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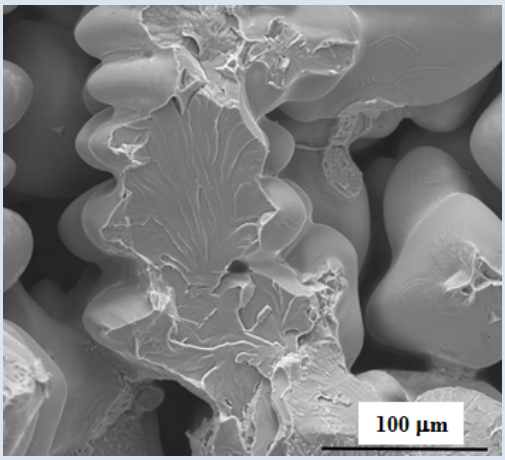
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SEM CHARACTERIZATION OF COMPLEX PRECIPITATES IN AN AS-CAST NB-V-TI MICROALLOYED STEEL

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ABSTRACT

This article deals with the characterization of complex precipitates from commercial Nb-V-Ti microalloyed steel produced by continuous casting, using fracture surfaces from V-notch Charpy tests, and extracted precipitates. The samples were studied by means of scanning electron microscopy and X-ray energy dispersive spectroscopy, in combination with X-ray diffraction. Samples examination revealed micron size (Nb,Ti,V)(C,N) precipitates, most of them with a highly branched dendritic morphology, and Ti rich precipitates, corresponding to (Ti,Nb,V) (C, N). Also dendritic Nb(C,N) without Ti was observed. By means of the method used in this investigation, it was possible to easily reveal the precipitates, being able to fully characterize their distribution, size and morphology, and also their chemical composition and crystal structure.

Keywords: *Carbonitrides, dendritic Nb Precipitates, microsegregation, fracture.*

CARACTERIZACIÓN MEDIANTE MEB DE PRECIPITADOS COMPLEJOS PRESENTES EN UN PLANCHÓN DE ACERO MICROALEADO DE NB, V Y TI.

RESUMEN

El artículo trata sobre la caracterización de precipitados complejos presentes en un acero comercial microaleado al Nb-Ti-V, producido mediante colada continua. Las muestras utilizadas son las provenientes de superficies de fracturas obtenidas mediante ensayos Charpy y precipitados extraídos de la matriz. Las muestras fueron analizadas mediante microscopía electrónica de barrido equipado con EDS y a través de análisis de difracción de rayos X. Se observaron precipitados de (Nb,Ti,V)(C,N) con tamaños de micrones, la mayoría de ellos con estructura dendrítica, y precipitados ricos en Ti que correspondieron a (Ti,Nb,V) (C, N). Adicionalmente precipitados dendríticos de Nb(C,N) sin Ti fueron observados. La metodología de análisis utilizada en el estudio, permitió caracterizar completamente los precipitados, su distribución, tamaño y morfología, así como su composición química y estructura cristalina.

Palabras claves : *Carbonitruros, precipitados dendríticos de Nb, microsegregación, fractura.*

1. INTRODUCTION

Microalloyed steels are widely used for automotive applications to decrease vehicle weight [1]. and for pipeline applications at the oil industry that demands materials with high strength, good toughness and weldability [2-3]. The common microalloyed elements used for these applications are V, Nb, and Ti, which yield to substantial improvement on the mechanical properties by different hardening mechanisms. To optimize the precipitates effect and keep good control of ferrite grain size, it is desirable to completely dissolve the particles at the reheating temperature, and to precipitate them at lower temperatures [4]. The dissolution process is more critics in steels with multimicroalloying components, which can lead to the formation of precipitates with complex chemistry due to the mutual solid solubility of carbides and nitrides, with the subsequent effects on the mechanical properties of the material [5-9]. Therefore, it is of significant importance to identify the characteristics of precipitates present in the slab, in order to adjust the pouring and solidifications conditions and also to select suitable combinations of microalloy additions and appropriate processing conditions. The characterization of precipitates is usually done by transmission electron microscopy. In industrial practice, for instance, a characterization of precipitates present in as-cast slabs by a simple analysis is crucial, for setting the correct solidification and thermomechanical processing parameters that guarantee an appropriate microstructure. This study focuses on a comprehensive microstructural analysis of large precipitates that could be present on a as-cast slab of a Nb-V-Ti microalloyed steel produced by continuous casting. The analysis was centered on morphology, chemistry and crystal structure of precipitates, by using impact tests samples surfaces and extracted precipitates, analyzed by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS), in combination with X-ray diffraction (XRD) of precipitates, extracted from the matrix by chemical dissolution and filtration.

