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Co-existence of γ'_N phase and γ_N phases on nitrided austenitic Fe-Cr-Ni alloys- I. Experiment

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ABSTRACT

The formation of a metastable and nitrogen-supersaturated f.c.c. interstitial solid solution layer on Fe-Cr-Ni austenitic stainless steel at a moderate temperature around 650-720 K is not entirely understood. In the present work, three groups of austenitic Fe-Cr-Ni alloys, containing systematic variations of chromium, nickel and iron contents were nitrided by plasma-based low-energy ion implantation at 653 K for 4 h and investigated with light-optical microscopy (LOM), electron probe microanalysis (EPMA), (grazing incidence) X-ray diffraction (XRD) and transmission electron microscopy (TEM). Commercial AISI 304L was included for comparison. For the austenitic alloys with a Cr content below 12 wt. %, a duplex layer is observed in the nitrided case where the interface between the top layer, consisting of γ' -Fe₄N like ordered γ'_N , and the disordered γ_N (nitrogen enriched austenite) zone underneath is associated with a decrease in N content. For the alloys with a Cr-content over 12 wt. %, a featureless continuous zone is observed with LOM and a gradual decrease in nitrogen content is measured with EPMA. Nevertheless, a similar duplex structure of outer γ' -Fe₄N like ordered γ'_N and inner γ_N is confirmed by XRD and TEM for all nitrided alloys, irrespective of the Cr content. The results are discussed in terms of the short-range order (SRO) promoted by the Cr-N interaction and long-range order (LRO) caused by the Fe-N interaction.

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1. Introduction

The supersaturated interstitial solid solution of nitrogen (or carbon) in austenitic stainless steel developing in the surface region during low temperature nitriding (or carburizing) is preferably referred to as expanded austenite, shortly γ_N (or γ_C). It is characterized as a metastable, precipitate-free and super hard phase that forms by dissolving a large amount of nitrogen in the octahedral interstices of Fe-Cr-Ni austenitic stainless steel, which thermodynamically tends to develop CrN. The applicability of expanded austenite relies on the combination of excellent wear resistance and excellent localized (pitting or crevice) corrosion performance. Dissolution of nitrogen into austenitic stainless steel is usually achieved by plasma nitriding [1-4], nitrogen ion beam implantation [5-8], plasma immersion ion implantation [9-11] or gaseous nitriding in an ammonia-based atmosphere [12], in the temperature range 650-720 K. At the atomic scale the structure of the nitrogen-modified surface zone is mainly reported as: i) a disordered nitrogen-supersaturated solid solution, wherein the N atoms are “trapped” by Cr atoms in octahedral interstices, thus forming a short-range ordered distribution [13-17]; ii) a zone containing both Cr-N short-range order and Fe₄N-like long-range order of nitrogen atoms [18,19]; iii) a mixture of the stoichiometric nitrides γ' -Me₄N and/or ϵ -Me₂₋₃N phases, in a disordered high nitrogen solid solution, and even the nano-scale CrN precipitates dispersed in an expanded Fe₄N-like long-range ordered phase [2,20,21].

On the basis of X-ray diffraction (XRD) analysis, which does not show superlattice reflections, expanded austenite has been concluded to be a solid solution of nitrogen in an f.c.c. lattice without LRO among the nitrogen atoms [13-15]. Using transmission electron microscopy (TEM) with selected area diffraction, Lei and Zhu [22,23] observed that there is no other LRO arrangement, but only f.c.c. spots in the nitrided zone. Bell [16] summarized that the relatively strong affinity of Cr atoms to N atoms is responsible for the large solubility of nitrogen and short-range ordering of Cr and N. Parascandola et al. [24,25] proposed a trapping-detrapping model assuming that each Cr atom traps one N atom during the nitrogen diffusion process, thus assuming Cr-N short-range ordering. The assumption was consistent

with a trapping-detrapping model for diffusion which provided nitrogen concentration-depth profiles. Oddershede et al. [17] proved the occurrence of Cr-N short-range order in nitrogen-stabilized expanded austenite by an extended X-ray absorption fine structure (EXAFS) investigation that showed local distortions around Cr atoms and the N coordination of Cr atoms.

