University of Groningen

TEM study of Ti-N and Cr-N precipitate formation in iron alloys

Chechenin, N.G.; Bronsveld, Paulus; Chezan, A.R; Craus, C.B.; Boerma, D.O; De Hosson, J.T.M.; Niesen, L

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

[Link to publication in University of Groningen/UMCG research database](#)

TEM Study of Ti–N and Cr–N Precipitate Formation in Iron Alloys

N. G. Chechenin[1]), P. M. Bronsveld, A. Chezan, C. B. Craus, D. O. Boerma, J. Th. M. de Hosson, and L. Niesen

Materials Science Center, University of Groningen, Nijenborgh 4, NL 9747 AG Groningen, The Netherlands

The formation of precipitates of Ti and Cr nitrides in cold-rolled Fe + Ni(4at%) Ti(2at%) and Fe + Ni(4at%) + Cr(3at%) after a pre-nitriding step was investigated by Mössbauer spectroscopy (MS) and transmission electron microscopy (TEM). From MS data we conclude that initially most of the Ti and Cr were atomically dispersed. Using TEM and high-resolution TEM (HRTEM), we found that the Baker-Nutting (B-N) orientation relationship (OR) holds for platelets one to two interatomic distances thick, producing streaking around the (200) reflections, while for thicker precipitates the Nishiyama-Wasserman (N-W) OR is more favorable. We also observed a transient phase, Cr_2N, the formation of which was possible due to the relatively low nitriding temperature, a low nitriding potential, and the presence of Cr inclusions of relatively large initial size.

1. Introduction

The formation of nitrides in iron is an issue with a long history. A suitable nitriding process should lead to increased corrosion resistance and hardness in industrial applications. Unfortunately, the instability of the Fe–N system becomes a crucial factor at high applied temperatures, where the pores filled with gaseous N_2 cause difficulties in applications. The problem may be avoided by using a low temperature during nitriding [1]. Alloying elements, like Ni, may enhance the formability of the nitrided iron. Precipitates of alloying element nitrides, formed in the diffusion layer of the iron matrix, also can significantly improve the properties of iron alloys [2, 3]. For example, indentation hardness can be increased several times by nitriding iron alloys, containing Ti [4, 3, 5], Cr [3, 6], V, Al and some other elements [4].

Relevant questions are: whether or not the precipitates formed are coherent with the matrix and, if so, what is the orientational relationship (OR), what is the equilibrium shape and size of the precipitates, what kind of plastic and elastic deformations of the matrix are required to nucleate and coarsen the precipitates, etc. Most of these issues have been studied before in the above-mentioned references [2 to 6] and also by the groups of Jack [7] and Mittemeijer [8].

For f.c.c. precipitates in a b.c.c.-matrix the most familiar OR are the ones due to Bain [9], Nishiyama-Wasserman (N-W) [10, 11], and Kurdjumov-Sachs (K-S) [12]. Interconnection between these OR is described in depth in [13] and also in a number of books

---

[1]) Corresponding author: e-mail: ngch@phys.rug.nl

Also at Institute of Nuclear Physics, Moscow State University, 119899 Moscow, Russia.

(see, e.g. [14]). The last two relationships are based on the idea that closest-packed planes in each phase should be parallel to each other. Related to the f.c.c.-precipitate formation in a b.c.c.-matrix they imply that (111)f.c.c. is parallel to (110)b.c.c. and this is written as: for N-W: (110)b.c.c. // (111)f.c.c., [001]b.c.c. // [$\bar{1}$01]f.c.c.; and for K-S: (110)b.c.c. // (111)f.c.c., [1$\bar{1}$1]b.c.c. // [0$\bar{1}\bar{1}$]f.c.c. For the case of CrN and TiN precipitates, the Bain OR holds: (001)b.c.c. // (001)f.c.c., [100]b.c.c. // [110]f.c.c. which sometimes is called after Baker and Nutting (B-N) [15]. Following the B-N OR, a strained coherence between the α-Fe matrix and precipitates is possible with (001) habit plane, but not in the transverse [001] direction. That determines the disc shape of the precipitate. According to [7], the thickness of the TiN platelets is about 0.4 nm.