2. EXPERIMENTAL PROCEDURE

The microstructure examination was carried out upon an Nb-V-Ti steel in the as-cast condition, with chemical composition given in Table 1.

The material was provided by SIDOR (Iron and steel of the Orinoco Alfredo Maneiro), in the form of slab of 200 mm thick, produced by continuous casting. The samples for the study were cut out from the centerline segregation area of the as-cast slabs. The pieces were sectioned in various specimens for metallographic examination, Charpy impact tests, and precipitate extraction by chemical dissolution of steel matrix. The Charpy impact tests were conducted to reveal the precipitates at the fracture surface, and performed at 0°C on samples with parallel faces oriented along centerline segregation. The test pieces had dimensions of 10 x 10 x 55 mm3, with a machined V-notch, 2 mm deep. To extract the precipitates, the matrix was chemically dissolved in a HCl water solution at 50%, and heated in a sand bath at 70°C. The solution was left for 24 h in a beaker to allow the solids to sink. Subsequently, it was filtered using a 45µm Millipore filter. To avoid the interference in the analysis of microalloyed precipitates, previous to sample dissolution, the iron carbides were dissolved, by heating the sample at 750 ºC for 30 minutes and then quenched in iced water. The fracture surfaces and extracted precipitates were assessed by SEM with EDS, using an ESEM FEI-Quanta 200 and Oxford-Inca 200, respectively. The filters with precipitates were analyzed in backscattered images mode, using low vacuum. Additionally, XRD analysis was conducted on precipitates extracted from the steel matrix and directly collected in the filter. XRD data were obtained using Cu Kα radiation, a scan step of 0.030°, a step time of 2 s, and a 2θ range from 10 to 70° in a D4 Bruker diffractometer.

Table 1. Chemical composition of the steel examined in the present study (wt %).

C	*S*	*Si*	*Mn*	*V*	*Nb*	*Ti*	*N*
0.120	0.003	0.282	1.360	0.064	0.053	0.016	0.0064

3. RESULTS

3.1 Microstructural analysis by SEM-EDS

Figure 1 displays the characteristics of the fracture surface. The fractographic analysis revealed a mostly brittle fracture (Fig. 1a) with small contribution from the ductile mode (Fig. 1b). Figure 1a shows that the failure exhibited a combination of different brittle fracture modes, such as

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transgranular cleavage, with the characteristic flat facets, and intergranular fracture along the boundaries of dendrites colonies.

