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Dissolution and coarsening of large niobium carbonitrides in a microalloyed steel

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Observations and measurements of the kinetics of coarsening and dissolution of large cuboidal niobium carbonitrides during solution treatments of a high nitrogen niobium microalloyed steel are reported. At temperatures between 1473 and 1573 K a competitive coarsening and dissolution process was established where the larger niobium carbonitrides grew at the expense of the smaller, or employing niobium and nitrogen which remained in solid solution. In this temperature range growth or dissolution rates and critical sizes could be determined from the analysis of the evolution of particle size distribution. At higher temperatures (1623–1723 K), only a dissolution process existed, where the dissolution rates as a function of particle size was found to increase with increasing temperature.

1. Introduction

An excess of nitrogen in the liquid state of microalloyed steels is known to be deleterious because nitrogen enhances the formation of large carbonitrides of some microalloying elements during casting [1–4]. Once formed, the large (typically cuboidal) carbonitrides are known to be very stable and may represent at least a partial waste of the valuable microalloying elements.

The main contribution of niobium, vanadium, titanium or other elements in fabricating microalloyed steels is the formation of very small carbide, carbide or carbocarbonitride precipitates. These precipitates are formed in the austenite field and have the role of retarding grain growth and recrystallization during or immediately after the hot-rolling process [5–7]. Therefore, the transformation yields a fine-grained ferrite. The very fine precipitates also strengthen the ferrite [8, 9].

The blast furnace–basic oxygen steelmaking practice of microalloyed steels is followed by a ladle metallurgy stage where the final alloy adjustment is made. In the ladle, a nitrogen jet for the agitation of the liquid steel is frequently employed. Excessive exposure of the melt to the nitrogen jet causes an increase in the nitrogen in the steel to excessive levels which make favourable the formation of large niobium carbonitrides. Controlled additions of titanium or aluminium are sometimes made as nitrogen traps to prevent the formation of the large niobium carbonitrides [1].

The present work was undertaken to study the kinetics of the coarsening and/or the dissolution of large cuboidal carbonitrides of a high nitrogen niobium microalloyed steel at high temperatures, large particles being > 250 nm. Relevant works concerning precipitates in microalloyed steels have considered these kinetic processes, but only for particles smaller than 50 nm, both theoretically and experimentally [8–10]. In practice, the extent of dissolution of these particles depends critically on the particle size distribution. It has been reported that while for large particles the dissolution temperature is above 1600 K, the dissolution temperature for small particles of 1 nm size may be as low as 1290 K [1, 11–14]. In this work the kinetics of the coarsening and dissolution of the large cuboidal niobium carbonitrides was characterized by analysing the evolution of particle size distribution in samples treated at high temperatures [14, 15]. We were able to determine the rate of growth or dissolution of particles as a function of size, the critical size for zero growth at given temperatures and a curve for the volume fraction of the steel occupied by the precipitates also as a function of the treatment temperature.

2. Experimental procedure

Steel billets and hot-rolled steel bars from a special heat of steel which was designed aiming to develop weldable microalloyed reinforcing steels under the British specification B4999, were used. As stated before, the fabrication process is a conventional blast furnace–basic oxygen converter, followed by ladle metallurgy where the alloy adjustment was made and

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where the sample for the chemical analysis was taken. In the ladle the steel was agitated using a nitrogen jet. The liquid steel was poured in a continuous casting machine to produce billets of square section of about 15 cm each side. The billets were reheated at 1423 °C and rolled in a mill to obtain deformed bars of 12 mm diameter.

To perform the experiments described in this paper, we obtained a slice of one billet and a segment of a bar. From the centre of the slice of the billet a set of samples of about 1 cm^3 were machined. The solution treatments of the samples were made in a high-temperature Lindberg furnace with temperature controller within a 5 K range. Reference annealing of 1800 s at 1373 K, was performed and five heat treatments at 1473, 1573, 1623, 1673 and 1723 K, also for 1800 s were carried out. Subsequently samples were quenched in agitated oil.

The metallographic examinations were performed on samples of the billet as-received, annealed and quenched. Deep grinding was used to avoid the thick decarburized layer formed during the annealing. Polishing was done using sand paper and 1 and 0.3 µm alumina powder. The samples were further etched using a saturated aqueous Nital. Observations were performed in a Jeol JSM-T200 scanning electron microscope, assisted with an EDAX analyser. With this instrument the large cuboidal niobium particles could be clearly identified in the ferrite–pearlite structure of the steel billet as-received or in the structure of the annealed and quenched material. The EDAX detector was not able to detect elements as light as carbon or nitrogen, therefore we could not establish with this instrument if the large cuboidal particles were simple nitrides of niobium or if they were carbonitrides. The latter is more accepted by other authors in the literature, therefore we decided to employ carbonitrides [1, 6, 9].