The objectives of this study are: development of hard and formable Fe–N-based dilute alloys for industrial applications with small additions of alloying elements, and a study of the formation of precipitates of Ti and Cr nitrides in α-Fe. We investigate the properties of the precipitates, i.e. their size, shape, coherence of the interphase boundary, in order to use this information for optimization of further nitriding steps where these precipitates may serve as nuclei for the growth of iron nitride phases.

2. Specimen Preparation

Slices of bulk Fe + Ni(4at%) + Ti(2at%) and Fe + Ni(4at%) + Cr(3at%) materials were cold-rolled to 2 to 4 μm thick foils, which were nitrided afterwards during ≈1 h at a temperature in the range 450 to 500 °C in a NH_3 + H_2 mixture of 1 atm and at a nitriding potential ln (r_N) = ln $[p(NH_3)/p(H_2)^{3/2}]$ ≈ −7.0, where the pressures of ammonia, $p(NH_3)$, and hydrogen, $p(H_2)$, are in Pa. The nitriding potential corresponds to the α-region of the Fe–N Lehrer phase diagram [16, 17], so that no formation of Fe nitrides is expected. We call this process "pre-nitriding".

Before inspection in TEM, the samples were thinned by two-beam ion milling until a small hole was formed. In most cases, the samples were exposed to air only about 10 min, which is short enough to avoid any significant surface oxidation. For the study, CTEM JEM 200CX and HRTEM JEM 4000 EX/II electron microscopes were used with electron beam energies of 200 and 400 keV, respectively.

3. Results

3.1 Mössbauer spectra

Figure 1 shows the evolution of the MS spectra upon nitriding the FeNiTi samples. Before nitriding an extra component in the spectra due to Fe atoms with a nearest, or a next nearest Ti atom neighbor, can be observed, with a relative intensity corresponding to the amount of Ti dissolved, Fig. 1a. Based on this dependence, our estimates indicate that a major fraction of Ti and Cr was atomically dispersed in the Fe-matrix of as-rolled foils. We note that Ni atoms reduce just slightly the hyperfine field in the Fe-matrix and broaden the Fe-sextets in MS spectra, but do not produce a well-defined extra component [18]. During pre-nitriding at temperatures around 400 to 450 °C the Ti neighbor satellite is replaced by a broader component with a different shift, Fig. 1b. We tentatively associate this component with the formation of isolated TiN molecules. After annealing at temperatures around 700 °C the formation of TiN precipitates can be observed by the disappearance of the extra component, Fig. 1c. Similar results were obtained for FeNiCr samples.
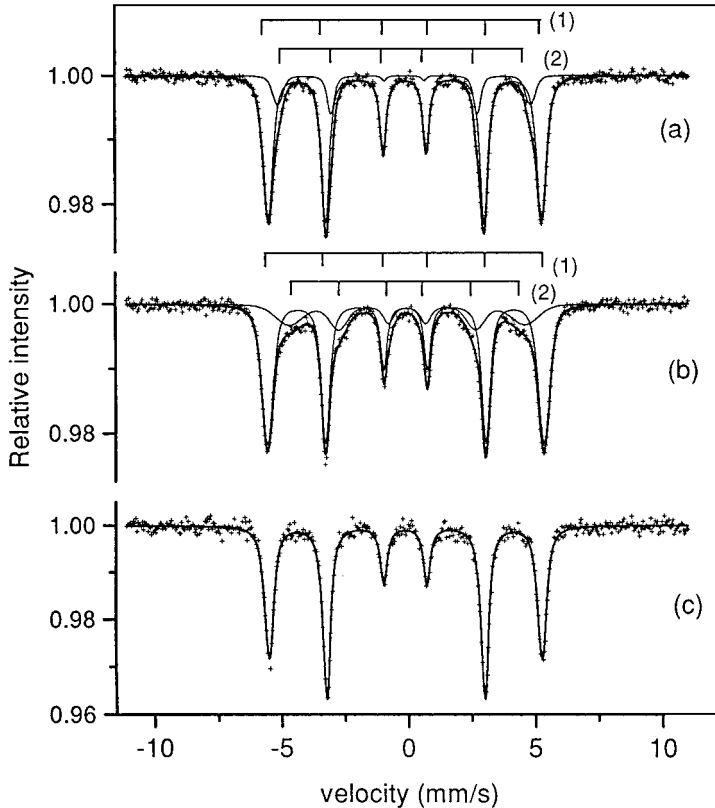
Fig. 1. MS spectra of FeNiTi foils: a) as-rolled; b) pre-nitrided at 400 °C, 1 h, $\ln(r_N) = \ln[p(NH_3)/p(H_2)^{3/2}] = -7.34$; c) 700 °C, 2 h, in pure H_2. The lines are fitted deconvolutions of experimental data, showing the main contribution due to pure iron plus substitutional Ni atoms (deep curves) and an additional contribution of nonmagnetic Ti neighbors (shallow curves). The peak positions of the matrix (1) and second (2) components are indicated

