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Microanalysis of TiNb Carbonitrides in HSLA Steels

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Abstract. The microchemistry and morphology of Ti- and Nb-rich carbonitrides formed during continuous casting in some HSLA steels, differing only in their Nb content, have been investigated in order to characterize the effect of Nb on the nucleation and growth process of these particles. Precipitates were extracted using the carbon extraction replica technique and analyzed in a VG-HB 5 STEM by EDS. They exhibit large composition gradients and their morphology is roughly correlated to their size. A model based on the formalism of ternary solubility products in liquid iron and in austenite is developed to explain satisfactorily these composition gradients, and gives the composition of newly formed nuclei in austenite and that of the last deposited layer of precipitates. Nuclei appear as spherical particles, grow by interface instability to polyhedral particles, then to dendrites, with secondary protrusions developed from the primary arms also as a result of an interface instability process.

Dans des aciers faiblement alliés à haute limite élastique ne différant que par leur teneur en niobium et produits par coulée continue, on a analysé la morphologie et la composition des carbonitrides riches en Ti et Nb pour caractériser l'effet du niobium sur les processus de germination et de croissance de ces précipités. Les précipités sont prélevés dans des répliques d'extraction de carbone et analysés par spectrométrie à dispersion d'énergie dans un microscope électronique à balayage et à transmission VG-HB 5. Ils présentent d'importants gradients de composition et leur morphologie est reliée à leur taille. Un modèle fondé sur le formalisme des produits de solubilité ternaires dans le fer liquide et l'austénite a été développé de manière à rendre compte de ces gradients de composition, et fournit la composition des nouveaux germes produits dans l'austénite pendant le refroidissement ainsi que celle de la dernière couche des précipités. Les germes apparaissent sous forme arrondie, croissent selon un mécanisme d'instabilité d'interface; les précipités deviennent alors polyédriques puis dendritiques dont les bras secondaires proviennent également d'un processus de croissance avec instabilité d'interface.

Introduction

Optimization of the properties—i.e., weldability, toughness, and strength—of HSLA steels containing Ti and Nb can be achieved if the

influence of each alloying element, Ti and Nb, on the evolution of the microchemistry, morphology, and distribution of Ti- and Nb-rich carbonitrides during the processing of the steels is well understood. Additions of Ti to some HSLA steels produced by continuous casting were shown to modify a complex series of precipitation reactions that occur during the subsequent thermal history of the alloys and depend strongly on the initial as-cast microstructure [1, 2]. This initial stage is characterized by a fine distribution of Ti- and Nb-rich carbonitrides, as revealed by a STEM analysis, which exhibit various morphologies such as cuboids or dendrites and whose mean Ti/Nb concentration ratio and dimensions depend also on the nominal Ti content of the steel and increase with it. Consequently, investigations of the nucleation and growth mechanisms of such particles formed during continuous casting are important from a scientific and industrial viewpoint. For the already mentioned HSLA steels [2], two thermodynamic models deriving the volume fraction and composition of precipitates at the equilibrium for temperatures up to 1500°C were developed on the basis of the formalism of solubility products [3] and either (a) coprecipitation of binary compounds TiN, TiC, NbN, and NbC, i.e., without any mixing of the precipitating species; or (b) complete intersolubility of the precipitating compounds to give rise to mixed $Ti_xNb_{1-x}[C_yN_{1-y}]_v$ carbonitrides. These models contributed to explain satisfactorily the Ti, Nb, and N concentrations found in precipitates after continuous casting and various subsequent thermomechanical treatments.

The present communication is concerned with STEM investigations on the microchemistry and morphology of Ti- and Nb-rich precipitates formed during continuous casting in Ti- and Nb-bearing HSLA steels containing different nominal Nb contents. It reports the effects of Nb additions and cooling rates in the range 0.15–0.27 C°/sec on these precipitation reactions. Some evidence is given that dendritic growth of precipitates occurs in the solid state in this system.

