DISSOLVING BEHAVIOR OF LARGE DENDRITIC PRECIPITATES IN V-Nb-Ti MICROALLOYED STEELS

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Abstract

The dissolution process of complex dendritic precipitates of as-cast V-Nb-Ti microalloy steel slab was addressed, using scanning electron microscopy, transmission electron microscopy and inductively coupled plasma-optical emission spectrometry. The progress of the dissolution process was followed by re-heating the as-cast sample at 1250°C and 1300°C for 30 and 90 minutes. The as-cast microstructure was comprised by complex Ti-rich (Ti,Nb,V) and Nb-rich (Nb,Ti,V) carbonitrides, as well as nanometric precipitates based on the three microalloys. The former were found in micrometric sizes with cuboidal, plates and dendritic morphologies. The primary and secondary arms of dendrites were rich in Ti, while the tertiary arms were rich in Nb. During re-heating incomplete dissolution of large-dendritic precipitates was observed even at 1300°C, resulting in spherodized (Nb, Ti, V) particles and Ti-based carbonitrides, practically unaffected by the heat treatment. Vanadium did not dissolve completely in austenite at this condition, remaining bound to Ti within Ti-rich precipitates and in less proportion to Nb-rich carbonitrides, being both the Ti-rich and Nb-rich carbonitrides with vanadium thermodynamically stable at least up to 1300°C. The process of dissolution will be discussed.

Keywords: Dissolution**,** precipitates, slab, microalloy steel, reheating

COMPORTAMIENTO DE DISOLUCIÒN DE PRECIPITADOS DENDRÌTICOS DE GRAN TAMAÑO EN ACEROS MICROALEADOS V-Nb-Ti

Resumen

Se abordó el proceso de disolución de los precipitados dendríticos complejos de una acero microaleado con V-Nb-Ti en estado, utilizando microscopía electrónica de barrido, microscopía electrónica de transmisión y espectrometría de emisión óptica de plasma acoplada inductivamente. El progreso del proceso de disolución en el recalentamiento a 1250 ° C y 1300 ° C durante 30 y 90 minutos, mostró que la microestructura en la condición de colada estaba compuesta por carbonitruros complejos ricos en Ti (Ti, Nb, V) y ricos en Nb (Nb, Ti, V), así como precipitados nanométricos basados en los tres microaleantes. Los primeros se encontraron en tamaños micrométricos con morfologías cuboidales, placas y dendríticas. Los brazos primarios y secundarios de las dendritas eran ricos en Ti, mientras que los brazos terciarios eran ricos en Nb. Durante el recalentamiento, se observó una disolución incompleta de precipitados dendríticos grandes incluso a 1300 ° C, dando como resultado partículas esferodizadas (Nb, Ti, V) y carbonitruros a base de Ti, prácticamente no afectados por el tratamiento térmico. El vanadio en esta condición no se disolvió completamente en la austenita, permaneciendo unido al Ti dentro de precipitados ricos en Ti y en menor proporción a los carbonitruros ricos en Nb, siendo los carbonitruros ricos en Ti y ricos en Nb con vanadio termodinámicamente estable al menos hasta 1300 ° C. Se discutirá el proceso de disolución.

Keywords: Disolucion**,** precipitados, planchón,acero, microaleado, recalentamiento

INTRODUCTION

Commercial microalloyed steels are usually based on the addition of Ti, Nb and V alone or combined, to improve the overall mechanical properties and welding. The Ti prevents austenite grain growth in the heat affected zone due to the formation of very stable TiN [1] in sizes lower than 0.1 μm [2,3]. On the other hand, Nb retards recrystallization and refines the austenite microstructure during steel processing by precipitation of fine carbides or carbonitrides in austenite [4,5] and by solute drag effect of Nb in solution [6]. It leads thereby, to an augment in the density of sites available for nucleation of ferrite during $\gamma \rightarrow \alpha$ phase transformation, giving rise to a refinement of ferrite grain microstructure. On the other hand, vanadium increases the strength of microalloyed steels by precipitation hardening in ferrite [7,8]. Thus, precipitation of particles for both microstructure refinement and dispersion hardening depend, among other factors, on the amount of microlloyed elements available for precipitation, and hence on the dissolution of precipitates formed in the cast structure during the reheating stage prior to hot rolling.

