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Atom Probe Tomography I. Early Stages of Precipitation of NbC and NbN in Ferritic Steels**

By F. Danoix, E. Bémont, P. Maugis and D. Blavette

The results reported in this paper give new information regarding the early stages of precipitation in model low niobium steels. It clearly appears that the kinetic paths for carbides and nitrides precipitation in the investigated model alloys are very different, more continuous in the case of carbides, and through GP zones formation in the case of nitrides.

1. Introduction: The Early Stages of Phase Separation

Materials of industrial interest frequently derive their mechanical performance from the presence of a hardening second phase. Among the most important questions, the phase composition is a key parameter because it controls the lattice misfit and the volume fraction of the hardening phase. Identification of the decomposition regime (nucleation and growth versus spinodal decomposition) and the precipitation kinetic pathway (existence of cascade of metastabilities, clustering, metastable phases) is of utmost importance not only for academic reasons but also because it is crucial for the optimisation of materials through the control of microstructure. Because the early stages of phase separation take place at the nanometer scale, limited experimental investigation related to this field have been reported so far.

Among the relevant techniques for observation and microanalysis at the nanometer scale, Atom Probe Tomography (APT) has several unique possibilities, as the only 3D quantitative analytical microscope with an atomic resolution. The Tomographic Atom Probe (TAP,^[1]), developed in France in the early nineties, allows to map out chemical species within the small volume that is analysed ($10 \times 10 \times 100 \text{ nm}^3$) in three dimensions, with a resolution of a few tenth of cubic nanometer. The depth resolution of one single atomic layer, makes it possible to image chemical ordering.^[2] Segregation to crystal defects can also be evidenced. 3D reconstruction of Cottrell atmospheres in boron doped FeAl intermetallics at the atomic-scale is one of the best illustrations of the instrument potential.^[3]

This paper reports the contribution of Atom Probe Tomography in the investigation of the early stages of precipitation of carbides and nitrides in model ferritic steels. These researches were conducted in collaboration with ARCELOR in the framework of the joined program "CPR Precipitation (2001–2006)".

2. The Precipitation of NbC in Model FeNbC Steels

The enhanced mechanical properties of high strength low alloy (HSLA) steels are achieved by a fine dispersion of very

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small and stable carbides, nitrides and carbonitrides precipitating from Nb, Ti and V microalloyed steels.^[4] This paper is focussed on low carbon steels containing niobium. Nb is one of the most frequently added microalloying elements because of its strong effect on microstructure and mechanical properties of steels.^[5-8] In sheet steels, niobium addition is known to refine the austenite grain size during hot rolling through the retardation of austenite recrystallisation. In addition, NbC precipitation in ferrite during coiling and/or annealing induces a structural strengthening of the matrix.

The early stages of precipitation of NbC carbides at 600 °C in a model HSLA steel (composition given in Tab. 1) were studied. Note that these alloys cannot be considered as nitrogen free, but rather as low nitrogen steels as compared to higher nitrogen steel studied, as reported in the third section of this paper, and in which niobium and niobium carbonitrides precipitate.

NbC carbides have the NaCl structure. NaCl-type carbides are known to adopt the Baker-Nutting orientation relation in ferrite,^[9,10] defined as following :

$$(100)_{\text{bcc}} // (100)_{\text{fcc}} \text{ and } [011]_{\text{bcc}} // [010]_{\text{fcc}}.$$

The lattice parameters of the bcc ferrite and the fcc NbC (NaCl type) phases are respectively 0.286 and 0.447 nm. The misfit that exists between the two phases is around 40% in the direction perpendicular to the (001) habit plane and around 10% in the direction parallel to the habit plane. Such a high misfit raises the question whether the carbides can precipitate directly as semicoherent precipitates or form via a cascade of metastabilities, that is the formation of solute clusters and/or transient metastable precipitates that have a composition and a structure different from that of the stoichiometric equilibrium phase NbC. The role of clusters in the homogeneous intragranular nucleation of a second phase have been recently discussed by J.F. Nie et al.^[11]