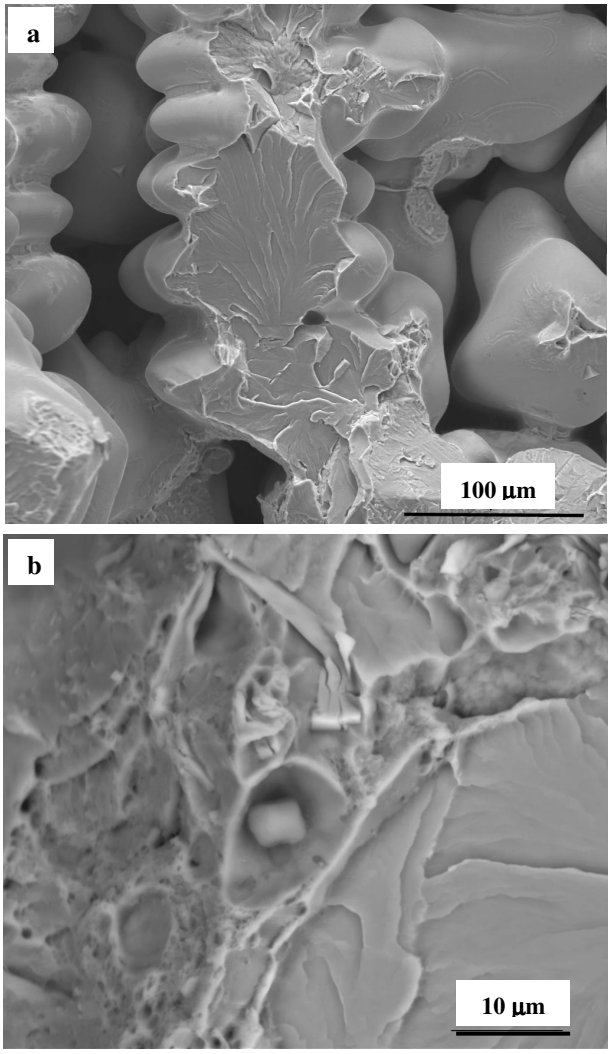


Figure 1. Fracture surface of samples taken from centerline zone of continuous casting slab. a) Brittle fracture, b) Combination of ductile and brittle fracture modes.

Close examination of the fracture surface at the matrix interdendritic zones, revealed large particles also dendritic-shaped, highly branched, as seen in the backscatter images of Figures 2a and 2b. Bulk microprobe analysis of these particles, Figure 2c, indicated that they were rich in Nb, Ti and V, which corresponds to complex precipitates which is in agreement to other authors [10]. Another feature worth to mention is the periodic contrast observed along the branches, showing light and dark zones (see Fig. 2a), which could be attributed to compositional differences.

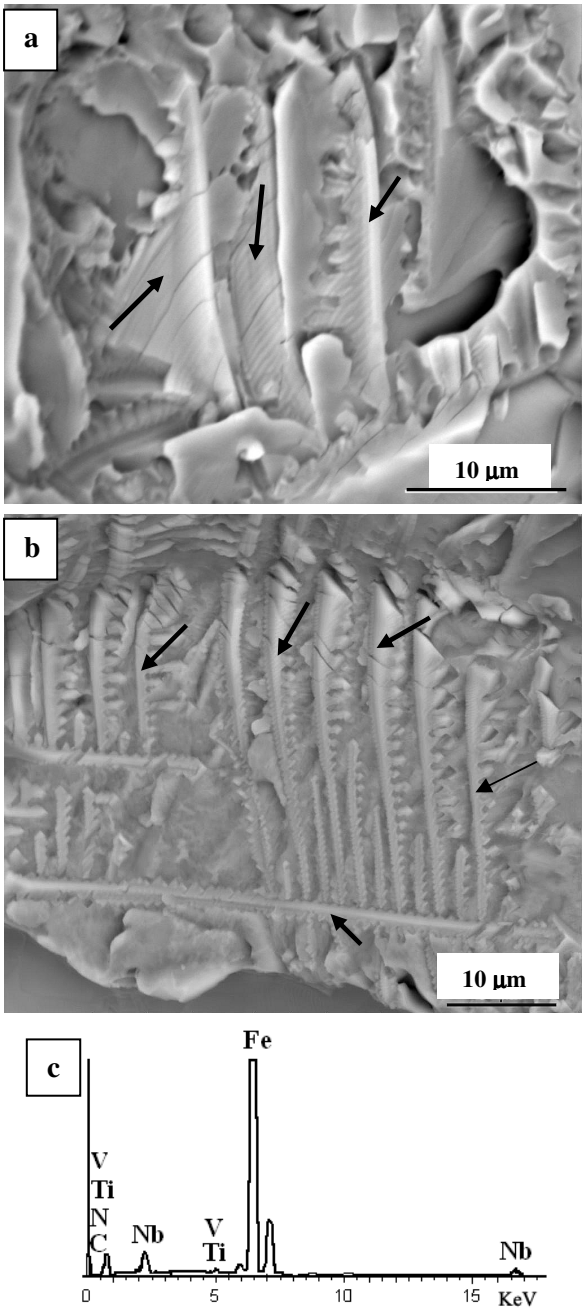


Figure 2. Dendritic Precipitates at the interdentric zone.of δ- ferrite, a and b (indicated by arrows) and their EDS (c).

