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EELS analysis of the nitrogen content of carbide particles in a commercial γ′-strengthened nickel-base superalloy

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ABSTRACT

Carbide particles contribute to the high strength of nickel-base superalloys. It is a long standing question whether these carbide particles contain nitrogen. Here we examine the nitrogen content of the titanium–molybdenum-carbide in the commercial superalloy NIMONIC PE16 using a combination of electron energy loss spectroscopy (EELS) with energy dispersive X-ray (EDX) analysis. Careful examination of the molybdenum M_3- and M_2-edges, which overlap with the nitrogen K-edge, leads to an upper limit for the nitrogen content of the carbide: 1.8 at.%.

The high strength of nickel-base superalloys derives mainly from nano-scale precipitates of the γ′-phase, the composition of which is approximately described as $Ni_3(Al,Ti)$ [1–11]. Carbide particles are essential for the realization of the full technical potential of γ′-strengthened nickel-base superalloys. At grain boundaries discrete carbide particles may suppress grain boundary sliding and also in the interior of the grains these particles may contribute to the strength of the material. However, they may also give rise to detrimental effects: (i) clusters of them can initiate cracks and (ii) titanium-rich carbides which form along grain boundaries, cause depletion of Ti in seams and thus suppress the formation of the strengthening γ′-precipitates. Such seams are commonly referred to as precipitate free zones (PFZ) [7,10]. Even though nitrogen may substitute for part of the carbon content of carbide particles, they are usually referred to as carbides only. One reason for this may be that since producers of superalloys normally quote the overall carbon content in their analyses, but not the nitrogen content, authors tend to completely disregard the latter constituent. Particles of titanium nitride are known to form already in the melt and to serve as nuclei for carbide particles in the solid [2]. Taylor and Sachs [12] reported the following composition of an M_6C-type carbide (M stands for various metals plus silicon) in a complex iron-free nickel-base alloy containing cobalt, chromium, molybdenum, tungsten, and silicon: $(Ni_{0.58}Co_{0.30}Si_{0.12})_3(Mo_{0.49}W_{0.07}Cr_{0.44})_3(C_{0.95}N_{0.05})$. Consequently, in order to indicate the nitrogen content of carbides, they are also sometimes referred to as carbonitrides [1,2,5,9,11,13–16]. MC (M primarily represents Ti) is one of the most frequently observed carbides in nickel-base superalloys.

The microstructure and the mechanical properties of the commercial γ′-strengthened nickel-base superalloy NIMONIC PE16 have been the subjects of many investigations, e.g. [1,3,4,7,10,14]; Refs. [1] and [4] are reviews and Refs. [7] and [10] deal with carbides and γ′-PFZs along grain boundaries. NIMONIC PE16 was chosen as an example for the entire class of γ′-strengthened nickel-base superalloys. According to its producer Glossop Superalloys Ltd., UK, the atomic percentages of the constituents of NIMONIC PE16 are: Ni 41.3, Fe 34.4, Cr 17.5, Mo 2.02, Ti 1.50, Al 2.59, C 0.25, P 0.12, Si 0.11, Co 0.05, Mn 0.05, Cu 0.04, Bi 0.02, Zr 0.01, V 0.01. The nitrogen content of the alloy is unknown. The bulk specimens were subjected to a sequence of thermo-mechanical treatments described elsewhere [10]. Their final heat treatment was at 1119 K for 210 h. The resulting grain size, defined as the average spacing of grain boundaries along straight lines, was approximately 280 μm and the volume fraction of the strengthening spherical γ′-precipitates was about 0.029 with an average radius of 59 nm.

The aim of the present investigation was to determine locally by analytical transmission electron microscopy (TEM), the nitrogen content of MC carbide particles in NIMONIC PE16 [1,3,4,7,10,14]. In the following the MC carbide in NIMONIC PE16 will be referred to as PE16-M(C, N) indicating that it may contain nitrogen. While it has been shown that electron energy loss spectroscopy (EELS) is a suitable method to determine the nitrogen content in carbonitrides

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[15], the presence of molybdenum in our particles and the subsequent overlap of the Mo M_3- and M_2-edges with the N K-edge (nitrogen K-edge) present a serious challenge for the present quantification. Hence the nitrogen content is determined using a combination of EELS with energy dispersive X-ray (EDX) analysis. EDX is used to calculate the relative Ti, Mo and Cr content of the carbide. The region of the EELS spectrum containing the Mo M_3- and M_2-edges is carefully examined for the presence of an N K-edge. An upper limit for the nitrogen content is then calculated by assuming that all the counts in the N K-edge region arise from nitrogen and none from molybdenum. Since the counts arising from Mo are included in this calculation, this method leads to an upper limit and indeed to an overestimate of the N content. To the best of our knowledge this method is used for the very first time to estimate an upper limit for nitrogen in the presence of heavier elements. This approach may be used to estimate an upper limit for any light element with an overlapping edge in the EELS spectrum.

Slices of 0.3 mm thickness were spark cut from the thick un-deformed ends of the dumb-bell shaped cylindrical tensile tested specimens used in the investigation of the effects of γ′-PFZs on the yield strength of NIMONIC PE16 [10]. These slices were ground to approximately 70 μm in thickness. Subsequently thin foils for TEM were prepared by electro-polishing using a Tenupol-3 twin-jet device and a solution of 17% perchloric acid in ethanol. Electro-polishing was carried out at 13 V and −20 °C for 2–3 min. Samples were plasma cleaned (air plasma) just prior to analysis. Since during the electro-polishing procedure PE16-M(C, N) particles dissolve somewhat more slowly than the remainder of the material it was possible to excavate them at the edge of the thin TEM foil (cf. Fig. 1). EDX analyses showed no indication of residual matrix present on the free-standing area of the PE16-M(C, N) particle.

