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The evolution of primary and secondary niobium carbonitrides in AISI 347 stainless steel during manufacturing and long-term ageing

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Abstract

Nb(C,N) precipitates were studied in a niobium-stabilised stainless steel (AISI 347) statically aged at 700 °C. Scanning electron microscopy and energy filtered transmission electron microscopy were used to determine the volume fraction and precipitate size of primary and secondary Nb(C,N) after ageing times between 0 and 70,000 h. The experimental data were correlated with simulations of Nb(C,N) formation based on the assumption that the process is controlled by diffusion. These simulations provide a rationale for the existence of two sets of niobium carbonitrides in commercial tubes of AISI 347. Growth of primary Nb(C,N) occurred essentially during manufacturing, with no significant growth at 700 °C. Rapid dissolution and re-precipitation of secondary Nb(C,N) occurred during manufacturing. Coarsening at 700 °C of secondary particles was modelled using the Lifshitz–Slyozov–Wagner theory, which overestimated the coarsening rate. These problems were overcome with a model developed by the authors. This model takes both growth and coarsening into account.

Keywords: AISI 316 stainless steel; Niobium carbonitrides; Growth; Coarsening; Long-term ageing

1. Introduction

In niobium-stabilised steels such as AISI 347, niobium carbonitrides, Nb(C,N), form because of the high affinity between niobium and interstitials. There are two different purposes in adding niobium. One is to stabilise the material against intergranular corrosion, the other to provide good creep resistance in the material. If good creep resistance is the primary aim, a solution heat treatment is performed to dissolve Nb(C,N) (in the following termed NbX for simplicity). Subsequent precipitation then occurs during creep with increased strength as a consequence [1]. The material is suitable for superheater tubes in steam power plants, and due to the stabilisation with niobium, steels of type 347 have good resistance to intergranular corrosion [1].

Coarse (primary) NbX are formed in the later part of the solidification process. This is evident from the morphology of these carbides (see Fig. 1(a)) and from the fact that they form eutectically between the dendrites [2]. The NbX precipitates grow during manufacturing and solution annealing of the material. There is also a dispersion of fine (secondary) NbX homogeneously distributed in the matrix as shown in Fig. 1(b). They form during manufacturing and solution annealing, but because of their small size they are affected by the process parameters and dissolve and re-precipitate during manufacturing.

The solubility and the stoichiometry of NbX are essential in determining the behaviour of steel with regard to static ageing and creep. It should be mentioned in this context that C is the major interstitial constituent in NbX because

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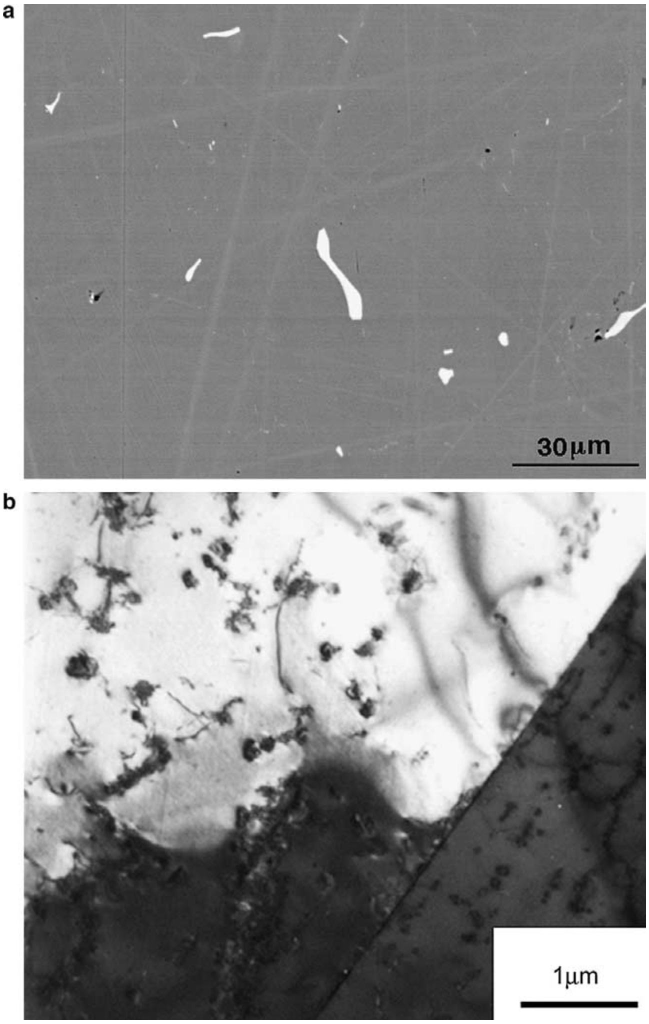