Experimental Procedures

CASTING PRACTICE

Four steels containing different amounts of Nb and having the same basic composition were produced in the laboratory from electrolytic iron (Table I). Continuous casting was simulated in such a way that the cooling rates obtained were of the same order of magnitude as those currently realized in industrial practice. Casting of the steels was done into sand molds with iron chills on two opposing faces to allow different cooling rates throughout the slab thickness. The slabs have dimensions of 203 × 127 × 254 mm. Cooling rates of the order of 0.27 C°/sec at the surface

TABLE I
Chemical Analysis of the Steels (wt.%)

Steel designation	C	N	Ti	Nb	S	P	Si	Mn	Al	Mo
1	0.07	0.006	0.011	0.005	0.004	0.003	0.23	1.80	0.025	0.31
2	0.075	0.006	0.011	0.01	0.003	0.003	0.22	1.78	0.028	0.31
3	0.075	0.006	0.01	0.04	0.003	0.003	0.23	1.85	0.02	0.31
4	0.065	0.006	0.01	0.06	0.004	0.003	0.24	1.74	0.03	0.32

and 0.15 C°/sec at the ingot center, measured at the solidus temperature in the molds during solidification, were achieved.

SAMPLE PREPARATION FOR STEM ANALYSIS

In order to exhibit the influence of the cooling rate on precipitation mechanisms, two sets of carbon extraction replicas were prepared from each slab: one comprising replicas obtained from rapidly cooled samples taken from the slab surface; the second one constituting replicas prepared from slowly cooled samples coming from the ingot center.

The preparation of carbon extraction replicas was conventional. After mechanical polishing and a final operation using 1- μ m diamond paste, samples were etched in a 5% Nital solution to reveal the precipitate distribution. Carbon evaporation was carried out under 10^{-6} torr and the carbon films stripped off from etched surfaces in a 2% Nital solution under 5 V.

Microanalysis was performed with a vacuum generator HB 5-dedicated STEM equipped with a Tracor Northern TN 2000/4000 EDS x-ray system. X-ray spectra were interpreted using the assumption of the thin-film criterion and the Cliff-Lorimer ratio technique [4], for which the K_{TiNb} constant, relative to the Ti K series and Nb L series x-rays was previously determined to be 0.53 ± 0.06 [1]. Ti and Nb concentration gradients observed inside precipitates were studied with the finest electron spot size available, ~ 2 nm, under 100 kV.

Results and Discussion

MORPHOLOGY AND MICROCHEMISTRY OF Ti- AND Nb-RICH CARBONITRIDES

Although no quantitative assessment of the size distributions of precipitates was performed, the results indicate that the morphology of a precipitate depends roughly on its size, but not on the nominal Nb content

of the steel (Table 2). Small Ti- and Nb-rich carbonitride nuclei, $\varnothing < 20$ nm, when visible, look fairly spherical (Fig. 1a, n°1), suggesting that nucleation occurs in the solid state, and not only in liquid iron as might be expected [2]. Indeed, a cube-cube orientation relationship between the NbC and γ -Fe structures has been reported [5] that gives rise, in that system, to a spherical three-dimensional γ -plot of the interfacial energy γ between the NbC phase and austenite, and therefore to spherical NbC nuclei. This particular orientation relationship could also exist in the case of nuclei of Ti- and Nb-rich carbonitrides in austenite because Ti, Nb, and respectively C, N can be mutually intermixed in the same NaCl-type fcc structure [6]. This would justify the existence in these steels of nearly spherical nuclei enriched almost homogeneously in Ti and Nb. Because observed on replicas, these nuclei are likely to be formed late during the cooling in the lower part of the austenite temperature range, in which diffusion of the components Ti, Nb, C, and N in austenite becomes much slower, preventing growth of precipitates; the drastic change of composition between carbonitrides and the matrix, whatever the Nb content, requires long-range diffusion. If nucleation occurred only in liquid iron, nuclei possessing only faceted equilibrium shapes [7] would appear after cooling. However, these nuclei are not likely to be observed because of their very probable growth during cooling throughout the γ -Fe temperature range.