The particle size distribution of the cuboidal niobium carbonitrides was calculated in cumulative form computing on average, 150 measurements of particle sizes in each sample, covering an area of 0.5 mm^2 of each sample. A cumulative size distribution represents the number of particles per unit area or volume which are equal or larger than the given size. The two-dimensional histograms obtained in each sample were converted to three dimensions using standard techniques [17, 18]. Because the distributions could be closely approximated by log normal functions, especially when expressed in the form of cumulative distributions, this continuous expression was used instead of the original histograms. The calculation of the average rate of growth or dissolution of the particles as a function of the size was done by analysing the evolution of the cumulative distributions with a methodology described elsewhere [15]. The volume fraction occupied by the large niobium carbonitrides was calculated using the appropriate weight function in the integration of each size distribution.

For the TEM observations a thin foil was machined from a sample of the hot-rolled bar. Discs of 3 mm diameter were cut from the foil and etched in a twin-jet electropolishing machine using a 10% perchloric acid solution in ethanol. The TEM used was a Jeol 100CX.

3. Results and discussion

The steel composition (wt%) is 0.21C, 1.61Mn, 0.34Si, 0.022P, 0.018S, 0.046Nb, 0.003Al and 0.0073N. The microstructure of the steel billet in the as-received condition was formed by ferrite and pearlite. Cuboidal particles were found mainly in the ferrite field as is shown in Fig. 1. These particles could also be identified in the matrix of the solution-treated and quenched samples (Fig. 2). The EDAX pattern of one of these cuboidal particles is depicted in Fig. 3, where the

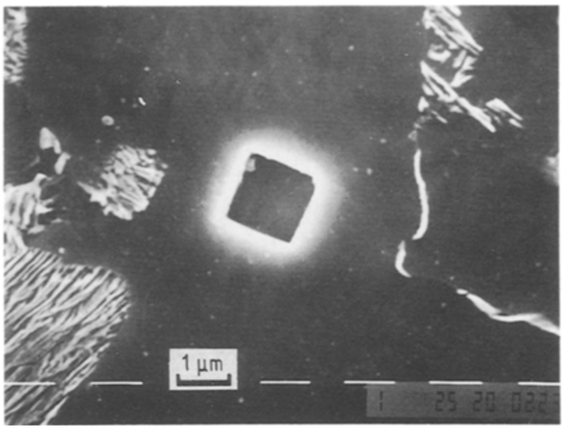

Figure 1 Large cuboidal niobium carbonitride in a ferrite grain.

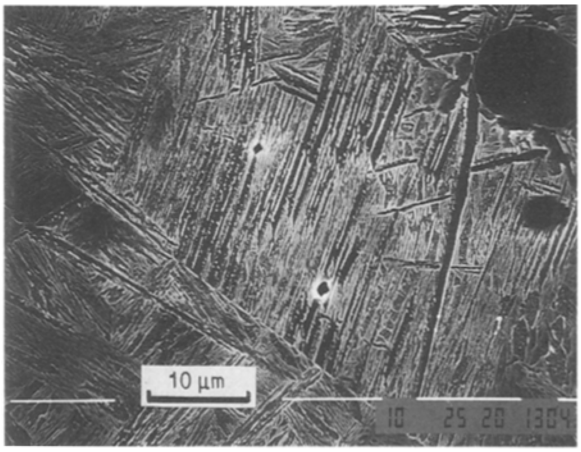

Figure 2 Cuboidal niobium carbonitride in a sample solution treated and quenched.

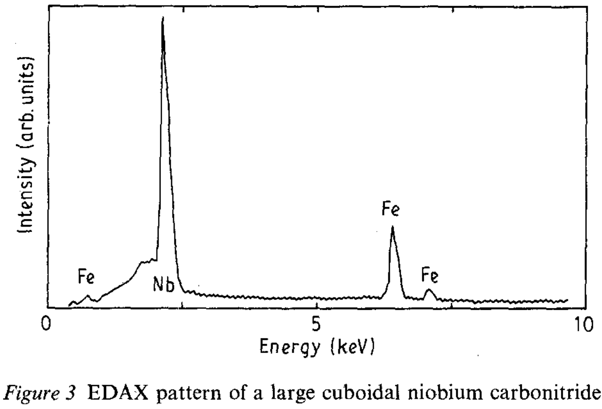

Figure 3 EDAX pattern of a large cuboidal niobium carbonitride.

niobium peak dominates over the iron intensity of the steel matrix. The EDAX detector used was not capable of detecting light elements such as nitrogen.