Thomson assumes that the NbC phase appears by means of intermediate metastable phases.^[12] Following these authors, the precipitation would proceed through the formation of transient carbides. On the other hand, Khatchaturyan and De Ardo both suggest that a nucleation of coherent NbC carbides is possible if precipitates adopt a thin disk-like shape.^[10,13,14]

The model steel (composition in Tab. 1) was melt and heat treated by Arcelor Research SA (research group of Arcelor group). Steels were heat treated in an horizontal furnace in vacuum-fastened glass tubes at 1523 K for 5 min and then water-quenched. This austenitizing treatment is shown to dissolve all the precipitates formed during hot rolling and then to give rise to random solid solution.^[15] The heat-treated sam-

ples were then aged for 5, 10 and 30 mins at 600 °C and finally water-quenched. Samples were stored at low temperatures (liquid nitrogen, 77 K) in order to prevent diffusion of interstitial atoms (carbon and nitrogen). Specimen stored at room temperature were shown to be susceptible to unmixing.

Atom-probe investigations of samples aged 5 min at 600 °C showed that carbon and niobium atoms segregate first in the form of isostructural diffuse atmospheres, 1 or 2 nm in diameter (Fig. 1). These atmospheres contain a majority of iron atoms (60–80 at.%) and around 2.8 times more carbon than niobium. The formation of these atmospheres can be understood by the C-Nb short range attraction and by the higher mobility of carbon interstitial atoms compared to niobium (that migrate through a vacancy exchange mechanism).^[15]

For longer ageing times (10 mn), diffuse atmospheres similar to those observed after 5 mins ageing still exist, and are found to enrich in niobium with ageing time, so as to reach an average atomic ratio C/Nb close to 1. Concurrently, the iron concentration decreases. In addition, iron containing (Nb,Fe)C particles were found to co exist with the atmospheres at this ageing time. The amount of iron in these particles was close to 30 at.%. 3D images did not exhibit anymore the continuity of atomic planes through these particles, suggesting their incoherence with the *a* solid solution: carbides have a distinct crystallography compared to that of the *a* parent phase. These iron-bearing particles were interpreted as metastable (Nb,Fe)C carbides. The presence of iron in these transient carbides is thought to ease the nucleation by lowering the lattice misfit, leading to a reduction of the nucleation barrier.

For longer ageing times (30 min), atmospheres were no more detected. Carbides get richer in solutes (Nb, C) and poorer in iron (Fig. 2). Most of the carbides examined after 30 mn at 600 °C were found to have a composition close to that of the expected NbC equilibrium phase.^[16] The iron level in the core of the particle analysed in Figure 2 is below 10 at.%.

These results suggest that the precipitation of the very high misfit incoherent NbC phase (misfit of 40% perpendicular to the (001) habit plane) in low nitrogen ferritic steels is not direct, but proceeds through a complex kinetic path, nota-

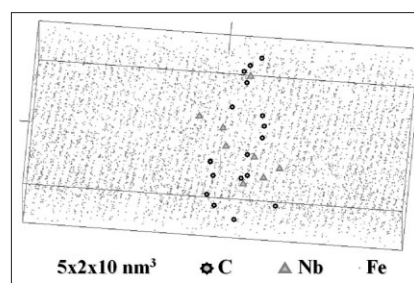


Fig. 1. 3D reconstruction of a small volume in the ferrite of the FeNbC alloys (aged 5 min at 600 °C) showing the presence of a diffuse atmosphere that is enriched in carbon. (011) planes of the ferrite are not disturbed by the presence of this atmosphere, showing that this is an isostructural atmosphere and not a nucleus of the NbC equilibrium phase.

Table 1. Composition of the low nitrogen model steel (at.%).

