Original article

Microstructural and fractographic investigation of a centrifugally cast 20Cr32Ni + Nb alloy tube in the ‘as cast’ and aged states

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Fracture surface and microstructure of tensile samples taken from a centrifugally cast 20Cr32Ni + Nb alloy tube were investigated in the ‘as cast’ state and after being submitted to isochronal aging at temperatures between 670 °C and 820 °C for 200 h. The results show that the main crack path is interdendritic at a macroscopic scale, but that the fracture surface is characterized by dimples at microscale in all samples, suggesting that the fracture micromechanism does not change, in spite of the large ductility loss observed in the aged samples (fracture elongation, \( \bar{\varepsilon}_f \approx 0.16 \) for samples aged at 770 °C) compared with ‘as-cast’ samples (\( \bar{\varepsilon}_f \approx 0.42 \)).

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1. Introduction

The phenomenology of cold ductility degradation of centrifugally cast tubes of alloy 20Cr32Ni + Nb was described by the present authors in previous work [1] considering tensile samples in the ‘as-cast’ and aged\(^1\) states. It was shown that ‘as cast’ samples displayed an average elongation of 41.7%, which reduced to 16% after aging for 200 h at 770 °C, in parallel, the average yield stress increases from 196.7 MPa in the ‘as cast’ samples to 246 MPa in the aged state. In other words, the elongation of the aged sample decreases to 38.4% of the value measured in the ‘as cast’ sample, while its yield strength is only about 25% larger in comparison with the ‘as cast’ state [1]. These results can be better appreciated with reference to Table 1, which is based on the results shown in Ref. [1]. This disproportion is, however, potentially more severe if one consider reports of virtually zero elongation for parts subject to long-time service [2].

This phenomenon is highly relevant to the technology in which these alloys are employed. Decreased ductility results in accidents during maintenance operations in outlet manifolds of pyrolysis or reforming plants, leading to scrapping of the part and increased costs [2]. The understanding of the phenomenon, however, requires identifying the mechanisms by which this ductility degradation takes place and, in spite of

\(^1\) Isochronal treatments of 200 h in temperatures between 670 °C and 820 °C. This heat treatment schedule is based on an empirical ‘aging resistance’ test, specified by project designers for acceptance of a material batch by the end user [1].
its importance, little is known about this matter. A working hypothesis attributes it to the precipitation of a brittle 'grain boundary' phase, known as 'G-phase' [2].

This phase corresponds to a nickel niobium silicide with Ni$_3$Nb$_2$Si stoichiometry, which is observed to precipitate in association with eutectic NbC particles at the interdendritic region [2–4]. The formation of the 'G-phase' is well documented in tubes made of alloys of the HP class (25 wt.% Cr, 35 wt.% Ni) which are also subject to this ductility degradation. Recent experimental results obtained in a thermodynamic assessment of the Nb–Ni–Si system [5] confirmed the stability, crystal lattice and stoichiometry of the G-phase at the 800 °C isothermal section. These results show that the G-phase is observed in equilibrium with the Ni-rich austenite at this temperature, and, in other words, that this silicide is likely expected to be a potential equilibrium phase in Ni superalloys with high Nb and Si contents.

Ecob et al. [3] investigated the isothermal precipitation kinetics of the 'G phase' in HP alloy tubes containing a very large surplus of Nb and showed that the maximum reaction rate is located around 775 °C, which correlates well with the temperature for maximum ductility degradation (see e.g. Ref. [1]). Powell et al. [6] investigated a wrought stainless steel of similar composition and confirmed the existence of the 'G-phase' and its relation with the NbC (N) carbides. Almeida et al. [4] confirmed the presence of the 'G-phase' in a centrifugally cast tube made of HP alloy and its close relationship with the NbC primary particles by means of Backscattered Electron images, which clearly showed a contrast in the interdendritic particles, with the light tones corresponding to NbC and the dark tones associated with silicon-rich areas, which were identified as G-phase particles. Finally Chen et al. [7] identified niobium and silicon rich precipitates associated with the primary NbC carbides in the microstructure of an ex-service tube made of the 20Cr32Ni + Nb alloy, which showed nil ductility at a room temperature tensile test, and concluded that these precipitates correspond to the 'G-phase'.

