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Characterization by Electron Diffraction of Two Thermodynamical Phases of Precipitation in Nb-Microalloyed Steels

M. Gómez[1], S.F. Medina[1], P. Valles[2] and A. Quispe[3]

[1]National Center for Metallurgical Research (CENIM), Av. Gregorio del Amo 8,

28040-Madrid (Spain), E-mail: smedina@cenim.csic.es

[2] National Institute of Aerospace Technology, INTA, Torrejón de Ardoz, Madrid, Spain

E-mail: vallesgp@inta.es

[3] National University "Jorge Basadre", Av. Miraflores s/n, University City,

Tacna (Peru), E-mail: abqc@unjbg.edu.pe

Abstract. Excellent mechanical properties (high strength and toughness) of microalloyed steels are mainly caused by induced precipitation during thermomechanical treatment (TMT) and grain refinement. It has been recently found that TMT of Nb-microalloyed steels can give rise to two different kinds of precipitates, manifested by the double plateau in the statically recrystallised fraction (X_a) against time curves. This work presents an electron diffraction study performed in a transmission electron microscope, equipped with an EDS Edax analytical system. Lattice parameters of a great deal of particles, smaller than 200 nm and with face cubic centred structure, have been measured. Frequency distribution of the values of lattice parameters shows that these are grouped in two sets whose mean values are close. Comparison of these values with those found in the literature for carbides, nitrides and carbonitrides usually present in microalloyed steels demonstrates that they are Nb carbonitrides with slight stoichiometric differences (NbC_xN_y).

Introduction

Most hot rolled microalloyed steels are steels which contain niobium, as these have the advantage of adequate solubility at normal rolling temperatures. Vanadium presents greater solubility in austenite than niobium and its precipitation as VN, and above all as VC, occurs at very low temperatures, making it difficult to obtain sufficiently deformed austenites before the $\gamma \rightarrow \alpha$ transformation. To this end, a good part of the research work on microalloyed steels has been focused on low or medium carbon niobium steels, obtaining highly deformed austenites at the end of rolling which give rise, after the transformation, to very fine ferrite/pearlite microstructures and consequently good mechanical properties.

In steels with a C content of approximately 0.2%, around 60 ppm of N, the solubility temperatures of niobium carbides and carbonitrides are not very different [1-4]. One of the consequences deriving from the above is the formation of complex carbonitrides which can be formed not as a precipitate as such but by the heterogeneous nucleation of one type of precipitates on another, forming relatively complex and coarse precipitates.

When strain induced precipitation starts, static recrystallisation is inhibited during a certain time, normally until the end of precipitation, before again advancing until recrystallisation is complete. This momentary inhibition of recrystallisation appears as a plateau on the recrystallised fraction against the logarithm of time curves [5-6]. It has been reported that some Nb-microalloyed steels

show double precipitation (two plateaus) and it takes place when the percentages of C and Nb are such as to favour the formation of carbides rather than nitrides, a singularity typical of some microalloyed steels with Nb and C contents in excess of 0.20 mass% [7-8]. Nevertheless the nature of these precipitates is not still clear, so in this paper the static recrystallisation is studied in a niobium microalloyed steel through the determination of recrystallised fraction against the time by means hot torsion tests. An study is made of the influence of the strain and differential thermal analysis and transmission electron microscopy (TEM) are used to assess the double precipitation and its nature .

Materials and Experimental Procedure

The steel to be studied have been manufactured by Electroslag Remelting (ESR) in a laboratory unit capable of producing 30 kg ingots and for their manufacturing consideration has been made of the thermodynamic activities of the slag components and of the alloying elements in order to obtain the desired composition (Table1). The ingot was forged and subsequently given a normalised treatment to reduce the band structure produced by deformation and to homogenize the microstructure.

The torsion specimens, with a gauge length of 50 mm and 6 mm in diameter, were austenitized at high temperature above to the solubility temperature, for 10 min, and then the temperature was rapidly reduced to the testing temperature. During the test the specimens were protected by an argon atmosphere in order to prevent their oxidation. Torsion magnitudes (torque, no. of revolutions) and equivalent magnitudes (stress, strain) have been related according to Von Mises criterion [9].