Element	Nb	C	N
Concentration (at. %)	0.0471	0.0380	0.0024

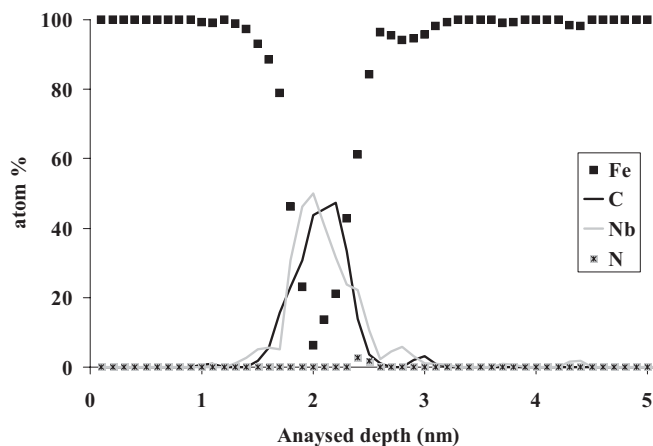


Fig. 2. Concentration profile through a small carbide (< 2 nm). The iron concentration in the core of the particle is less than 10 at.% (30 min at 600 °C).

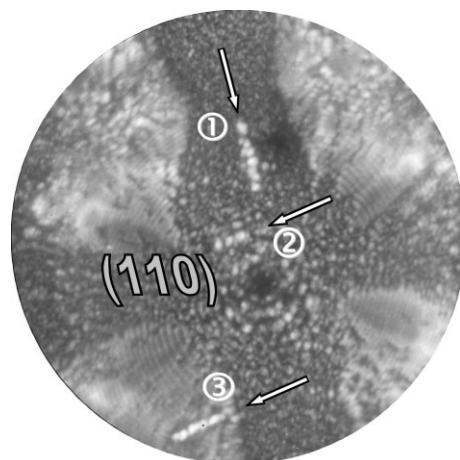


Fig. 3. (110) oriented field ion micrograph showing three alignments of bright spots, associated with the plate shaped precipitates.

bly the formation of isostructural diffuse atmospheres, which are gradually replaced by an iron-containing (Fe;Nb)C metastable phase, which in turn enriches in solutes and finally transforms into the expected NbC equilibrium phase.

3. The Precipitation Pathway in Nitrogen Containing Steels FeNbCN

A heat with a higher nitrogen content was also studied. Its composition is given Table 2. The interstitial (C + N) content approximately balances the substitutional niobium content, initially planned to favour carbo-nitrides precipitation.

High resolution electron microscopy of specimen aged 5 min at 650 °C revealed, in addition to carbo nitrides, the presence of plate shaped precipitates, lying in the {100} planes of the parent ferrite matrix.^[17] These platelets were shown to be monoatomic in thickness. Specimens were investigated by Field Ion Microscopy and Atom Probe Tomography.

During field evaporation in the field ion microscope, lines of brightly imaging spots were observed, as shown Figure 3.

The presented field ion micrograph has been obtained under a specific operation mode of the field ion microscope. In classical operation, field ion micrographs are recorded when the surface is stable with respect to field evaporation, i.e. evaporation of surface atoms is prevented by reducing the applied electric field. Under these conditions, atomic resolution at the specimen surface can be achieved, but only a few bright spots can be imaged for each individual alignment. In the present case, the field ion micrograph was recorded

during field evaporation of the specimen. According to Miller et al., the obtained micrographs can be referred as evapographs.^[18] The number of bright spot is then cumulated, and makes these latter much easier to observe. The counterpart is that atomic resolution is lost. Three alignments of bright spots are clearly revealed.

It should be remembered that the field ion micrograph is an image of the hemispherical cap of the specimen apex. Therefore, the micrograph must be interpreted as a curved 2D interception of 3D features present in the observed specimen. In this framework, the bright spots alignments can be interpreted, consistently with the HREM observations, as the trace of {100} oriented platelets, emerging at the specimen surface.

Information related to the relative orientation of the platelets can also be derived from the orientation of the bright spots lines, but must be interpreted with care in terms of projection and interception. Three variants of {100} platelets exist, perpendicular to each others. If intercepted along one common habit direction, two different variants can lead to parallel traces, and be misinterpreted as belonging to the same variant. This may be in particular the case for platelets 2 and 3, and only 3D investigation could elucidate this point. Conversely, if the trace are perpendicular, this unambiguously indicates that they belong to different variants. Platelets 1 and 2 on one hand, and 1 and 3 on the other hand are perpendicular, and thus belong to different variants.