Larger diameter precipitates appear as polyhedral or cuboidal particles (Fig. 1a, n°2). This change of morphology may be caused by interface instability [8], and is characterized by the formation of edges on spherical nuclei when the particle diameter exceeds a critical value [9, 10], roughly 20 nm. Such perturbations on spherical particles are controlled either by surface diffusion at the interface, or volume diffusion in the matrix and/or the precipitate, into a matrix that becomes continuously supersaturated in Ti, Nb, C, and N during the cooling. No Fe or other residual elements were detected inside the precipitates analyzed, located in prior austenitic grains, so that the elimination of iron from growing particles may also

TABLE 2
Correlation between the Size and Morphology of Precipitates Formed during Cooling at 0.15 or 0.27 C°/s in Steels 1, 2, 3 and 4

Particle diameter	Morphology
<~20 nm	Roughly spherical particles (Fig. 1a, n°1)
~20~50 nm	Polyhedral or cuboidal particles (Fig. 1a, n°2)
~50~200 nm	Cuboidal, small dendritic (Fig. 1a, n°3), or angular particles
>200 nm	Dendritic or angular particles; dendritic particles exhibit often secondary protrusions developed from primary arms

FIG. 1. Morphology and composition gradients of particles formed in steels 1 to 4: (a) spherical (n°1), cuboidal (n°2), dendritic (n°3) precipitates in steel 4 cooled at 0.27 C°/s; (b) angular particles in steel 2 cooled at 0.27 C°/sec; (c) dendritic particle formed in steel 2 after cooling at 0.15 C°/sec; (d) dendritic precipitate in steel 4 cooled at 0.27 C°/sec; (e, f) composition gradients inside particles featured respectively in (c) and (d), where values indicate equi-Ti/Nb weight concentration ratios inside particles.

FIG. 1. (continued)

FIG. 1. (continued)

represent a factor that alters the growth process, for instance by modifying surface diffusion.

Subsequent growth of cuboidal particles takes place at corners, which represent points of very small radius curvature on the surface of precipitates. This phenomenon has been studied theoretically in the case of liquid-solid [11] and solid-solid [9, 10] interfaces, but is rarely observed [12]. The extension of corners generates a dendritic morphology of precipitates (Fig. 1a, n°3). Minimization of the total elastic strain energy of the matrix and the precipitate [7, 10], associated with the growth of a spike at a corner in γ -Fe, may be responsible for the unsymmetrical

growth of spikes and so-called angular-shaped particles (Fig. 1b). Simultaneous with the extension of these primary spikes, secondary protrusions develop by interface instability [8, 9]. Sinusoidal perturbations are generated along primary spikes and accompany their lateral growth, giving the precipitates the aspect of solidification dendrites (Figs. 1c and 1d). Except for very small particles of fairly homogeneous Ti and Nb concentration, all the particles analyzed exhibit steep concentration gradients of Ti and Nb. These variations, over a few nanometers or even less, are frequently observed (a) at the corners of polyhedral particles; (b) around the centers of particles in dendritic or angular particles; (c) along the primary arms in dendritic or angular particles; and (d) on the edges of secondary protrusions of dendritic particles. The existence of such gradients inside precipitates shows that the volume diffusion rate of the constitutive species (Ti and Nb) is very slow inside carbonitrides, even in the γ -Fe temperature range. This very low diffusivity can be considered to be the result from the fact that the particles possess a very high melting point [13]. Maps indicating the Ti/Nb weight-concentration ratio inside two dendritic precipitates are given in Figs. 1e and 1f. Ti and Nb x-ray peak intensities, serving as a basis for calculating ratios, correspond to average concentration values relative to Ti and Nb atoms contained in the volume irradiated by the incident electron beam, which has a 2 nm spot size. The beam-broadening effect and the absorption corrections do not strongly modify these values so these maps can be considered to represent fairly well longitudinal sections of the three-dimensional variations of the Ti/Nb ratio inside particles.