The examination of the precipitates chemistry becomes more straightforward in samples containing the precipitates extracted from matrix, since it is not disturbed by the presence of iron. Figure 3a shows a backscatter image of a dendritic precipitate and its chemical composition, by way of mapping images of Nb, Ti, V and N, figures 3b, 3c, 3d y 3e, respectively. The mappings in Figures 3b

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and 3c, delineated two types of precipitates, one faceted and rich in Ti, and another with dendritic morphology and rich in Nb, that seems to be growth from the Ti rich precipitate. The Ti rich precipitates have dissolved some amount of Nb and V, as seen in Figure 3b and 3c and 3d, while the Nb rich precipitate does not contain Ti, and appears to have lesser amount of V. These precipitates seems to be a (Ti,Nb,V)(N,C) and (Nb,V)(N,C), respectively. However, Figure 4 shows that Nb rich precipitates can be found with Ti as well. The sizes of primary dendritic arms reach lengths up to 40 µm with secondary dendrite arm spacing between 1 to 8 µm.

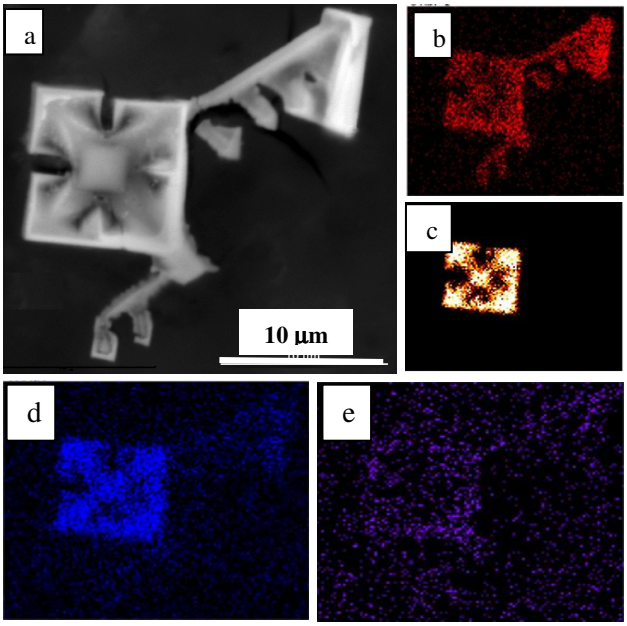


Figure 3. Backscatter image of chemically extracted precipitates from matrix (a), along with mapping images of Nb ,Ti , V , and N (b. c. d y e, respectively).

Precipitates with morphologies different from dendritic were also observed. Figure 5 is an example, which corresponds to an image of precipitates extracted from the steel matrix (a) and EDS spectrum of precipitates (b). These precipitates have cruciform (star like) and rounded morphologies, and are rich in Nb, which are commonly reported fore these types of microalloyed steel [11]. Besides their morphology, they were also distinguishable from the dendritic-shaped particles by their smaller size, typically inferior to 0.2 µm.

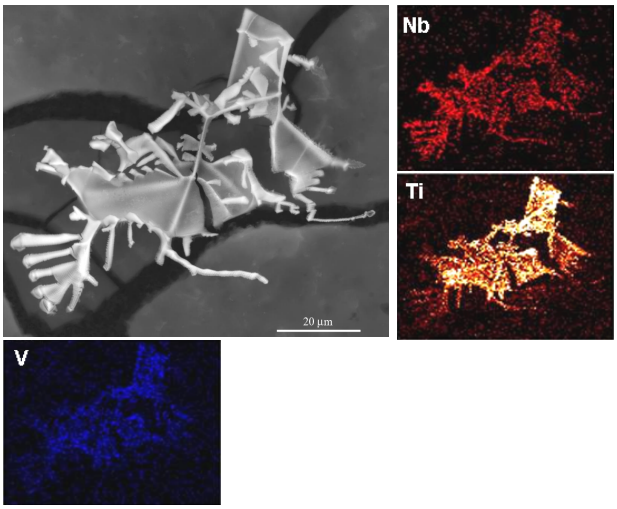


Figure 4. Backscatter image of chemically extracted precipitates from matrix, along with mapping images of Nb ,Ti and V