Therefore, the presented field ion micrograph confirms the hypothesis of planar platelets as revealed by HREM, showing, on the same micrograph, at least two different orientational variants. The combination of HREM and FIM proves the existence of planar GP zones in this 'high' nitrogen model steel.

Concerning the thickness of these platelets, HREM gives good indication that they must be monoatomic. Additional field ion microscopy investigations reported elsewhere also confirms this result.^[19] At last, preliminary investigation by Atom Probe Tomography indicate that these zones are close

Table 2. Composition of the 'high' nitrogen model steel (at.%).

Element	Nb	C	N
Concentration (at. %)	0.0493	0.0274	0.0255

to the stoichiometry NbN.^[20] It is not clear yet how much iron substitutes to niobium, but a clear indication is that carbon is virtually absent from these zones. They can therefore not be regarded as a transient phase in the precipitation sequence of carbon nitrides, as for the previously described carbon and niobium atmospheres. TEM examination of the same material after prolonged ageing time shows the presence of a NaCl structure based niobium nitrides.^[20] The NbN platelets can possibly be regarded as the precursors of this NbN cubic phase.

The NbN platelets have the same morphology as the so called GP zones in the AlCu system (one or few Cu rich planes in the Al matrix). It is therefore tempting to build a parallel between both types of precipitates, and refer the NbN platelets as GP zones. If a general definition of GP zones is 'isostructural metastable inclusions in the parent matrix', then the NbN platelets are most likely to be of this nature, at least concerning the substitutional element Nb. Indeed, as shown by HREM, the platelets are fully coherent with the ferritic matrix. In addition, as the platelets have a well defined composition, and are shown to disappear after longer isothermal holding times at 650 °C, they can be regarded as metastable. Therefore, the observed platelets will be referred as GP zones, in agreement with the published literature in the field of nitriding of steels.

4. Comparison of the Precipitation Sequences

The results reported in this paper give new information regarding the early stages of precipitation in model low niobium steels. Two different type of precipitation sequences have been observed.

In the case of the low nitrogen alloy, precipitation of carbides is observed for prolonged ageing time at 600 °C. In the early stages of phase transformation ($t = 5$ min), isostructural diffuse atmospheres of niobium and carbon are formed, with a high carbon to niobium ratio (average of about 2.8). This ratio is thought to be due to the much higher mobility of carbon atoms compared to niobium. When ageing proceeds, these diffuse atmospheres get richer in solute elements, and the carbon over niobium ratio tends towards unity. Concurrently, the solute enriched zones reject the remaining iron, so as to reach the equilibrium NbC phase. The existence of a metastable iron containing carbide, with C/Nb = 1.2 is suspected.

In the case of the high nitrogen alloy, in addition to the described sequence leading to the NbC phase, monoatomic in thickness NbN platelets are observed. No precursor in the form of niobium and nitrogen (i.e. carbon free) diffuse atmosphere was observed. The transition from platelets to equilibrium NbN has not been investigated so far, and it is not known whether the platelets will act as nuclei for this latter. A more detailed description of the platelets, in particular atomic arrangements of niobium and nitrogen is necessary for this purpose, and is currently under investigation. A likely assumption is that niobium and nitrogen atoms adopt in

the platelets an atomic configuration close to the one in the equilibrium NaCl based NbN phase.^[20] Platelets could therefore act as nuclei for the NbN phase. Experimental evidences have not yet obtained to sustain this hypothesis.

5. Conclusion

It clearly appears that the kinetic paths for carbides and nitrides precipitation in the investigated model alloys are very different, more continuous in the case of carbides, and through GP zones formation in the case of nitrides.

Ab initio studies are planned to study the stability and energetic characteristics of the different intermediate steps observed by Atom Probe Tomography.

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