In this way MS allows to follow the development of nitrides on a molecular level. The TEM technique gives insight in structures on a scale from Ångstroms to μm.

3.2 TEM observations. As-rolled materials

Typically, as-rolled FeNiTi and FeNiCr foils show a relatively homogeneous distribution of "dot"-like particles with a size below 1 nm, except for some areas with a somewhat larger size of 2 to 4 nm. These "dots" could be associated either with defects or with microprecipitates. We do not expect Ni to precipitate because of its high solubility in Fe. The electron diffraction shows, in general, a regular b.c.c. α-Fe pattern, as is illustrated in Fig. 2 for the [001]-zone, where some superspots are also visible. These extra spots correspond to kinematically prohibited {100} reflections and could be associated with dynamical diffraction in a distorted b.c.c. lattice. This distortion can be caused both by a large amount of defects induced by the cold rolling and by incorporation of substitutional Ni and/or Cr atoms into the matrix. The [001] matrix orientation is in good correspondence with XRD results, which reveal a strong texture in the foils. In TEM,
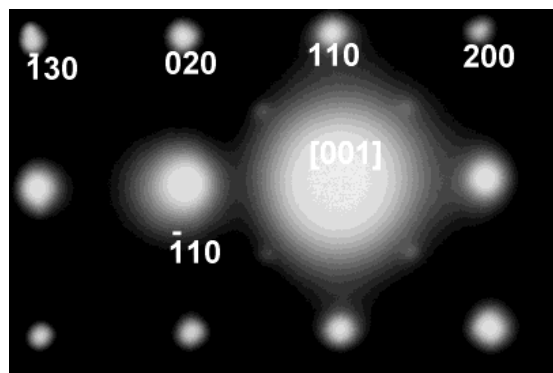
9*

Fig. 2. FeNiCr (as-rolled). The SAD shows regular pattern for the [001] zone of b.c.c. α-Fe with and kinematically forbidden {100} extra spots

however, ⟨011⟩ and ⟨111⟩-oriented crystallites were also observed frequently. The reason of this over-representation of the other grain orientations may be due to a higher sputtering rate during the ion beam milling of the samples for grains with a (001) plane parallel to the surface. In some selected area diffraction (SAD) pictures for FeNiTi samples weak reflections of small hexagonal Ti crystallites were observed, indicating the presence of precipitates of relatively large (more than several nm) sizes. We did not observe such reflections for Ni, nor for Cr precipitates, though we note that it could be difficult to detect reflections from small Cr crystallites, even if present, because of the small difference in parameters of the b.c.c. lattices of Cr and α-Fe.

3.3 Precipitate formation in pre-nitriding

After pre-nitriding of FeNiTi foils, homogeneously dispersed particles of small size (below 4 nm) were predominant. In selected areas, like those shown in Fig. 3a, large clusters up to 40 nm were sometimes visible. The interior of these clusters was not homogeneous, but consisted of a dense composition of smaller particles of nm size.