The TEM observations of the hot-rolled samples allowed us to determine that after the solidification of the billet, a significant amount of niobium remained in solid solution or in the form of small precipitates. Also during and after hot rolling, the niobium in the solid solution may have precipitated in the form of small particles. The ferrite grain in the sample of the hot-rolled bar is rich in small niobium precipitates as is apparent in Fig. 4, where the diffraction pattern allowed the small precipitates to be identified as hexagonal carbonitrides of niobium where the (0 0 1) direction of the precipitate is parallel to the (1 1 0) direction of the ferrite.

The effect of the solution temperature on the volume fraction of the large cuboidal precipitates is depicted in Fig. 5. The treatments at temperatures below 1600 K do not affect significantly the precipitate volume fraction. The apparent increase in the volume fraction of the precipitates in the sample treated at 1473 K may not be a statistical fluctuation, because it is conceivable that the large cuboidal particles may have coarsened at the expense of the niobium, carbon or nitrogen which remained in solid solution after solidification. The volume fraction of the precipitates was clearly reduced in the samples annealed at temperatures 1623, 1673 and 1723 K. This latter result is consistent with reports of other workers where the dissolution temperature for large niobium particles has been established at 1605 K [1].

Fig. 6 contains the cumulative particle size distributions of the samples treated at 1473 and 1573 K, respectively. Each distribution should be compared with the reference heat treatment at 1373 K. As mentioned before, from a comparison of the cumulative distributions in each case it is possible to assess some features of the kinetics of growth and dissolution of the precipitates [15]. In Fig. 6 it is apparent that the population of particles of sizes smaller than 1.1 μm decreases during treatment at 1473 K, while the contrary occurs for the population of larger particles. The calculation of the rate of growth or dissolution of the particles as a function of the size is depicted in Fig. 7. Naturally the growth rate at 1 μm is nil, negative for the smaller particles and positive for the larger. Fig. 7 also shows the curve for growth and dissolution of the particles in the sample treated at 1573 K. Here the critical size for zero growth is larger, 1.3 μm, and the rates of dissolution and of growth are larger in magnitude. The reported stability of the large particles in similar steels treated at temperatures below 1600 K [1, 11–14] is rather a manifestation of a competitive

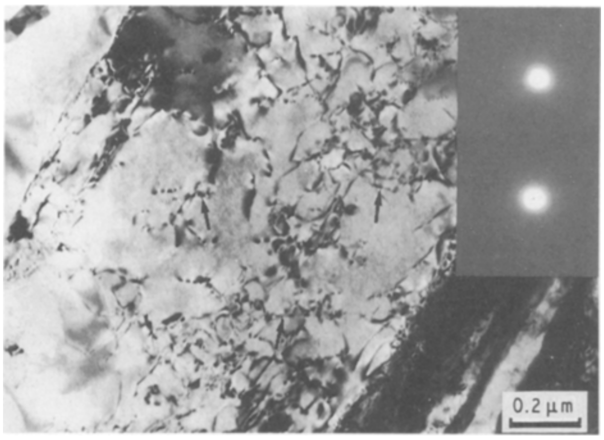

Figure 4 Bright field of fine precipitation in a ferrite grain of a hot-rolled sample of the steel.

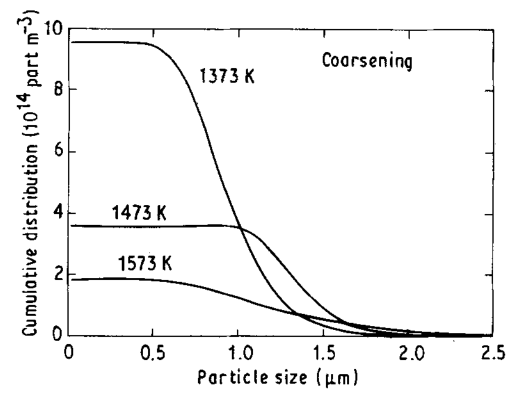

Figure 6 Cumulative particle size distributions of the samples treated at 1473 and 1573 K compared with the reference sample treated at 1373 K. The population of particles smaller than 1 μm is reduced while the number of larger particles is increased. The treatment at 1573 K reduces considerably the population of the particles smaller than 1.3 μm, while the population of larger particles is slightly increased.