These results suggest that in service precipitation of 'G-phase' is correlated with the ductility degradation. This supposition is based on the ad hoc assumption that silicides are inherently brittle and that this phase precipitates at grain boundaries and interdendritic spaces, hence the ductility degradation would be linked with a change in failure mechanism, with the 'as cast' alloy being more ductile due to a lower propensity to interdendritic fracture. The aim of the present work is to test this hypothesis by the investigation of the microstructure and fracture surface morphology of the tensile samples used in previous work by the present authors [1].

### 2. Materials and samples

Tensile samples extracted from a centrifugally cast tube made of alloy 20Cr32Ni + Nb (ASTM A351 CT15C) were analyzed both in the 'as cast' and in the aged (670–820 °C for 200 h) states.

The samples, oriented along the tube axis, were extracted, whenever possible, from the same position along the tube length, to avoid that minor compositional deviations, characteristic of the casting process, affected the results. Further details about sample extraction can be found in Ref. [1], it is, however, important to state that all tensile samples were extracted rigorously from the same position relative to the exterior tube wall (that is, their centers were located at the same radial coordinate referring to the tube axis). This is important, since the tubes have a mixed equiaxed/columnar solidification microstructure, with the equiaxed region located in the inner part of the tube wall and the columnar region located in the exterior part and the relative amounts of these regions could, potentially, influence the outcome of the tests. By taking the samples from the same position we used the expected radial symmetry of the tube, to assure that, apart from minor statistical variations characteristic of the casting process, these amounts were equivalent in all samples. The average composition of the tube was 0.12%C, 0.85%Si, 1.08%Mn, 0.017%P, 0.007%S, 19.8%Cr, 31.9%Ni, 0.01%Mo, 0.02%Co, 0.98%Nb, 0.02%Cu and 0.056%N (compositions given in wt.%). Particular care was also taken in the heat treatments to allow for the reproducibility of the thermal regimes. The three tensile samples for each heat treatment temperature, in particular, were submitted to the same thermal regime, since the heat treatments were performed simultaneously in a tubular furnace, with the samples symmetrically distributed in relation to the furnace axis.

The heat-treated samples were fractured in a hydraulic testing machine. Samples were machined according to ASTM A370-12a specification, with diameter D = 8.75 mm and gauge length, G = 35.0 mm. The center of the specimens was located 12 mm away from the tube surface. One half of the broken sample was reserved for fracture surface analysis, while the second half was sectioned along the axial direction. The fracture surfaces were carefully preserved for observation in a scanning electron microscope (SEM), equipped with energy dispersive X-ray spectrometry (EDX) accessory. The second half was mounted in plastic resin and prepared for metallographic observation by grinding with silicon carbide paper up to #600 grit, followed by final polishing in diamond paste down to 1 mm. The polished samples were observed both in optical and in Scanning Electron microscopes, with and without etching in aqua regia (50% HNO$_3$ + 50% HCl). These samples were used to identify the subsuperficial damage produced during loading. A separate set of metallographic samples was extracted from the heads of the tensile samples in order to