On the background of the [001]-zone pattern of α-Fe a number of extra spots are seen in Fig. 3b. The spots S5 and azimuthal arcs around them belong to {110} reflections of small grains of the α-Fe-phase. The streaking of the (200)-type of matrix spots points to the presence of thin platelets perpendicular to the streaking direction in reciprocal space. Thus, these platelets are oriented in accordance with the Baker-Nutting coherence relationship $(010)_{b.c.c.}$ // $(010)_{f.c.c.}$, $[001]_{b.c.c.}$ // $[011]_{f.c.c.}$, which has been found for thin platelets of f.c.c. TiN precipitates by Phillips [4], Jack [7] and other groups. This epitaxial relationship is schematically illustrated as a [010] view on the α-Fe/TiN interface in Fig. 3c. In the plane of precipitate the mismatch is small enough: $\varepsilon = (d_{f.c.c.(110)} - d_{b.c.c.(100)})/d_{b.c.c.(100)} = (0.300 - 0.287)/0.287 = 0.045$, whereas perpendicular to the habit plane the mismatch is about 33%. Such a mismatch favors the formation of thin platelets. The length of the streaks is inversely proportional to the thickness of the precipitate platelets, and since the length of the streaks is about half the reciprocal lattice spacing, the thickness of the platelets can be estimated as being of $(0.5/d_{200})^{-1} \approx 0.3$ nm.

Two contributions in Fig. 3b come from TiN particles of a larger size. Spots S1 correspond to (200)TiN reflections. These spots deviate by about 9° to 10° from $\mathbf{g}_{020}$. Spots S2 are (111) reflections of TiN and do not point directly to a specific OR. Satellites S4
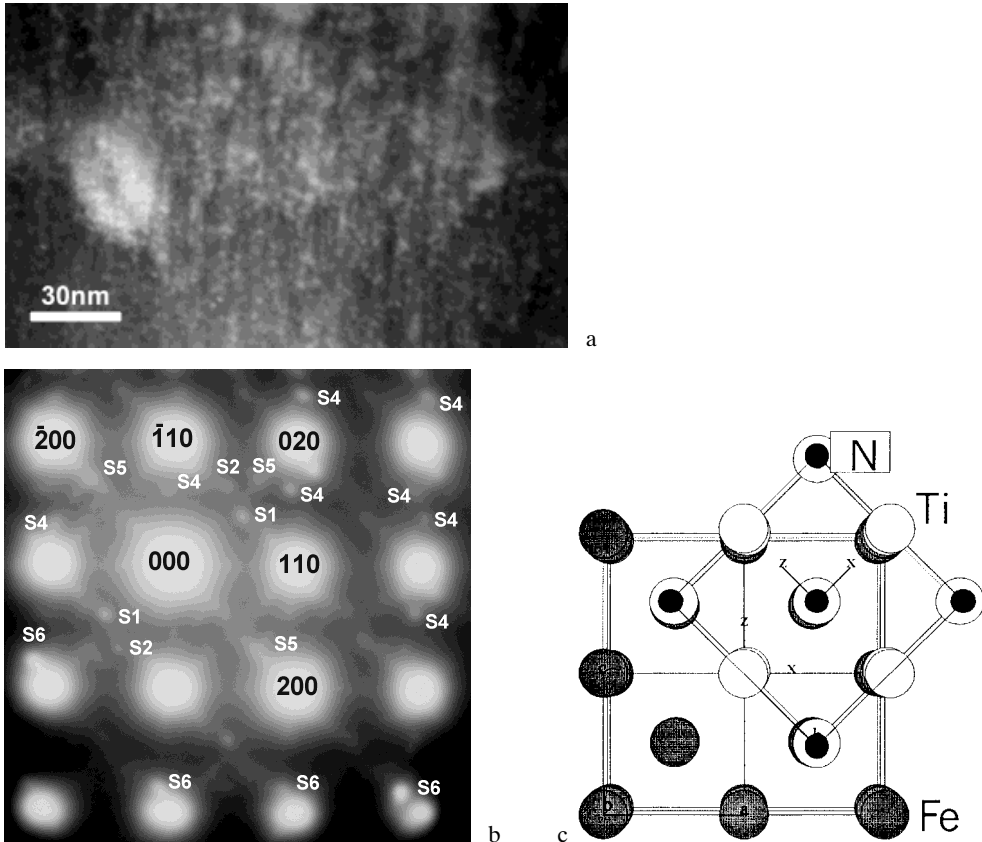
Fig. 3. FeNiTi foil pre-nitrided under the conditions of Fig. 1. Selected area DF image of TEM with a rare ≈40 nm cluster of precipitates. SAD pattern showing the [001] matrix pole with some admixture of grains of smaller size, which give speckles S5 and arcs on the {110} ring. TiN precipitates show up in streaking of the (200)α-Fe spots, in (200)TiN (S1) and (111)TiN (S2) spots. The satellites S4 and S6 may correspond to double diffraction. c) Schematic [010] view on the α-Fe/TiN interface