Ichii et al. [18] were the first to suggest the Fe_4N -type crystal structure of expanded austenite on the basis of a similarity of the f.c.c. structure and the occurrence of ferromagnetism; however no superlattice reflections were detected by XRD. Hannula et al. [19] observed a weak Fe_4N -like superlattice spot on the selected area diffraction in TEM observations, and regarded the supersaturated austenite as an expanded γ' - Fe_4N phase. Xu et al. [26] detected an ordered structure at the surface and a disordered structure at the subsurface on the nitrogen-modified layer by TEM, proposing that the nitrified surface consists of a supersaturated nitrogen solid solution containing γ' - Fe_4N -type arrangement with additional short-range order of Cr-N pairs the γ'_N phase, and the subsurface consists of the γ_N phase as the supersaturated γ -type solid solution with only short-range order of Cr-N pairs. Jiang and Meletis [27], and Stroz and Psoda [28], respectively, observed the γ' - Fe_4N -like ordered arrangement by high-resolution TEM, and the former marked the antiphase domains of N ordered arrangement. Brink et al. [12,29] reported a transition phase γ_T with a composition consistent with the stoichiometry M_4N during decomposition of the high-nitrogen γ_N phase. Apparently, the stoichiometric M_4N is thermodynamically favored over expanded austenite with short-range order of the N atoms at high nitrogen content. Recently, Brink, et al. found XRD super-lattice reflections associated with LRO of nitrogen in paramagnetic homogeneous expanded austenite at a high nitrogen occupancy¹, $y_\text{N} = 0.55$ [12].

A first proposal that N-supersaturated austenite can be conceived as a mixture of γ' - Fe_4N -like nitride and CrN-free N-saturated austenite was reported by Zhang and Bell [2]. On the basis of results obtained by deconvolution of XRD and conversion electron

¹ Nitrogen occupancy refers to the degree of occupied octahedral interstices, which for an f.c.c. lattice is equivalent to the number of nitrogen atoms per metal atom.

Mossbauer spectroscopy (CEMS), Gontijo et al. [20] concluded that expanded austenite is constituted of γ' -Fe₄N, and ϵ -Fe₂₋₃N phases and nitrogen-saturated austenite with different contents of nitrogen. Martinavičius et al. [21] showed on the basis of field ion microscopy and atom probe tomography that the nitrogen-supersaturated austenite zone can contain nano-scale CrN precipitates dispersed in a nitrogen-saturated austenite matrix even though the structure appeared single phase in an XRD investigation. A similar result was also obtained by Oddershede et al. [30], who observed that the presence of GP-zone like CrN precipitates were present in expanded austenite powder as detected by EXAFS, while the expanded austenite is inhomogeneous and contained CrN precipitates detectable by XRD. In subsequent work of Oddershede et al. [17] on a homogeneous expanded austenite powder, no evidence was found for the presence of mixed Cr-N clusters or CrN platelets in a short-range ordered arrangement around Cr atoms.

In the present work, the isostructural evolution of the nitrogen-supersaturated cases, formed by plasma-based low-energy nitrogen ion implantation at 653 K, on three groups of Fe-Cr-Ni austenitic alloys with systematic variations of the chromium, nickel and iron content were investigated, to elucidate the composition and crystallography of the nitrogen-stabilized expanded austenite layer in dependence of the alloying element contents. The influence of the alloy composition on the evolution of ordered and disordered distributions of nitrogen in supersaturated expanded austenite is discussed. AISI 304L was included as a reference material.