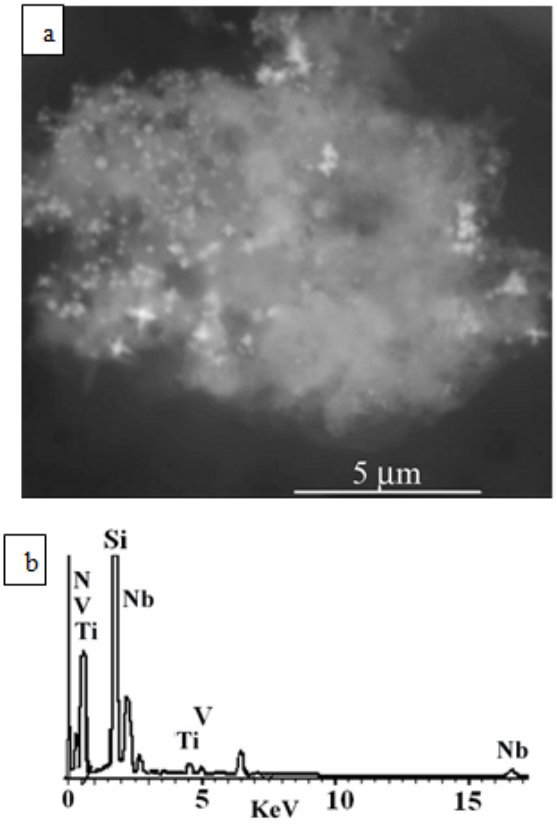


Figure 5. Backscatter image of chemically extracted precipitates from matrix (a), with the EDS spectrum (b).

3.2 X-ray diffraction (XRD) analysis of extracted precipitates from steel matrix

Figure 6 displays an X-ray diffraction pattern of the precipitates extracted from the steel matrix. The

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possible phases detected are listed in Table 2, mainly carbides and carbonitrides of the microalloying elements.

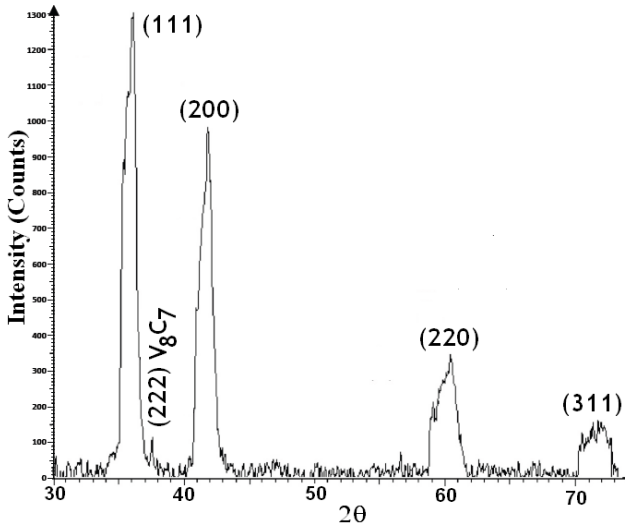


Figure 6. XRD pattern of chemically extracted precipitates from matrix.

Table 2. Phases identified from X-ray diffraction pattern of figure 5.

Phase	*Space Group*	*Lattice parameters (Å)*	*X ray Card Number*	*Ref.*
TiCN	Fm3m (225)	4.469	42-1488	[10]
TiCN		4.297	42-1489	
TiN		4.241	38-1420	
(Nb,Ti) C		4.427	47-1418	
NbC		4.469	38-1364	
VC		4.165	73-0476	
V_8C_7	$P4_132(213)$	8.334	35-0786	
$Ti_yNb_{1-y}C_xN_{1-x}$	Fm3m (225)	-	-	[11]

4. DISCUSSIONS

The features of a highly branched dendritic morphology of carbonitrides precipitates, in conjunction with their interdendritic distribution, suggest a nucleation in the liquid state, as a consequence of solute segregation during solidification. The tendency of Nb and Ti to segregate in the liquid during solidification, is illustrated by Figure 7, with represents a plot of C_L/C_o ratio as a function of liquid fraction [12]. C_L is the amount of Nb or Ti in the liquid, and C_o is the composition of Nb or Ti in the steel. According to Figure 7, at low liquid fraction, C_L in the case of Nb, can be several times C_o, which can cause segregation of Nb. As suggested by [12], the strong segregation of Nb could explain the precipitation of Nb carbonitrides in the remaining liquid, between dendrites of δ- ferrite, at the final stage of solidification. Segregation of Ti in the liquid can also occur, but in less extension than Nb.