The variation of the Ti/Nb ratio from the center of some precipitates toward their extremities is reported in Table 3. The precipitates are classified according to their morphology for each steel and cooling rate, where c, a, d indicate, respectively, cuboidal, angular, and dendritic particles. For each morphology, the first value represents the Ti/Nb ratio in the center of the particle, the third one at the extremity exhibiting the highest composition change, and the second one in an intermediate region of the particle. For each type of morphology, steel, and cooling rate, several particles were analyzed in detail. The composition gradients listed in Table 3 are representative of the major part of precipitates in the class of particles considered.

The results indicate that steel 1 behaves differently from steels 2, 3, and 4, which contain increasingly more Nb. Indeed, the precipitates formed in steel 1 present a Nb-enrichment in their external parts and extremities, whereas there is a Ti-enrichment of the outer layers of precipitates found in steels 2, 3 and 4. Moreover, in these three steels, some precipitates exhibit Ti-enriched regions at their center and extremities

TABLE 3
Evolution of the Ti/Nb Weight Concentration Ratio Inside
Some Particles Formed in Steels 1 to 4, at Cooling Rates 0.15
and 0.27 C°/s

Steel designation	0.15 C°/sec	0.27 C°/sec
1	c: 15< <30 a: no d: 13.5-11-10	c: 15< <30 a: no d: no
2	c: no a: 0.47-0.61-0.89 d: 1.08-0.70-0.44	c: no a: 1.48-0.70-1.27 d: 0.35-0.30-0.57
3	c: 0.10-0.30-0.49 a: — d: 0.17-0.17-0.33	c: 0.10-0.30-0.50 a: — d: 0.14-0.10-0.32
4	c: 0.11-0.15-0.21 a: 0.11-0.13-0.16 d: 0.15-0.16-0.18	c: 0.08-0.15-0.20 a: 0.09-0.11-0.16 d: 0.30-0.25-0.50

no = Not observed on replicas; c = cuboidal particle; a = angular particle; d = dendritic particle. First value is center of the particle; second value is intermediate position; third value is extremity exhibiting the highest composition change.

with an intermediate region depleted in Ti (Table 3, Fig. 1f). This Ti-depleted zone can be observed in large precipitates, $\varnothing > 0.2 \mu\text{m}$ (i.e., essentially angular and dendritic particles), while smaller particles possess only a Ti-enrichment of their external layers and no Ti-rich center.

Additions of Nb to these steels increases the average niobium content of precipitates for when the nominal Nb content goes from 0.005 (steel 1) to 0.06% (steel 4), the average Ti/Nb ratio decreases continuously from 30 to 0.1. Slightly enhancing the cooling rate from 0.15 to 0.27 C°/sec does not seem to modify the Ti and Nb concentration variations inside particles but does increase the distribution of particles of smaller diameter. This is expected because growth of particles is diffusion-controlled and a slower cooling rate allows more diffusion to take place.

Because Ti- and Nb-rich nuclei look homogeneous in composition and microdiffraction on polyhedral, angular, dendritic particles does not indicate any change in their crystalline structure, the precipitates can be considered as mixed monocrystalline Ti- and Nb-rich carbonitrides and

not an aggregation of several binary precipitates (TiN, TiC, NbN and NbC) formed by heterogeneous nucleation during the cooling.