Carbonitrides formed in the cast-slab during and after solidification can have a different composition, morphology and size distribution, depending on the steel composition and solidification conditions. These characteristics influence the dissolution behavior of precipitates during reheating. Most of the studies found in the literature on this subject deal with Nb or Nb-Ti [9,12] microalloyed-steel, and a few of them address the case of Nb-V-Ti multimicroalloyed steels [13,14]. Studies agree on the higher stability of Ti nitride [1,15]. In addition, when V, Nb and Ti are added altogether in the microalloyed steel, mixed precipitates with complex chemistry appeared [16,17], which were more stable than the simple carbides or carbonitrides. Furthermore, Nb-rich-and Ti-rich particles prevailed in the Nb-V-Ti steels. Z. Chen et al. [3] reported Nb rich-dendritic precipitates stable up to 1150°C. Likewise, Nöhrer et al. [18] found that Nb and V dissolved almost completely

at temperatures of 1250°C, and S.G. Hong et al. [14] in a Nb-Ti-V microalloyed steel, reported Nb and Ti rich precipitates without V before and after re-heating. It is often assumed that niobium and vanadium dissolve completely at the common reheating temperature in industrial thermomechanical practices (1250°C), given their poor thermal stability compared with Ti-based carbonitrides. However, in multicomponent V-Nb-Ti microalloyed steel it could not be the case. Consequently, the present study addressed the evolution of precipitates during reheating in terms of their dissolution behavior and composition.

2. EXPERIMENTAL PROCEDURE

The material used in this study was a commercial 200 mm thick-slab of V-Nb-Ti microalloyed steel, produced by continuous casting. The chemical composition of the material is given in Table 1. The evaluation of dissolution behavior of precipitates in the austenite region was carried out on samples of 20x4x4 mm^3 cut from the central segregation region of slab. The specimens were encapsulated in quartz tube and kept in vacuum to avoid oxidation, then heated at 1250°C for 30 min and at 1300°C during 30 and 90 min, follow by quenching in an aqueous-10% NaCl solution. Afterwards, the iron matrix of quenched-samples and cast samples, was dissolved by chemical dissolution and filtering, according to the procedure described elsewhere [17]. The residues collected in filters were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS), through backscattered electron image mode, using ESEM FEI-Quanta 200 and Oxford-Inca. To quantify particle size, image analysis was carried out using the IMAGE PRO PLUS 4.1.5 software. The sample in the as-cast condition without heat treatment was additionally analyzed by Transmission Electron Microscopy (TEM) in STEM mode (HAADF/EDS), to evaluate the nanometric precipitates. For this analysis, the precipitates were separated by centrifugation and suspended in ethanol. A drop of the suspension was placed on a 600-mesh copper grid coated with a thin

film of carbon. The equipment used for this part of the study was a TEM TALO, FEI- 200KV. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), using a Perquin Elmer 5300V, was used to quantify the amount of Nb in solution and precipitated in the as-cast and heat-treated samples.

Table 1: Chemical composition of microalloyed steel

Element wt %						
C	Si	Mn	V	Nb	Ti	N
0.120	0.282	1.360	0.064	0.053	0.016	0.0064

RESULTS AND DISCUSION

As-cast microstructure

The as-cast microstructure was comprised by nanometric particles and micrometric-precipitates of different morphologies and composition, as exhibited in figures 1 and 2, respectively. The EDS mapping that accompanies the TEM image in Figure 1, displays particles rich in Nb of circular and cruciform shapes, ranging from 30 to 45 nm, and spherical particles enriched in V in sizes between 10 and 20 nm. The Nb particles contained Ti and V, but the V appeared to be free or to have very small content of Ti and Nb. Given the solubility product and kinetic of formation, the V based nanometric particles are more likely to precipitate in ferrite, while the nanometric Nb-rich carbonitrides could had nucleated in austenite [19].