<table>
<thead>
<tr>
<th>State</th>
<th>Yield strength ($\sigma_f$) [MPa]</th>
<th>UTS [MPa]</th>
<th>Fracture elongation ($\varepsilon_f$) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>196.7 (1.5)</td>
<td>523.3 (1.7)</td>
<td>41.3 (2.0)</td>
</tr>
<tr>
<td>670 °C</td>
<td>214.3 (2.0)</td>
<td>553.3 (4.4)</td>
<td>28.3 (0.9)</td>
</tr>
<tr>
<td>720 °C</td>
<td>239.0 (2.1)</td>
<td>546.7 (4.4)</td>
<td>20.0 (0.6)</td>
</tr>
<tr>
<td>750 °C</td>
<td>253.7 (1.7)</td>
<td>541.7 (3.3)</td>
<td>19.3 (0.3)</td>
</tr>
<tr>
<td>770 °C</td>
<td>246.0 (2.6)</td>
<td>531.7 (4.4)</td>
<td>16.3 (0.3)</td>
</tr>
<tr>
<td>820 °C</td>
<td>234.0 (2.3)</td>
<td>516.7 (8.3)</td>
<td>19.0 (1.5)</td>
</tr>
</tbody>
</table>

Table 1 – Results of the tensile tests in samples of alloy 20Cr32Ni + Nb in the ‘as cast’ state (AC) and after aging at the indicated temperatures for 200 h. Results are averages of three samples and the values in parentheses are the standard deviation of the average.

2 That is, for all tested temperatures, except 750 °C.
Fig. 1 – Optical micrographs corresponding to the base microstructures of the samples in the states: (a) ‘as cast’ ($\varepsilon_f = 41.3\%$, $\delta_y = 196.7$ MPa), (b) aged at 670 °C for 200 h ($\varepsilon_f = 28.3\%$, $\delta_y = 214.3$ MPa), (c) aged at 720 °C for 200 h ($\varepsilon_f = 20.0\%$, $\delta_y = 239.0$ MPa), (d) aged at 750 °C for 200 h ($\varepsilon_f = 19.7\%$, $\delta_y = 253.7$ MPa), (e) aged at 770 °C for 200 h ($\varepsilon_f = 16.7\%$, $\delta_y = 246.7$ MPa), (f) aged at 820 °C for 200 h ($\varepsilon_f = 19.0\%$, $\delta_y = 234.0$ MPa).
investigate the base microstructure obtained by the different heat treatments, for the sake of reference.

3. Results and discussion

3.1. Base microstructures

Fig. 1a–f shows the typical sample head microstructures (i.e. undeformed) of the ‘as cast’ and aged samples. Average values of recorded elongation $\dot{\epsilon}_f$ and yield stress, $\sigma_f$ [1] are also shown in this figure, for the sake of comparison. The microstructures show austenite dendrites and $\gamma + NbC$ eutectic at the interdendritic spaces. The NbC carbides at the interdendritic spaces are virtually unaffected by the aging heat treatment and the only microstructural change in the aged samples, when compared with the ‘as cast’ one, is the profuse precipitation of a chromium-rich carbide in the matrix (presumably $M_23C_6$). These results are in good agreement with previous works in similar steels [4].

Comparing the different aging temperatures, we identify morphological differences in the secondary carbide precipitation. At 670 °C and 720 °C the precipitation occurs at preferential sites in the austenitic matrix, while it becomes more homogeneously distributed at higher aging temperatures. The amount of precipitates is also different and they are more abundant in the samples aged at 750 °C and 770 °C. The case of the sample aged at 750 °C is noteworthy. The volume fraction of secondary carbides in this sample is clearly higher compared with the other samples. This observation is attributed to the fact that the samples were extracted from a different position along the centrifugally cast tube length (hence, overall composition is slightly different from the other samples). This maximum volume fraction correlates well with the maximum average yield stress, but not with the minimum average elongation, which occurs for the samples aged at 770 °C (see Ref. [1]). The elongation loss in the aged samples, hence, cannot be simply attributed to the precipitation of secondary carbides and their strengthening effect.

These results fundamentally agree with the ones published by Chen et al. [7]. These authors identified eutectic NbC precipitates associated with dispersed MC and $M_{23}C_6$ carbides in the matrix of an ‘as cast’ sample of the 20Cr32Ni1Nb alloy. These authors also investigated an ex-service sample of the same material after four years ($3.5 \times 10^4$ h) of service at 760 °C [7]. In the ‘ex-service’ sample, small precipitates ($M_{23}C_6$) precipitates are identified in the matrix and the interdendritic boundaries are decorated with NbC and $M_{23}C_6$ particles, were the MC particles show silicon-rich areas at the interface with the matrix, which were identified as G-phase regions. Comparing these results with the present ones, we observe that the heat treatment time of the later is considerably higher, as well as the silicon content. Both conditions would favor G-phase precipitation in the alloy.