and S6 may correspond to periodic elastic deformations of the matrix due to the presence of precipitates, as will be discussed in Section 4.

Similar to the case of FeNiTi, in FeNiCr we saw, in general, a homogeneous distribution of small "dot"-like precipitates, but in some selected areas we observed an enhanced concentration of larger (up to ≈5 nm) size precipitates, similar to those shown in Fig. 4a. The SAD pattern, Fig. 4b, showed streaks which extend almost through the whole first primitive reciprocal cell, indicating the presence of CrN platelets with a thickness of one or two interplanar distances. The platelets are oriented parallel to the {010} plane as predicted by the B-N OR which has been reported in [6] for CrN in Fe. The misfit parameters for f.c.c. CrN and b.c.c. α-Fe lattices are very similar to those of TiN, therefore, CrN also tends to form platelets in b.c.c. α-Fe. There are also reflections, which correspond to larger CrN precipitates. A couple of {111} CrN spots is seen in Fig. 4b nearby $\{1\bar{1}0\}$ and $\{\bar{1}10\}$ matrix spots, indicating the correspondence with the N-W OR for a b.c.c./f.c.c. interface: $(110)_{b.c.c.}$ // $(111)_{f.c.c.}$, $[001]_{b.c.c.}$ // $[\bar{1}01]_{f.c.c.}$, or K-S
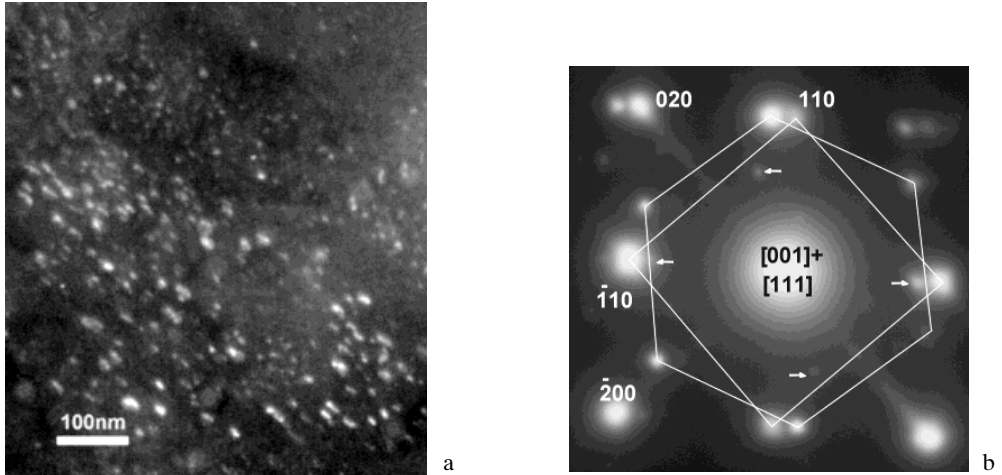
Fig. 4. Pre-nitrided FeNiCr. a) Dark field image. b) SAD pattern with [001]-zone + admixture of [111]-zone. The indexing is given for the [001]-zone pattern. Large streaks through the first primitive reciprocal cell indicate the presence of platelets of CrN precipitates, one to two interatomic distances thick, with their wide side parallel to the (010)-plane. The arrows show the reflections of CrN precipitates of a larger size, which give also double diffraction spots seen nearby the (020) type of matrix spots