MODELING OF THE SEQUENCE OF PRECIPITATION

To describe the sequence of precipitation that occurred in these steels during cooling, a model based on the coprecipitation of the binary compounds TiC, TiN, NbC, and NbN was used to calculate the mole fractions of precipitates at the equilibrium in austenite versus temperature, in the range 700–1400°C [2]. Though equilibrium is probably not reached during the cooling, mole fractions deduced from this model are supposed to be those that would, effectively, be found during continuous casting. Calculations were performed under the following assumptions: (a) zero-mixing of the precipitating compounds TiC, TiN, and NbN in liquid iron or solid iron (austenite); (b) each precipitating compound maintains unit activity; (c) each precipitating compound has perfect stoichiometry; (d) concentrations of solutes in liquid iron and austenite are given by their ternary solubility products [3] once precipitation begins; (e) equilibrium is maintained in austenite throughout the cooling. The results are shown in Fig. 2.

It appears that no precipitation occurs in liquid iron. Precipitation starts in each steel at ~1370°C, with the nucleation of titanium nitrides in aus-

FIG. 2. Predicted mole fractions of precipitated carbonitrides as a function of temperature in steels 1 to 4.

tenite. This first stage is followed in steel 1 by the precipitation of TiC and NbC, and by that of NbC and then TiC in steels 2, 3, and 4. This inversion is responsible for the complete difference between the composition gradients internal to precipitates found in steel 1 and those exhibited by particles formed in the three other steels. To explain this using the above model, particles, which appear as mixed Ti- and Nb-rich carbonitrides, should be considered as composed of the infinitely small-sized binary compounds TiN, TiC, and NbC taken in the right proportion, homogeneously distributed, with no mixing between them. In this extent, the model, dealing only with binary compounds, can be extended to mixed carbonitrides homogeneous in composition and may be used to provide an evaluation of the composition of nuclei formed at a certain temperature T in austenite and also of the composition of the last layer deposited at T on a growing precipitate, thus allowing the prediction of composition gradients inside precipitates.

If x , y , z , t , and $\delta T/\delta t$ designate, respectively, the mole fractions of TiN, TiC, NbC, time, and cooling rate, the slight increase in the precipitation that occurs at T in austenite, caused by the decrease δT in the temperature during δt , is characterized by a Nb/Ti ratio that can be expressed as: $r = \delta z/(\delta x + \delta y)$, where δx , δy , δz , as functions of T , are the respective increases in the TiN, TiC, NbC mole fractions during δt . This increase in the precipitation corresponds either to the formation of Ti-Nb-rich nuclei by homogeneous nucleation in austenite or to the deposition of a Ti-Nb-rich layer on already-formed particles, whose composition (homogeneous), in terms of the Nb/Ti ratio, is given in both cases by the ratio r . The evolution of this ratio r , being calculated for δt -intervals all equal to 60 sec, or more precisely $r/1 + r$, is reported in Fig. 3 versus time from 1370°C ($t = 0$), for a cooling rate of 0.15 C°/s and the Nb contents corresponding to steels 1 to 4.

This description of precipitation in terms of r variations agrees fairly well with the results listed in Table 3. In steel 1, r increases late at the bottom part of the γ -Fe temperature range, which explains why precipitates nucleated early during the cooling possess Nb-rich outer regions and Ti-rich centers. In steels 2, 3, and 4, particles nucleated in phase 1 present a Ti-rich center ($r = 0$) followed by Nb-rich layers (r max) and finally a reenrichment of Ti on the external layers (r diminishing); however, when nucleated in phase 2, their centers are enriched in Nb (r max) and their outer layers exhibit some Ti-enrichment (r decreasing). The duration of phase 2 in steels 2, 3, and 4, during which precipitation of Nb is predominant (r max), is the longer the higher the Nb content of the steel, which causes the increase in the average Nb content of particles with the nominal Nb content of the steel.

FIG. 3. Evolution of the ratio r , the Nb/Ti weight concentration ratio, with time during the cooling of steels 1 to 4 at a rate of 0.15 °C/sec.

MORPHOLOGY INSTABILITY

A more detailed analysis of the nucleus size at which instability occurs and of the wavelength of the sinusoidal perturbations occurring on primary arms of dendritic particles will be presented in a future paper. Results will be compared to existing models [14].

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