The recrystallised fraction was determined at different temperatures corresponding to the austenite phase, at equivalent strain 0.35, lower than the critical strain which leads to the start of dynamic recrystallisation, and at a strain rate of $3.63s^{-1}$ (=1000 rev/min).

Table 1. Chemical composition (wt-%) of the steel studied.

C	Si	Mn	P	S	N	O	Al	Nb
0.21	0.19	1.14	0.023	0.015	0.0061	0.0046	0.008	0.058

The characteristics of the precipitates were determined by transmission electron microscopy (TEM), using the carbon extraction replica technique. The study of the dissolution of precipitates was carried out by differential thermal analysis, where the heating rate of the samples was 15 °C/min and they were protected from oxidation by an argon flow of 20 ml/min.

Results and discussion

The austenitization temperature was chosen taking into account that in this type of steels preliminary reheating to the deformation temperatures must guarantee total dissolution of the precipitates. In this sense, the solubility temperature for carbides, nitrides or carbonitrides, hypothetically present in this steel, is below the selected austenitization temperature of 1250 ºC.

As has been mentioned, the recrystallised fraction was determined for different temperatures and strain of 0.35, respectively, using the method known as "back extrapolation"[10]. Fig. 1 shows the recrystallised fraction against time curves. When the deformation temperature was equal to or less than 1050 ºC, the double plateau was formed. Once the kinetics of the first precipitation (first plateau) ends and recrystallisation again continues, the second precipitation starts to occur and once this finalizes recrystallisation continues until it is complete.

The DTA curve (Fig. 2) shows three reactions. The one which occurs at a lower temperature, of endothermic nature, is the phase transformation of pearlite and ferrite into austenite (during heating), and two exothermal reactions corresponding to the dissolution of the precipitates. Comparison of the final temperatures of each reaction with the calculated solubility temperatures for niobium nitrides and carbides does not clearly show, at least not definitively, the nature of the precipitates.

Nevertheless, it seems obvious that there is a dissolution of two types of precipitates, corresponding to the formation of the two peaks respectively.
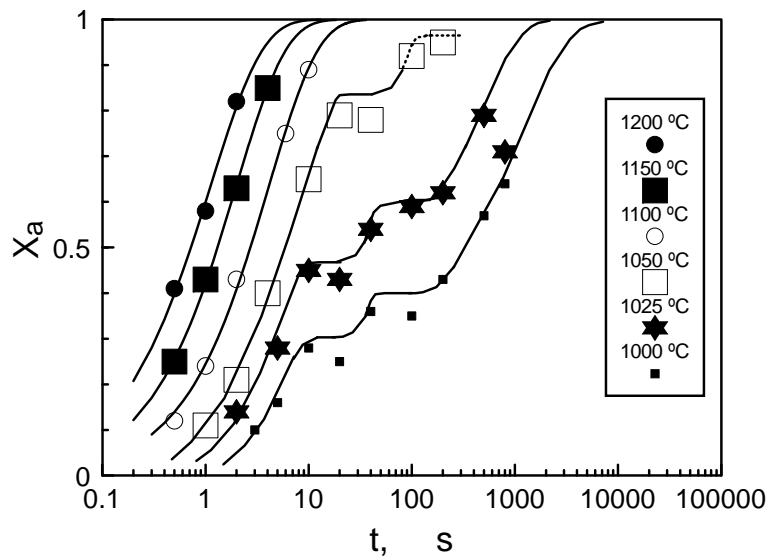
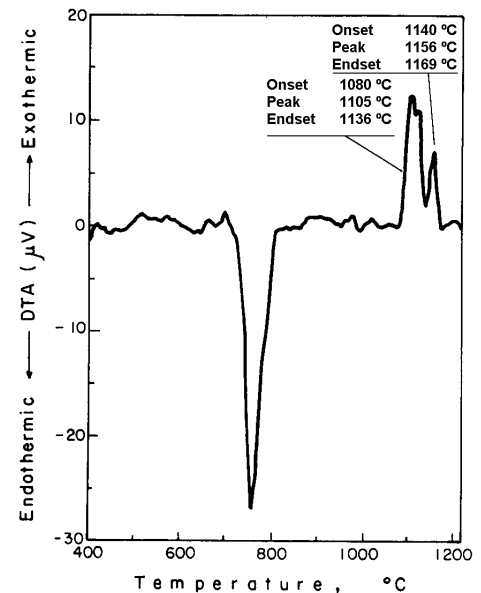Fig. 1. Recrystallised fraction (Xa) against time (t).