Fig. 1. (a) The morphology of primary NbX shows that they are formed interdendritically already during solidification (SEM, back scattered electrons). (b) Micrograph showing secondary NbX embedded in the austenitic matrix (TEM).

of the relatively low concentration of N in the original melt of AISI 347. During service in air at 800 °C and above nitridation can occur leading to successively higher portions of N in NbX but this does not occur at 700 °C [3]. Stabilisers like Nb are known to reduce the solubility of C in austenite. However, until the solubility limit is reached at the solution heat treatment temperature, addition of Nb and X will increase the amount of NbX at the service temperature, thereby increasing the creep resistance. Great efforts have been made to find the optimum Nb:C ratio to precipitate as much NbX as possible while maintaining a low coarsening rate [4–6].

When examining aged specimens in the present work, it became quite apparent that there is one family of relatively coarse ($r \sim 1.5$ μm) and one family of very small NbX particles ($r \sim 20$ nm). At first it was believed that the small ones had been formed during ageing. However, it was a surprise to find that both two families appear already in solution annealed material, in which only a distribution of coarse primary NbX had been expected. Irrespective of origin, the NbX precipitates were found to be of the same type with a face-centred cubic structure (space group Fm3m) [3]. The microstructural evolution of NbX during production of AISI 347 has not been described previously. A project was therefore initiated to gain a deeper understanding of the microstructural changes occurring during the production and service of seamless tubes, including all steps from casting via extrusion to final heat treatment and subsequent ageing at 700 °C.

2. Experimental

2.1. Investigated material

A niobium-stabilised stainless steel of type 347 with the composition 0.065C–0.02N–17.6Cr–11.4Ni–0.78Nb was studied. Nb and C are often added in stoichiometric quantities (Nb/C ~ 7.7). It is common practice, however, to overstabilize with respect to Nb. The ratio Nb/C was in this case 12. The steel was manufactured using an electric arc furnace followed by decarburisation in an AOD converter. After ingot casting extrusion billets (hollows) were produced by hot rolling, forging and trepanning. This led to a break-down of the original cast structure and a uniform metallurgical structure. After expanding the hollows, seamless tubes were produced by hot extrusion. The tubes were solution annealed at 1100 °C for 3 min and subsequently quenched before delivery. A schematic diagram of the manufacturing process for the investigated material is shown in Fig. 2. To be able to model the NbX precipitation during manufacturing, the cooling rates for the different parts of the processes were estimated for this specific ingot. The holding times used, at specific temperatures, were also considered. The cooling rates achieved after the various manufacturing steps have to be estimated carefully since they affect the precipitation behaviour considerably. The complete chemical composition of the tube provided by Sandvik Materials Technology is given in Table 1.

Creep specimens were taken from the tube wall and put into a multi-specimen creep machine where they were subjected to creep deformation until final rupture. The creep specimens were tested at 700 °C for 824 h at 130 MPa, 6658 h at 90 MPa, 15,352 h at 70 MPa and 69,752 h at 45 MPa. The experimental material was available in the form of solution heat treated, creep deformed and aged material. The grip part of the specimens was regarded as stress-free and therefore defined as statically aged material in the present investigation.

As the material was produced during the 1980s, i.e. before creep testing started, it was not possible to follow the microstructural changes during production step by step. Instead, it was attempted to model the microstructural development based on the production parameters and compare this to the material that is still available. As there were no significant microstructural differences between creep deformed and statically aged material crept material was excluded from the investigation.