3.2. Fracture surfaces

Fracture surface morphology is complex and presents a hierarchy depending on the magnification scale. Fig. 2 shows the fracture surface of one of the samples aged at 750 °C for 200 h at low magnification as observed in the SEM via a secondary electron image. Virtually the entire fracture surface can be visualized at this figure. The fracture surface at this scale is indistinguishable in all samples (including the ‘as cast’ ones) and has a heterogeneous morphology. Two regions are identified: at the lower part of the figure dendrites can be easily recognized, while in the upper part a rougher morphology is observed. These two regions correspond to the heterogeneous tube solidification macrostructure, which shows a columnar region in the outer tube wall, which changes to an equiaxed microstructure at about 10 mm toward the inner tube wall.

Fig. 3a–d shows the fracture surfaces of samples in the ‘as cast’ state (a and c) and aged at 750 °C in the (b and d) at the columnar (a and c) and equiaxed (b and d) regions. Analysis of these images confirms that there is no correlation between the decreased elongation of the aged samples and the fracture surface appearance. Furthermore, the fracture surfaces in the equiaxed and in the columnar regions of the sample are similar, differing only by the relative orientation of the dendrites (aligned in the columnar region and random in the equiaxed region), showing that at this scale the fracture path is interdendritic everywhere in the sample’s fracture surface.

Inspection of the fracture surfaces of the samples in the ‘as cast’ and aged at 770 °C states at higher magnification (Fig. 4a and b) shows that at a finer scale it consists of flat portions consisting of parallel terraces, intermixed with areas covered by dimples. These regions probably correspond to carbide-covered and carbide-free areas of the main crack path. At this scale, therefore, the fracture surfaces are characteristic of a quasi-brittle fracture process, since at least part of the flat areas resemble river marks (e.g., at the bottom right corner of Fig. 4a), showing that cleavage potentially takes place there. The relevant fact, however, is that the images are practically the same in spite of the large difference in average elongations of both samples (respectively $\dot{\epsilon}_f = 41.3\%$ and $\dot{\epsilon}_f = 16.7\%$). It is
therefore unlikely that the ductility loss is associated with a major change in the micromechanical damage process.

Sustaita-Torres et al. [8] investigated the effect of aging in a centrifugally cast 35 wt.% Cr–45 wt.% Ni heat resisting alloy, aged at 750 °C for 500 and 1000 h. This steel presents a similar microstructure to the 20Cr32Ni + Nb alloy. These authors identified the presence of a silicon-rich precipitates associated with the NbC particles, which could not, however, be unambiguously indexed as G-phase. As in the case of Ref. [4], the investigated steel contains substantially higher silicon content and was aged at higher times, and, as previously stated, both factors favor the formation of G-phase. More interestingly, the fracture surfaces present similar features as the one observed in the present work, showing that the fracture micromechanism is essentially the same, with or without silicides in the microstructure.

3.3. Subsuperficial damage

Fig. 5 shows the microstructure close to the fracture surfaces of the samples in the ‘as cast’ state and aged at 770 °C (the arrow shows the loading direction and points to the position of the fracture surface). These images show that, irrespective of the large variations in elongation, the NbC carbide particles are already fragmented prior to the final fracture. Also, these microfractures do not penetrate the matrix, which shows sufficient toughness to stop crack propagation. It is interesting to observe that only the particles which are aligned with the loading direction are fragmented, mimicking a typical fracture behavior of fiber-reinforced composites [9].