Fig. 2. DTA curve for steel used.

From the differential thermal analysis it is obviously not possible to deduce what percentages of niobium have been distributed between nitrides and carbides and therefore it is not possible to compare the solubility temperatures with the final temperatures of the two transformations. Thus, it cannot be stated with complete certainty that the precipitates are carbonitrides only and that there is not a presence of some nitrides and carbides.

Observation of the precipitates was carried out on the same specimens deformed and quenched to observe the recrystallised fraction of the austenite. In order to clarify the double precipitation (double plateau) occurred, a lot of electron diffraction analyses were performed and the lattice parameters were determined. Observations were made for the two specimens tested of the steel C at 1025 °C, strain of 0.35 and times of 15 s and 100 s, respectively. From the curve of the recrystallised fraction (Fig. 1), it is seen that the times selected are placed on the first and second plateau, respectively.

The resolution of precipitates using the carbon extraction replica technique by TEM, is shown in Fig. 3 a-b. The spectrum in Fig. 3c shows the presence of Nb and the lattice parameter determined from Fig. 3d reveals a f.c.c. cubic lattice with a value of a = 4.39-4.44 $\mathring{A}$, which is identified, in accordance with the reference value found in the literature [7, 8] as a niobium carbonitride (NbCN), although it could be a nitride (NbN) or carbide (NbC) too, as the lattice parameter of them are similar.

The statistical study of results showed the formation of only a kind of precipitates on the first plateau and two different precipitate groups on the second plateau. In the specimen tested at 15 s, corresponding to the first plateau, the electron energy dispersive X-ray spectrum showed the presence of Nb and the lattice parameter determined from electron diffraction image revealed a f.c.c. cubic lattice with a value of a = 4.39-4.44 $\mathring{A}$, which is identified, in accordance with the reference value found in the literature as a niobium carbonitride, carbide or nitride. The Fig. 4 shows the distribution of lattice parameter of this type of precipitates.

In the fine precipitates at 100 s after deformation two series of different lattice parameter were observed. The first series presented a lattice parameter of 4.41-4.44 $\mathring{A}$, similar to the above precipitates and for the second series it was of 4.46-4.58 $\mathring{A}$ (Fig. 5). In accordance with above, the first precipitates should correspond to carbonitrides or nitrides and the second precipitates to carbides. Nevertheless, the coarser precipitates presented a lattice parameter close to 4.46 $\mathring{A}$ (Fig. 6).
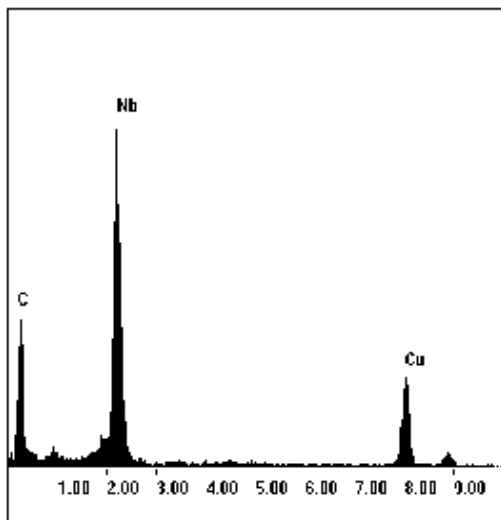
The last result means likely that the second precipitation is slightly heterogeneous and it is homogeneous above all.
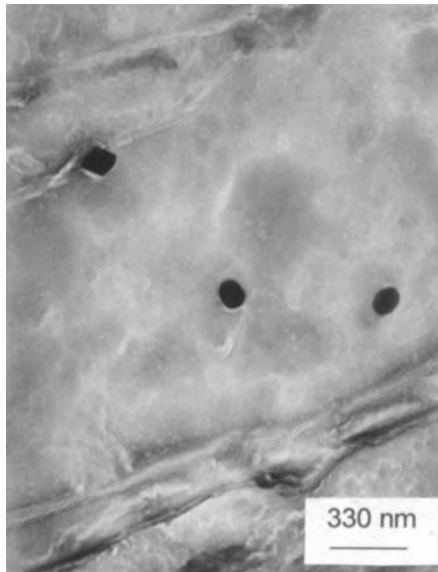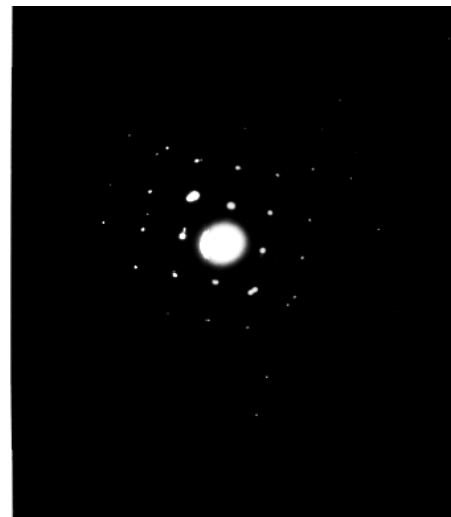
Fig 3. TEM images: (**a**) Image showing precipitates for specimen tested at 1025°C, t = 15 s. (**b**) Image showing precipitates for specimen tested at 1025°C t= 100 s; (**c**) EDAX spectrum of precipitate; (**d**) electron diffraction image.