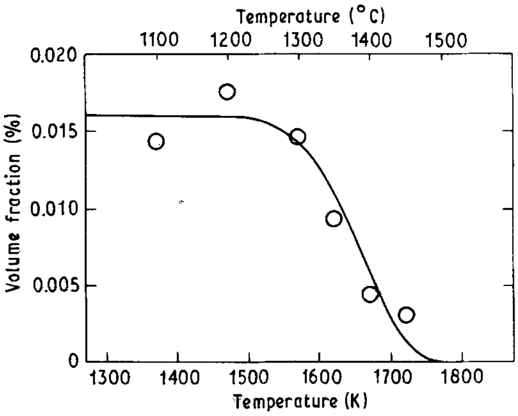

Figure 5 Volume fraction occupied by the precipitates as a function of the treatment temperature.

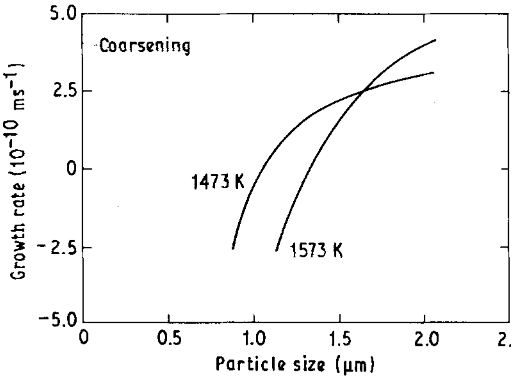

Figure 7 Coarsening and dissolution rates of the large cuboidal niobium carbonitrides in the samples treated at 1473 and 1573 K.

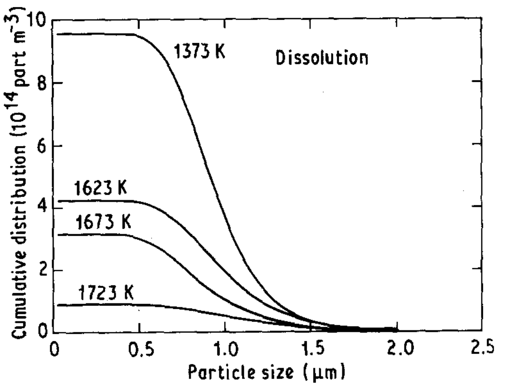

Figure 8 Comparison of the cumulative distributions of the samples treated at 1623, 1673 and 1723 K with that of the reference treated at 1373 K. In this case the populations of particles of all sizes are reduced.

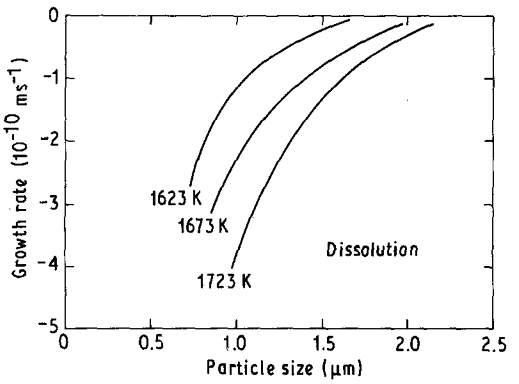

Figure 9 Negative growth rates of the large niobium carbonitrides in the samples treated at 1623, 1673 and 1723 K.

process where the larger particles actually grow at the expense of the smaller.

Fig. 8 shows the cumulative distributions of particle sizes of the samples treated at 1623, 1673 and 1723 K which are also compared to the distribution of the reference sample treated only at 1373 K. The samples treated at these higher temperatures do not exhibit any particle coarsening, because none of the distributions intersect that taken as reference. The particles of all sizes have been dissolved to some degree. The rate of dissolution of the particles as a function of size was calculated from the distribution obtained at each temperature, compared to that of the reference treatment. The results are plotted in Fig. 9. All the growth rates are negative. The rate of dissolution is larger for the smaller particles or at higher treatment temperatures. Our investigation allowed us to confirm that it is only at temperatures around 1623 K or above where the dissolution of the large cuboidal carbonitrides is generalized for all particle sizes.

4. Conclusions

The high nitrogen content of the microalloyed steel studied here developed a microstructure rich in large cuboidal carbonitrides. The solution treatment caused significant changes in the size distribution of the cuboidal carbonitrides considered. When treating at temperatures below 1623 K, the population of the smaller carbonitrides was clearly reduced, while the larger coarsened at the expense of the smaller or of material remaining in solid solution. The growth rate of the larger particles and the dissolution rate of the smaller were calculated as well as the approximated critical size for zero growth. The treatment at temperatures of 1623 K and above, caused the dissolution of precipitates of all sizes and progressively higher negative growth rates were calculated.

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