3.4. Fracture micromechanism

These results, in synthesis, positively shows that no major change in the fracture micromechanism can be observed in the samples, despite the large variations in elongation obtained in tensile tests at room temperature. The presence of cracks in the NbC particles well below the fracture surface shows that:

1. NbC is already ‘brittle’, in the sense that it cracks well below the final fracture,
2. NbC cracking cannot, therefore, be the determinant factor for final sample fracture and
3. The austenitic matrix is sufficiently tough to stop initial cracks generated in the carbide particles (as demonstrated by Fig. 5).

Furthermore, the observation of the fracture surfaces shows that final fracture is a grain boundary (more precisely, interdendritic boundary) phenomenon already in the ductile ‘as cast’ state.
According to the observations, the following picture can be drawn for the events which precede final fracture of all samples:

1. as the stress raises, austenite matrix deforms and cracks appear in the NbC particles oriented along the loading axis,
2. at some critical stress level, NbC particles located at grain boundaries fracture by cleavage (corresponding to the terraces observed in the fracture surfaces), and finally
3. the nucleated carbide microfracture triggers ductile fracture along the austenite grain boundary, which leads to final fracture.

It is important to stress again that this micromechanism is supposed to act in all samples, irrespective of the final elongation observed for the tensile test. There is, of course, always the possibility that the supposed ‘critical stress level’ of the interdendritic NbC particles decrease during aging, but the observation that the terraces does not seem to be affected by aging (see Fig. 4), seems to contradict this hypothesis. The influence of a more brittle silicide to trigger the ductility degradation seems to be unnecessary, which is consistent with the observation that no silicon-rich particle was ever observed in EDX measurements in the present microstructures. This does not mean that the G-phase, if present, could be responsible for a more severe ductility decrease of the sample. The present results only proves that the G-phase is not necessary for the observation of the ductility degradation.

Peng et al. [10] recently investigated a similar phenomenon (aging embrittlement at 700 °C/500 h) in a 25Cr–20Ni–Nb–N heat resisting steel, which presents similar matrix composition as the ASTM A351 CT15C alloy. These authors showed, using microhardness testing, that the strength of the grain boundary region is inferior in comparison with the bulk matrix and attributed this effect to alloy depletion in the grain boundary matrix via the precipitation of M_{23}C_{6} carbides. This mechanism could be adapted to explain the present results, since profuse secondary carbide precipitation is observed in the ASTM A351 CT15C alloy during aging, but two major differences are observed in the present case:

1. the carbide precipitation is distributed in the case of the ct15c alloy and not localized at the grain boundary region, as observed by Peng et al. [10], for instance, the 750 °C case shows nearly homogeneous secondary carbide distribution (see Fig. 1d) and yet, these samples are embrittled, and
2. Peng et al. [10] observed a clear transition from ductile fracture toward a cleavage-like fracture surface in the embrittled steels, which is not observed here.
Finally, the present results cannot point out a reason for the observed ductility degradation, these are probably linked to processes which occur at a much finer resolution or to the ability of the austenite matrix to distribute plastic deformation (perhaps due to an increase of strength in grain bulk), as observed by Peng et al. [10], prior to the onset of interdendritic fracture. Further investigations are required to solve this issue.

4. Conclusions

The characterization of the fractures surfaces of ‘as cast’ and aged samples of samples extracted from a centrifugally cast ct15c alloy tube was performed in the present work and shows that, in spite of the large ductility decrease observed in the aged samples, the fracture micromechanism is the same, namely, intergranular (interdendritic) cracking via microvoid nucleation and coalescence, intermixed with cleavage in the carbide particles.

Although no positive answer can be given on the cause of this embrittlement, the present results clearly shows that the presence of a (more) brittle phase is not a necessary condition for its observation.

Eutectic NbC carbide particles are observed to be fragmented deep below the main fracture surface, suggesting that this process occurs relatively early in the sample’s loading history, hence, fragile carbide cracking cannot be the controlling factor of final fracture.

Conflicts of interest

The authors declare no conflicts of interest.

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