For TEM analysis a FEI Titan 80-300 equipped with a Gatan Tridiem spectrometer and an EDAX EDX-system was used. The TEM was operated at 300 kV. The EELS-data were evaluated using Digital Micrograph™ (GATAN Inc.). EELS and EDX data were acquired from several nano-scale PE16-M(C, N) particles.

In the following a data-set taken from one particle is analyzed in detail. For EDX as well as EELS analyses, the carbide particle as marked by the arrow in Figure 1 was tilted off a zone axis to minimize crystallographic effects. EELS- and EDX-measurements were carried out in scanning-TEM (STEM) mode using a spot size of 4 nm. The effects of contamination could be reduced by scanning areas of typically $20 \times 20\ nm^2$ during data acquisition.

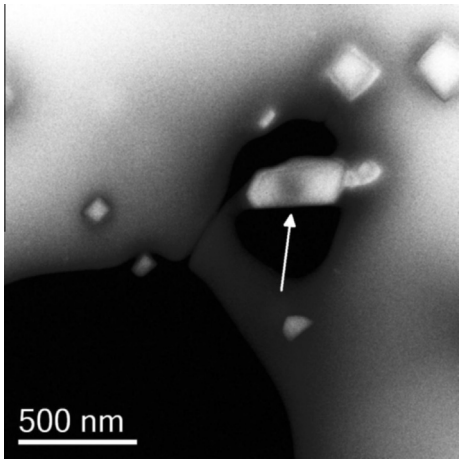

Figure 1. Dark field STEM image of a NIMONIC PE16 thin foil. The free-standing PE16-M(C, N) carbide particle used for EELS and EDX analyses is indicated by the arrow. It bridges a hole in the thin foil. A crack connects the two holes in the foil.

EDX measurements were performed with a tilt of 15° of the sample in the direction of the Si(Li) detector (S-UTW-window at 20°). The counting time was ~120 s (resolution 134 eV) leading to a maximum of ~150 counts/channel of the signal and 2–5 counts/channel in the background which was fitted by a multi-polynomial function (3rd order). Peak fitting and quantification of the K lines were performed in the FEI TIA™ software with a mixed model (using standards and standardless) and a thickness correction. The statistical evaluation led to a composition of (40.0 ± 1.8) at.% Ti, (9.6 ± 2.5) at.% Mo, and (0.43 ± 0.3) at.% Cr. The sum of the Ti-, Mo- and Cr-content was normalized to 50 at.%. Former estimates [7] of the respective atomic percentages were: 40 at.% Ti, 10 at.% Mo, and 50 at.% C. The minimum detectable atomic percentage of carbon in the present EDX measurements was estimated after [17] using the counts of the background and the counts of the carbon signal: 6 at.% C. Since nitrogen is a neighboring element to carbon, a similar value can be expected for the detectability limit of nitrogen using EDX. It should be pointed out, that a nitrogen signal could not be detected by EDX. Moreover, no other constituent of NIMONIC PE16 could be detected in the PE16-M(C, N) particle. It is emphasized that the error limits of the EDX-measurement are considerably smaller for the heavier elements Ti, Mo and Cr than for the light elements C and N.

EELS measurements were performed using a convergence angle of 10 mrad and a collection angle of 9.9 mrad; the EELS-energy resolution was approximately 1.0 eV. In addition low-loss spectra were recorded to measure the thickness [17]. Spectra were recorded from seven different areas, the respective data are numbered 1–7 in Figure 2 and Table 1. The energy window was shifted by an offset of 10 eV for each spectrum to physically shift the image of the spectrum on the detector. EELS quantification was performed using Hartree–Slater cross sections applied manually to each edge [15,17 and references therein]. The zero point of the energy scale of the experimental data was shifted such that the Ti L_3-edge appeared at the correct energy: 456 eV. After this shift, without any further adjustment, the C K-edge was found – within the experimental accuracy – at its correct position.

All seven raw EELS spectra are shown in Figure 2(a). The positions of the relevant edges are indicated. The Mo $M_{4,5}$-edges (molybdenum $M_{4,5}$-edges) (~227 eV), the C K-edge (carbon K-edge) (~284 eV) and the Ti L_3- (~456 eV) and Ti L_2-edges (titanium edges) (~462 eV) were detected as well as an O K-edge (oxygen K-edge) (~532 eV). To remove the background under the edges, a power law was fitted below the onset of the respective edges. All background functions were fitted in an energy range larger than 30 eV. The parameters of the background function for the N K- and Ti L-edges were very stable. As an example of the evaluations, the N and Ti edge regions of spectrum No. 6 are shown in Figure 2(b) and (c). The possible N K-edge (~401 eV) overlaps with the Mo M_3-edge (~392 eV) and the Mo M_2-edge (~410 eV). Moreover, the O K-edge overlaps with the extended Ti edge (cf. Fig. 2(a) and (c)). In Figure 2(b) and (c) the raw data are indicated by the thick black line, the fitted power law background function is drawn in red and the background subtracted edges in black; also indicated in blue are the Hartree–Slater cross-sections used in the quantification.

It should be pointed out, that no indication of an N K-edge is detected in any of the seven spectra of the carbide particle. For comparison, reference spectra from MoO_3 [18], N_2 [18], and TiN [19] are shown in Figure 2(b). However, we cannot rule out that some nitrogen may be present but masked by the overlying molybdenum edges. Thus in order to deduce an upper limit for the nitrogen content a procedure as described in the following was applied. Assuming that after background subtraction all counts in the N K-edge region, i.e. in the range 401–426 eV