OR: $(110)_{b.c.c.}$ // $(111)_{f.c.c.}$, $[1\bar{1}1]_{b.c.c.}$ // $[0\bar{1}1]_{f.c.c.}$. Further study by HRTEM evidence that the N-W OR seems to be more favorable. Another set of {200} TiN spots is seen close to a middle of the distance to (110) matrix reflection, deviating by about 10° from the direction to the (110) spot for the [111]-zone grain.

In the [001] HRTEM image of the FeNiCr pre-nitrided sample, we observed an f.c.c. CrN precipitate, incorporated into the b.c.c.-matrix on a low-angle intergrain boundary the approximate position of which is indicated in Fig. 5 by the line. The in-plane size of the inclusion is about 1.5×6 nm^2. Though a lack of ideal flatness of the film and/or defects prevent the ideal atomic resolution allover the image, one can still clearly see that the regular square-like arrangement of {110} fringes outside the precipitate is substituted by a hexagonal arrangement of {111} fringes inside the particle. The matrix $(\bar{1}10)$ plane fringes in this image are coherently transformed into (111)-plane fringes of CrN, and since the [001]-direction of α-Fe is kept parallel to the [011]-axis of CrN, it is linked to the Nishiyama-Wasserman orientational relationship.

The SAD pattern in Fig. 6 shows faint reflections, indexed in the Miller-Bravais h.c.p. notation, which were identified as being due to Cr_2N inclusions. In [6] this phase was considered as a transient nonequilibrium phase, with a larger Gibbs free energy than CrN. Indeed, in most published works [4, 6, 7] CrN particles have been reported and no visible Cr_2N phase. But in [6], it was shown that at low temperatures where kinetics slows down the nitriding processes, for small nitriding times and for relatively large concentrations of Cr, the transient phase could be present. Possible factors, enhancing the probability of formation of low-N Cr–N precipitates in our case, are short nitriding times, relatively low temperatures and the presence of relatively large inclusions of Cr in the as-rolled material. Although our SAD patterns, as mentioned before, did not provide evidence for such inclusions in as-rolled foils, be-
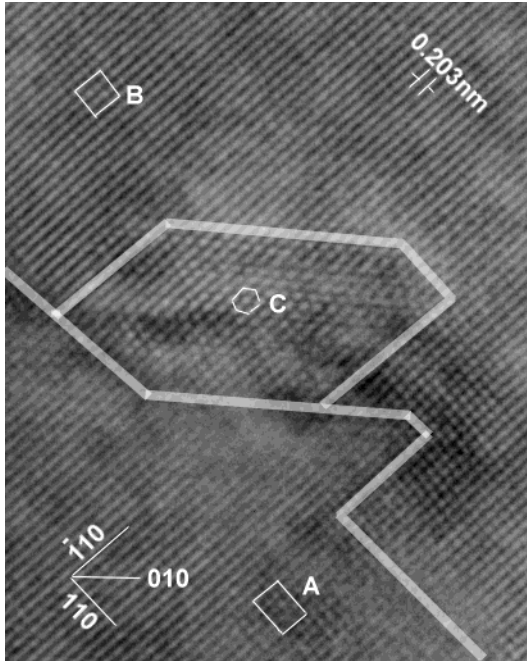
Fig. 5 Pre-nitrided FeNiCr. HRTEM image showing an f.c.c. CrN platelet in a b.c.c.-matrix on a low-angle grain boundary. The square-like arrangement of the (110) fringes of the matrix (regions A and B) is coherently transformed into hexagonal arrangements of (111)-plane fringes of CrN. The [001]-direction of α-Fe is parallel to [011]-axis of CrN

cause of the small difference in lattice parameters of the b.c.c. Cr and b.c.c. Fe, some of the relatively large particles, observed in both, bright and dark field, e.g. see Fig. 4a, may be related to these Cr clusters. Since the Cr crystals do not show up in XRD scans, their size is limited by nm scale and their fraction is low compared to atomically dispersed Cr.

