creep resistant steels by using windowless SDD on both SEM and TEM.

2. Experimental Methods
A creep resistant steel --- Alloy A was supplied by Doncasters Group Ltd. The alloy was crept at 1000°C and 40 MPa for 12 hours. Back-scattered electron (BSE) imaging and energy dispersive X-ray spectrometry (EDS) were used to investigate the element distribution. The size and distribution of the
secondary chromium carbides were analysed with an 80 mm$^2$ windowless X-Max$^N$ SDD at 3 kV on an FEG-SEM. Scanning transmission electron microscopy (STEM) was carried out on a Tecnai F20 TEM operating at 200 kV with an 80 mm$^2$ windowless X-Max$^N$ TLE SDD.

3. Results and discussion

3.1 As-cast microstructure

Figure 1 (a) shows the microstructure of as-cast Alloy A. The grains are surrounded by Nb-rich carbides and Cr-rich carbides which form a fragmented network. Nb is confined to the primary carbide network [4], whereas Si and Fe remain in solid solution in the Ni-rich matrix. The EDS analyses show that the concentration of carbon in the chromium carbide is around 30 at.%, which indicates that it should be the M\textsubscript{7}C\textsubscript{3} type. As shown in Table 1, Ni and Fe are found to substitute partially for Cr [5]. No fine precipitation has been observed in the matrix.

Table 1 EDS analyses obtained from the points shown in Figure 1

| Atomic %            | C     | Si | Cr     | Fe     | Ni     | Nb     |
|---------------------|-------|----|--------|--------|--------|--------|
| 1—Cr-carbides (as-cast) | 31.85±0.72 | --- | 59.63±1.13 | 7.30±0.68 | 1.21±0.22 | ---    |
| 2—Nb-carbides       | 41.73±0.81 | --- | 9.56±1.33 | 3.46±0.52 | 2.67±0.14 | 42.36±0.33 |
| 3—Matrix            | 6.99±0.67 | 2.12±0.54 | 22.41±1.04 | 35.77±0.43 | 31.94±0.20 | ---    |
| 4—Cr-carbides (crept)| 21.67±1.21 | --- | 66.26±0.84 | 8.35±0.39 | 3.02±0.47 | ---    |

Figure 1 BSE micrograph obtained from (a) as-cast Alloy A and (b) crept Alloy A

3.2 Microstructure evolution

The microstructure of the crept Alloy A is illustrated in Figure 1 (b). The content of carbon in primary chromium carbides decreased from 30% to 21% (c.f. Table 1), indicating transformation from M\textsubscript{7}C\textsubscript{3} to M\textsubscript{23}C\textsubscript{6}. The NbC morphologies are nearly unaltered during the creep, except for slight coarsening. Secondary precipitation can be observed within the matrix resulting from the supersaturated solid solution of carbon. Figures 2 (a-d) shows the results, using an SEM operating at 3 kV, of background and overlap corrected X-ray mapping (AZtec TruMap). The X-ray lines used in the SEM were low energy Cr L and Nb M, while the lines used in the TEM were Cr K and Nb K. Although the spatial resolution is not as good as that using TEM (c.f. Figures 2 (e-h)), they are in agreement that secondary chromium carbides are 100–250 nm. The secondary chromium carbides of such a size can act as barriers to dislocation movement contributing to good creep resistance.
3.3 TEM observations

As shown in Figure 3, the STEM analysis was carried on a selected area of crept Alloy A containing a primary chromium carbide. Nb carbides were mainly observed at the interface between the primary chromium carbide and the matrix. A Nb-Ni-Si particle was found associated with the primary chromium carbide; it has a fcc structure with a lattice parameter of 1.13 nm identifying it as G-phase (Ni\textsubscript{16}Nb\textsubscript{6}Si\textsubscript{7}). Although G phase does not appear to be intrinsically detrimental to the mechanical properties, the transformation from NbC (a=0.44 nm) into G phase (a=1.12 nm) induces a volume expansion and leads to cracking along the grain boundary.

The EDS spectrum shows that the fine particle highlighted in Figure 4 (a) is rich in chromium, niobium, carbon and nitrogen. However, the contents of Nb, Cr and N are different from that of a typical nitride such as Z-phase (NbCrN) in austenitic stainless steel [6]. The diffraction patterns
obtained from the particle were indexed as fcc with a lattice parameter of 0.429 nm close to NbC with its lattice parameter of 0.44 nm. EDS mapping shown in Figure 5 leads to a similar result --- observation of a (Nb, Ti)(C, N) particle combined with a chromium carbide.

![Figure 4](image1.png)

**Figure 4** Selected particles (a) bright field image; (b) selected area diffraction and (c) EDS spectrum

![Figure 5](image2.png)

**Figure 5** (Nb, Ti)(C, N) particle (a) bright field image and (b-h) overlap corrected TruMaps

4. **Conclusion**
- The existence of NbC, M$_7$C$_3$ and M$_{23}$C$_6$ was confirmed;
- The primary chromium carbides transformed from M$_7$C$_3$ to M$_{23}$C$_6$ during creep;
- Secondary chromium carbides M$_{23}$C$_6$ (100~250 nm) were observed within the matrix;
- Scanning transmission electron microscopy (STEM) showed the appearance of fine NbC, G phase (Ni$_{16}$Nb$_3$Si$_7$) and (Nb, Ti)(C, N) particles.

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