The micrometric precipitates can be distinguished as follows: 1) Cuboidal and large polyhedral precipitates, Figure 2a. They are rich in Ti and have a length between 3μm and 10 μm, respectively. Additionally, the cuboidal precipitates are partially covered with a Nb-rich layer, as showed by the individual EDS analyses of points 1 and 2 in Figure 2b. 2) Dendritic precipitates. They are found in sizes of few micrometers and larger than 100 μm, in the form of plates, well-ramified and rounded, as displayed in figures 2c to e, respectively.
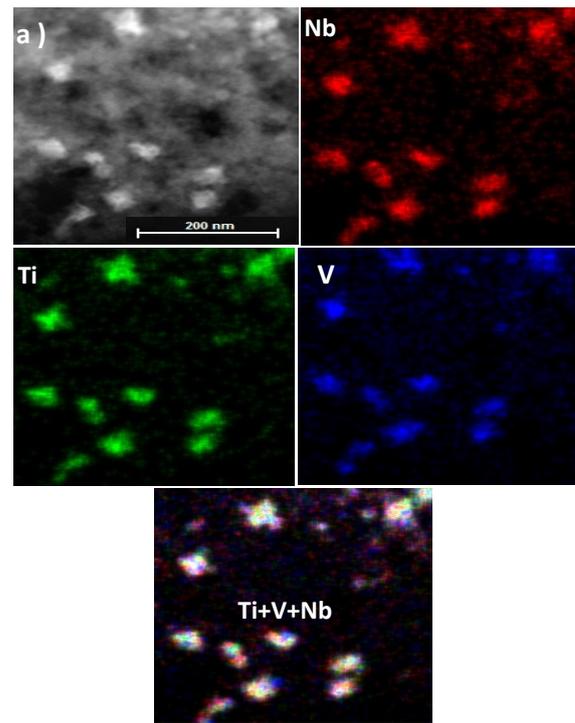
Figure 1. Nanometric precipitates in the as-cast steel with the individual mappings of Ti, Nb, V and the three elements superimposed.
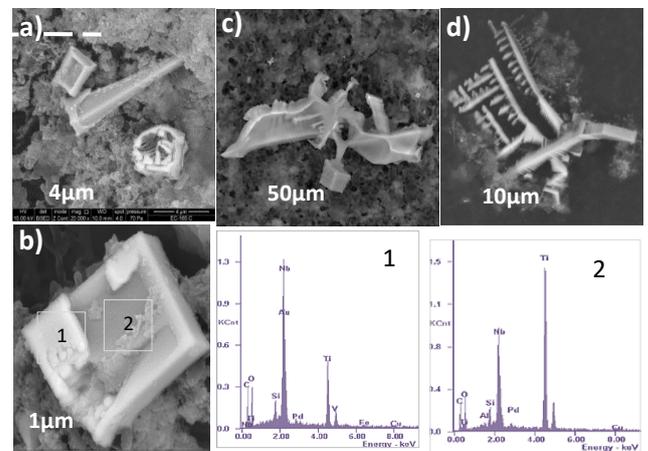
Figure 2. Micrometric precipitates in the as-cast steel. a) and b) Cuboidal and polyhedral shape precipitates respectively, with EDS spectrum in points 1 and 2 of image b. c), and d) Plate and ramified dendritic precipitates.

They could be classified in two types Ti-rich precipitates and Nb-rich precipitates, and both have vanadium dissolved in them, as shown in Figure 3. Given the brightness intensity of Ti in the elementary maps exhibited in Figure 3a, it is suggested that the primary and secondary arms of dendritic precipitates are