4. Discussion

Two types of orientational relationship were found to be operative for f.c.c. TiN and CrN precipitates in α-Fe. For one to two monolayer thick precipitates, which give streaking in (200)-type reflections, the OR of Baker and Nutting [15] works, in accordance with previous findings. But for larger precipitates we observe a preferred orientation, following the OR of Nishiyama and Wasserman [10,11]. The reason for that can be understood if we take into account a large ($\approx$30%) precipitate/matrix misfit in the

direction perpendicular to the (100) habit plane in the B-N type of coherence. E.g. for TiN/α-Fe the angle between (111)TiN and (110) α-Fe should be equal to $9.74°$. The observation of a 9° to 10° shift of S1 spots with respect to $\mathbf{g}_{020}$ in Fig. 3b indicates that the (111)TiN rotation
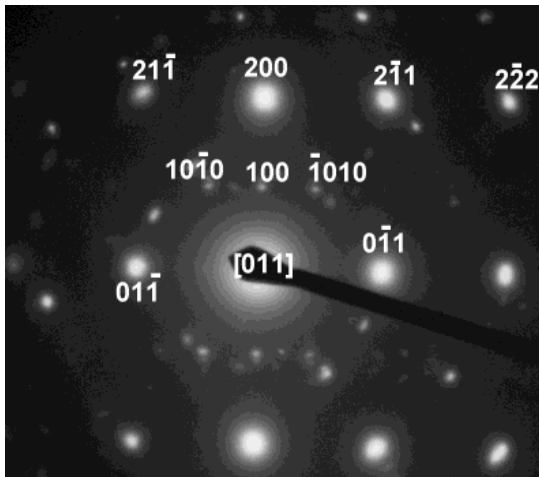

Fig. 6. Pre-nitrided FeNiCr. Besides the [011]-zone α-Fe matrix, SAD shows faint reflections, indexed in h.c.p. notation, which were identified as patterns of Cr_2N. Also reflections from smaller matrix grains are present

around the [011]-pole does take place. Further evidence for the N-W OR is obtained from a HR pattern, Fig. 5, where one set of matrix (110)-type fringes is coherently transformed into a parallel set of precipitate (111)-fringes. In this case the mismatch in the interplanar distances $\varepsilon_{1/1} = (0.245 - 0.203)/0.203 \approx 0.2$. Evidently, the mismatch will be negligible for every four (111)TiN and five (110)α-Fe planes: $\varepsilon_{4/5} = ((4/5) 0.245 - 0.203)/0.203 \approx -0.0345$. Similarly, every second (111)TiN plane will fall around a middle of interplanar space between (110)α-Fe matrix. The S4 satellites in Fig. 3b deviate by $|\Delta\mathbf{g}_{S4}| = 1/0.51$ nm^{-1} which may be associated with double diffraction on a periodically deformed matrix with periodicity of half the minimum mismatch of the 4-to-5 superstructure. In the region of a dense population of TiN inclusions, as shown in Figs. 3a and 4a, such a correspondence may cause a periodic deformation of the matrix, modulated with a period, equal to a multiple of half the distance of minimum mismatch between (111)TiN and (110) α-Fe which is about of 0.5 nm, as follows from above. The periodic deformation of a matrix by precipitates has been observed in the past (see, e.g. [19]), however, this issue requires further investigation.