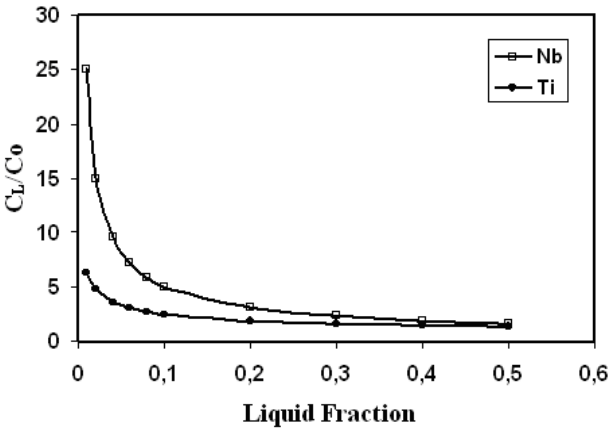


Figure 7. Variation of C_L/C_o as a function of liquid fraction [12].

The Nb carbonitrides have a cubic F structure. In these structures is common to have the primary dendrite branch, or trunk, growing in the <100> directions. Secondary branches appear in the [001] directions, perpendicular to the trunk [13], when the planar interface breakdown because the instability of the growing front. Tertiary arms could develop, when primary arms are largely spaced and such seems to be the case for some dendritic carbonitrides precipitates observed in the present study, as showed in Figure 2.

Small Nb rich particles were also observed in the sample. These particles, could have precipitated in the austenite phase, due to the oversaturation of Nb in austenite. These particles can coprecipitate on Ti rich particles and also on FeS inclusions. These results are consistent with previous work, using TEM analysis [14- 16].

The possible phases identified by X-ray diffraction, all, except one, have the same crystal structure Fm3m (225) with very close lattice parameters. It means that all the anions and cations of

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microalloyed elements, could be substituted among themselves. For this reason, the diffraction pattern shows wide peaks, especially around 2θ equal 60 and 72 degrees, due to the variation in interplanar distance because of the contribution of precipitates with variable composition and lattice parameter. This result could be related to the differences in contrast observed in the dendritic precipitates, as a consequence of changes in composition during their growth process. In this way, it is expected that the core of primary and secondary arms could be rich in Ti surrounded by a case rich in Nb, considering that Ti precipitates at higher temperatures than Nb or V. However, deeper study is required to corroborate this statement. On the other hand, it is important to point out that TiN can precipitate in liquid before starting the δ-ferrite solidification, leaving only a partial amount of Ti free to precipitate at the interdendritic zones of δ-ferrite.

Dendrite precipitates have been reported on studies done by TEM [17]. However, the observation and definition of highly branched dendritic precipitates as evident as the reported in the present study by SEM analysis are not showed in the revised literature. The observation of this morphology was facilitated by de use of fracture surfaces in combination with extracted particles, providing a better visualization of the complete volume of the precipitate. Additionally this methodology allows an easier localization of dendrite particles at the ferrite matrix. This type of observation is limited in samples prepared by the conventional mechanical grinding and polishing, which was also carried out in this study for comparison, without good results.

Thus, the identification of precipitates carried out during the present work, revealed a series of interesting precipitates characteristic, evident by the contrast of backscattered images, that distinguish it from other published studies, and introduce a different way to analyze the as-cast structures, without the need of using transmission electron microscopy.

The large and complex Ti-Nb-V-dendritic precipitates present in the steel under study, could have detrimental effects on the mechanical properties of the material due to the difficulties of having them completely dissolved during reheating process, which counteract the hardening potential effects of the microalloyed elements. Upon the bases of these results, it is important to evaluate the production conditions of the steel and to asses the dissolution kinetic of precipitates.

5. CONCLUSION

Large complex carbonitrides of the order of micrometers in size were identified in the continuous casting slab. These phases had dendritic morphology, precipitated in the liquid state between dendrites of δ- ferrite, and develop changes in composition during the growth process. Non-dendritic complex precipitates, smaller than 0.2 μm, were also present. Given the variations in chemical compositions, it may be more convenient to refer to these phases as solid solutions of (Ti,Nb,V)(C,N) or (Nb,Ti,V)(C,N), depending on which microalloyed element is in greater proportion in the precipitate.

The analysis of fractured samples and chemically extracted precipitates by SEM operated in backscattered images mode, together with EDS and XRD, provides useful information to fully characterize large precipitates in microalloyed steels.

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