richer in titanium that the tertiary arms, that seems to be enriched in niobium. The mapping of elements in figures 3a and 3b suggests a greater affinity of vanadium for Ti- carbonitrides than for Nb-rich particles, result that has been attributed to the larger differences in lattice parameters of VC and NbC compared to that of TiC [20].
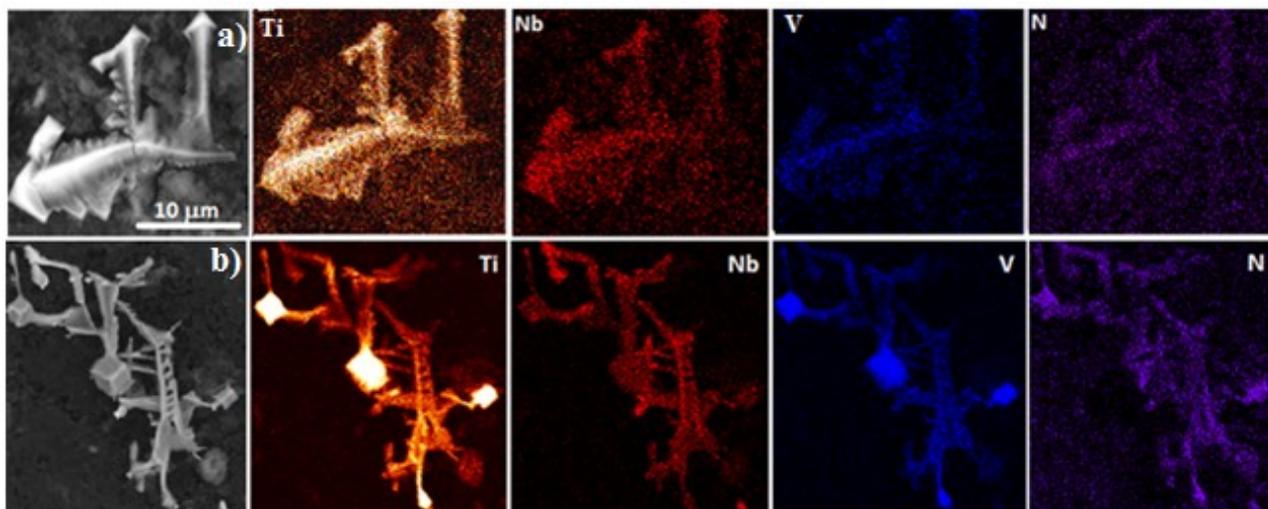
Figure 3. Mapping of Ti, Nb, V and N in dendritic precipitates in the as-cast condition.

Given the content of Ti and N in the microalloyed steel under study and considering the solubility product reported by Ken Inoue et al. [21], the TiN will be liquid at 1598°C and solid below this temperature. Therefore, it could be inferred that this phase nucleated in the molten iron during cooling. While the solidification advanced, a Nb-rich layer would form on pre-existing cuboidal precipitates, as observed by other researchers [1]. Furthermore, Nb-rich carbonitrides could form in the remaining liquid, between dendrites of δ- ferrite at the final stage of solidification, because of the strong segregation of Nb in the liquid, as suggested by C. Zhou [22]. Additionally, dendritic precipitates could grow from corner of cuboidal precipitates by interface instability, as shown in Figure 2b. In the solid state, particularly in the austenite phase, nanometric Nb-rich rounded and cruciform carbonitrides are more likely to form, while the V-rich particles nucleate in ferrite.

Dissolution process during re-heating

To investigate the dissolution behavior of carbonitrides, the residues extracted from the matrix of a quenched sample were analyzed after reheated at 1250°C for 30 min and 1300°C for 30 and 60 min. The evaluation was performed monitoring the changes in size, morphology, distribution and composition of carbonitrides with temperature and time. After heat treated at those conditions, the dendritic precipitates experimented partial dissolution, as showed in Figure 4. The incomplete reaction allows to follow the dissolution process, which starts preferentially at the periphery of secondary and tertiary arms rich in Nb, and at the skin rich in this element covering the core of Ti-rich primary arms. As observed in Figure 4a, the dissolution pattern in the sample heated at 1250°C for 30 min, displayed a row-like arrangement of carbonitrides at the early stage of dissolution. While the dissolution process continues, the rows of precipitates get fragmented in several parts, followed by spheroidization. The spherodized particles after reheating for 90 minutes at 1300°C are found in sizes ranging from 0,3 to 0,6 μm and present an aspect ratio between 1 and 1.5 (see Figure 5). They are rich in Nb as observed in the mapping of elements of Figure 6. This figure also shows that the Ti-rich precipitates in a plate-like and cuboidal morphologies, had a great degree of stability, remaining practically unaffected by the heat treatment. It is important to notice that V persisted associated to Ti-rich precipitates, even after