Conclusions

The above results showed clearly that the second plateau is formed by a new precipitation, whose particles had a lattice parameter something bigger than those corresponding to the first precipitation (first plateau).
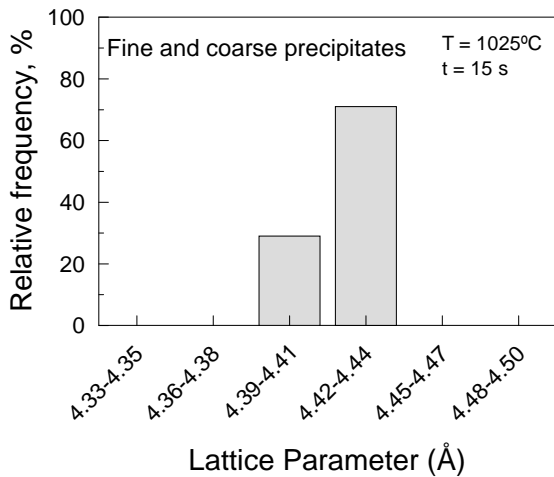
Acknowledgements

Fig. 4. Lattice parameter distribution; t = 15 s.

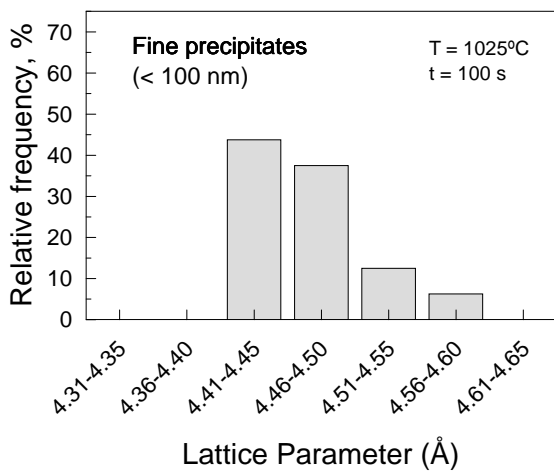

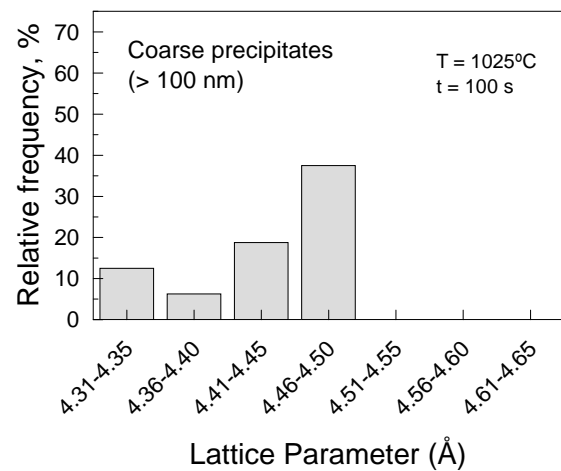Fig. 5. Lattice parameter distribution of fine precipitates; t = 100 s.

Fig. 6. Lattice parameter distribution of coarse precipitates; t = 100 s.

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