Cr and Ti differ in solubility in α-Fe and in affinity to nitrogen. A limited solubility of Ti favors clustering and variation of concentration of Ti along the sample, which we observed in EDAX measurements. It is also in correlation with TEM results reported here, in particular, with the formation of relatively large TiN precipitates, discussed in Section 3.3. Due to the rather high solubility of Cr, it could be reasonable to expect no clustering of metallic Cr in as-rolled material. Nevertheless, we have presented indications that these Cr inclusions exist. One of them is the presence of reflections, though weak, of CrN and Cr$_2$N, discussed in Section 3.3. These reflections can be formed by relatively large inclusions, which can hardly grow for the time and temperatures of nitriding in our studies. Nevertheless, most of the Cr and Ti content was atomically dispersed. Even if we estimate the content of Cr in the precipitates, for example, basing on Fig. 4a, and taking the light spots as due to large CrN particles, we still obtain a small fraction of only 1%. This is in correspondence with the results of MS spectra (Section 3.1), from which we estimate that the content of atomically dispersed Cr is close to the total concentration of Cr.

5. Conclusions

The formation of precipitates of Ti and Cr nitrides after pre-nitriding of cold-rolled FeNiTi and FeNiCr alloys was studied using Mössbauer spectroscopy and transmission electron microscopy. Initially, most of the Ti and Cr were found to be atomically dispersed. During pre-nitriding they form semicoherent plate-like precipitates with thicknesses of one or two {100}-interplanar distances. Some fraction of Ti and Cr forms larger precipitates, which give TiN and CrN f.c.c. reflections. We associate these larger precipitates with metallic clusters in as-rolled material. The metallic Cr clusters form during pre-nitriding the intermediate metastable Cr$_2$N-phase.

It was found that thin platelet precipitates follow the Baker-Nutting epitaxial relationship, while larger TiN and CrN particles grow with Nishiyama-Wasserman orientational relationship.

References

[1] D. K. Inia, M. H. Pröpper, W. M. Arnoldbik, A. M. Vredenberg, and D. O. Boerma, Appl. Phys. Lett. **70** , 1245 (1997).
[2] D. S.Rickerby, S. Henderson, A. Henry, and K. H. Jack, Acta Metall. **34**, 1687 (1986).
[3] D. S.Rickerby and A. Henry, Acta Metall. **34**, 1911 (1986).
[4] V. A. Phillips and A. U. Seybolt, Trans. AIME **24**, 2416 (1968).
[5] M. Ronay, Met. Trans. **12A**, 1951 (1981).
[6] B. Mortimer, P. Grieveson, and K. H. Jack, Scand. J. Metals **1**, 203 (1972).
[7] D. H. Jack, Acta Metall. **24**, 137 (1976).
[8] M. A. Somers, R. M. Lankreijer, and E. J. Mittemeijer, Phil. Mag. A **59**, 353 (1989).
[9] E. C. Bain, Trans. AIME **70**, 25 (1924).
[10] Z. Nishijama, Sci.Rep. Res. Inst. Tôhoku Univ. **23**, 638 (1934).
[11] G. Wassermann, Arch. Eisenhütt. **16**, 647 (1933).
[12] G. Kurdjumov and G. Sachs, Z. Phys. **64**, 325 (1930).
[13] U. Dahmen, Acta Metall. **30**, 64 (1982).
[14] D. A. Porter and K. E. Easterling, Phase Transformation in Metals and Alloys, Chapman & Hall, London 1992 (p. 514).
[15] Cited in [6] as R.G. Baker and J. Nutting, Precipitation Process in Steels, I.S.I. Special report, No. 64 (1959).
[16] E. Lehrer, Z. Electrochem. **30**, 383 (1930).
[17] E. H. du Marchie van Voorthuysen, B. Feddes, N. G. Chechenin, D. K. Inia, A. M. Vredenberg, and D. O. Boerma, phys. stat. sol. (a) **177**, 127 (2000).
[18] W. E. Sauer and R. J. Reynik, J. Appl. Phys. **42**, 1604 (1971).
[19] V. Daniel and H. Lipson, Proc. Roy. Soc. A **181**, 368 (1942).