reheating at 1300°C for 90 min. Nb-based particles at 1300°C dissolve smaller amounts of vanadium. Therefore, the vanadium remains preferentially bound to Ti within the Ti-rich particles, making part of the cuboidal and plate like Ti-rich particles, forming a stable mono-phase at least up to 1300°C.
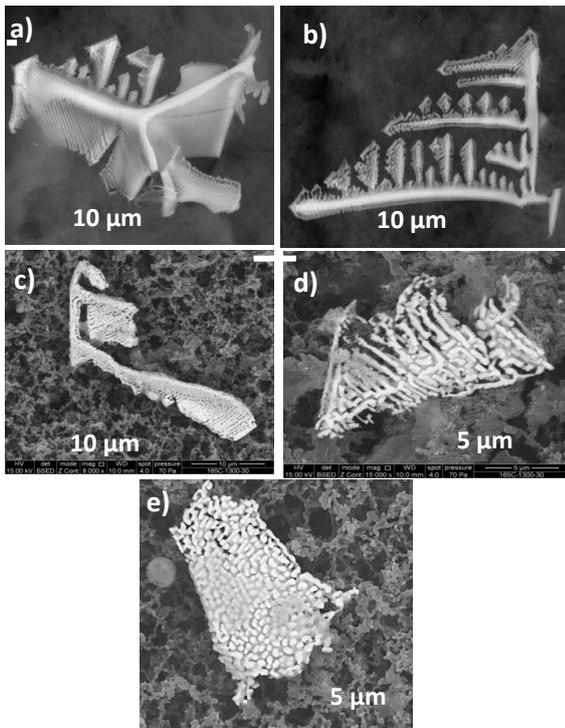
Figure 4. Dissolution process of particles during reheating. a y b) 1250°C-30 min. c y d) 1300°C -30 min. e) 1300°C-90 min.
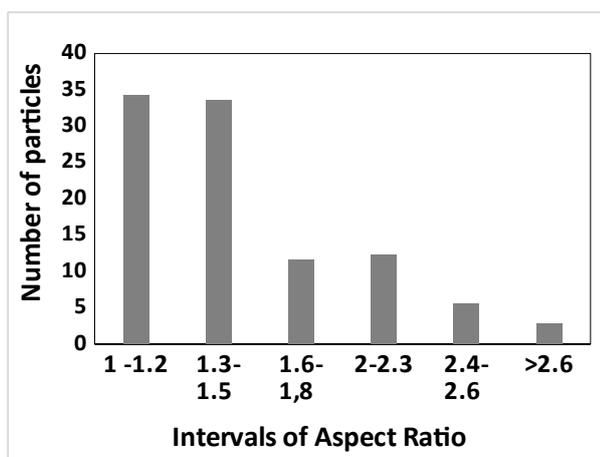
Figure 5. Aspect ratio ranges of spheroidized particles after heating at 1300 °C for 90 min.
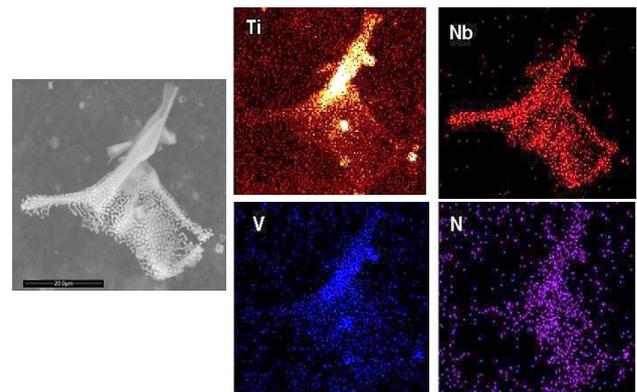
Figure 6. Mapping of Ti, Nb, V and N in dendritic pre cipitates observed during reheating 1300°C for 90 min

The results have shown that the reheating conditions used in this study do not warranty a complete dissolution of dendritic precipitates pre-existing in the as-cast material. Since the Nb-rich precipitates are the most likely to dissolve, while the Ti-rich based precipitates remain stable, the resulting microstructure is comprised of Ti-based precipitates almost unaffected by the reheating process, and isolated spheroids of Nb-rich particles formed by partial dissolution of dendritic precipitates. It is important to point out that in the steel heated at 1300°C for 90 min, vanadium remains soluble in the Ti-rich precipitate, but bounded in incipient amounts of Nb-rich particles. Other studies for example the one of Z. Chen et al.[3] in microalloyed steel with a composition of 0.082% C, 0.057 V, 0.039 %Nb, 0.019 Ti, and 0.0076 N, did not report the presence of Nb/rich precipitates at 1250°C, i.e. this phase had dissolved completely at this range of temperatures. Likewise, Nöhrer et al. [18] , who analyzed a steel with a composition of 0.2 wt% C, 0.041 wt% Nb , 0.11 wt%V, 0.018 wt% Ti and 0,013 wt% N, suggested a complete dissolution of Nb and V at temperatures of 1250°C. Regarding the presence of V in the Ti/based phase, I. I. Gorbachev et al. carried out a thermodynamic simulation study on carbonitrides formation in a Nb-V-Ti steel containing 0.1 wt % C, 0.007 wt % N and V in concentration of 0.1 and 0.05 wt %, which is very close to the composition of the steel under study. At 1100 and

1200°C they argued that Ti:N atomic ratio in steel is the main factor that influences the compositions of carbonitrides. The study also suggested that if Ti is below the content required to bound N in TiN based precipitates, it is possible to find Nb and V in large amounts in Ti-rich carbonitrides. This is the case of the present study, where the amount of Ti that can be bound to 0,064 N is 0.0219%, and the content of Ti in the steel is 0,016%. Moreover, considering the fraction of V, Nb and Ti in the microalloyed steel under investigation, at 1200°C, vanadium is expected to be within the Ti/based carbonitride, but not in the Nb/rich precipitates [23]. The first approach is in well-agreement with the founding in this study, detecting the presence of vanadium in Ti rich carbonitrides even at higher temperatures (1250 and 1300°C) than those used in the thermodynamic simulation, result also reported by others researches at temperatures of 1250°C [3]. Nevertheless, vanadium is also detected within the Nb-rich carbonitrides, contrary to expected by thermostability predictions [23]. According to the results obtained in this study, the stability of V and Nb in solid solution within Ti particles, was extended at temperatures greater than 1200°C. It could be stated then for the investigated steel, that Ti based (Ti, Nb, V) carbonitrides is a monophase stable at temperatures of 1300°C or even higher, evidencing a strong interaction of V and Nb with Ti. Consequently, it is highly feasible that the TiN formed in the first stage of solidification and that Nb and V dissolve within the precipitate during cooling, forming the Ti-rich (Ti, Nb, V) carbonitrides. Thus, a higher concentration of Ti in the steel supposes less V and Nb bounded to it in Ti-rich precipitates, and more V will be in the Nb-based carbonitrides, which is more likely to dissolve in austenite. The formation of these large Ti particles with V and Nb in their composition, is not convenient because they reduce the amount of Nb and V in solution for grain refinement and precipitation hardening.

Quantification of Nb in solution by ICP-OES

The dissolution of precipitates, expressed in terms of the niobium amount in solution, is shown in Table 2. In the as-cast condition most of the Nb is found in a precipitate form, remaining in solution around 10%. The results shown that after 30 min at 1300°C, near 70% of Nb has gone into solution, which is slightly affected by the soaking time at the same temperature at 90 min. The Nb in solution may be mainly provided by the dissolution of small particles rich in Nb, and by the incipient dissolution of large-dendritic precipitates. About 30% of Nb remains precipitated after reheating at 1300°C, which may be bounded to the large dendritic precipitates rich in Ti, which show great degree of stability. Therefore, the formation of this type of complex precipitates, limits the solubility of microalloy steels, including V, which is present within the Ti rich precipitates after heating at 1300°C, greater than the maximum reheating temperature typically used in industrial practice for this type of steel.

Table 2. Amount of Nb in precipitates before and after heat treatment.

Condition	Nb in solution (ppm)	Nb precipitated (ppm)
As-cast	47	488
1300°C-30 min	365	170
1300°C-90 min	375	160

CONCLUSIONS

The results obtained in the steel under study showed complex Nb-Ti-V carbonitrides, stable up to 1300ºC enriched in Nb or Ti. The microstructural analysis revealed an incomplete dissolution, during heating, of the Nb-rich as-cast precipitates, that only experiment partial changes in morphology, size and chemical composition. The increase in soaking time at 1300°C led to insignificant changes in the amount of Nb in solution, given the thermodynamically stability of the precipitates, limiting the availability of Nb and V for grain refinement and precipitation during hot rolling. Vanadium goes within both Ti as well Nb-rich

carbonitrides, at temperatures of 1300°C or even higher.

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