2. Experimental

Fe-Cr-Ni alloys were prepared from 99.999 wt. % nickel, 99.995 wt. % iron and 99.950 wt. % chromium using a vacuum arc furnace. A total quantity of 15 g of each of the alloys was prepared. The ingots were vacuum-sealed in a quartz tube and solutionized at 1423 K for 24 h and subsequently quenched into water. The solutionized ingots were cold-pressed to about 3 mm thickness, followed by annealing at 1373 K for 2 h in an Ar atmosphere and quenched in water. The weighed target compositions of the twenty alloys are listed in the Table 1 (cf. Fig. 1). The key point *k* is an alloy with Cr and Ni contents close to those of AISI

304 and AISI 316 austenitic stainless steels. In the group *lk*, the Fe content is basically maintained at about 70 wt. %, and the series is located parallel to the austenite to martensite transformation line in the Schaeffler diagram, while the Cr content changes from 0 to 17.66 wt. % by 3 wt. % increments. In the group *lm*, the Ni content is kept at 27 wt. %, and the Cr content changes from 0 to 17.66 wt. % at 3 wt. % increments and is balanced by a reduction of the Fe content. In the group *km*, the Cr content is constant and the Ni content changes from 12.67 to 27 wt. % and is balanced by a reduction of the Fe content. As alloys *l*, *lm1* and *lk1* are not fully austenitic after cooling, two more alloy compositions, alloys *lx* (essentially this is Invar) and alloy *lx1* were prepared. The Ni contents in these alloys are higher than for alloys *l*, *lm1* and *lk1* and, accordingly, the alloys are fully austenitic.

The final ingots were polished before nitriding. Commercial austenitic stainless steel AISI 304L with composition (in wt. %) C 0.020, Si 0.43, Mn 1.04, Cr 18.11, Ni 8.14, N 0.06, P 0.031, S 0.020, and Fe as the balance was included in the series of investigations. Introduction of nitrogen into the alloys was realized in a plasma-based low-energy nitrogen ion implantation device, using an electron cyclotron resonance (ECR) microwave plasma source, which is described elsewhere [31]. The specimens were biased with a pulsed negative potential of -2 kV at a process temperature of 653 K, which was regulated by an auxiliary heater. The total implanted dose of nitrogen ions follows from the average ion current density of 0.8 mA/cm² over a period of 4 h.

Cross sections of the nitrided specimens were prepared by standard metallographical preparation methods and the microstructure was revealed by etching in Marble's reagent, consisting of 10 g Cu₂SO₄ in 50 ml HCl (12mol/l) and 50 ml H₂O. Light-optical microscopy of the nitrided cases was performed using an OLYMPUS LEXT OLS4000 Laser Confocal Microscope. Nitrogen concentration-depth profiles were measured to a depth of 10 μm using a SHIMADZU EPMA1600, Quantification of the N contents was performed using BN as a reference. X-ray diffractometry for phase analysis was performed using CuKα radiation on a PANalytical Empyrean diffractometer for a symmetrical diffraction geometry at a speed of 4 °/min with a step size of 0.04°. Grazing incidence XRD (GI-XRD) was performed on a Bruker AXS D8 Discover XRD System for an incidence angle of 3° at a speed of 4 °/min

with a step size of 0.02° and scanned five times for each sample.

The surface regions of selected nitrided alloys were investigated in cross-sections using a FEI Tecnai G2 TEM. Sample preparation consisted of polishing the cross-section to a thickness of 40 µm followed by dimpling to 20 µm and finally ion-beam thinning until electron transparency was obtained.

3. Results and interpretation

3.1. Morphology of the nitrided case

Light-optical micrographs of cross-sections over the nitrided case for all twenty Fe-Cr-Ni alloys and AISI 304L are collected in Fig. 2. The entire case depth is about 5-6 µm. The *lx*, *lx1*, *l-lm3* and *lk1-lk3* samples exhibit a duplex microstructure adjacent to the surface, consisting of an outer layer with a thickness of 1-2 µm and the inner zone of 3-4 µm. The resistance against Marble's reagent is poor for the Cr-free alloys *lx* and *l*, so short etching times were applied to reveal the duplex structure. Acicular martensite is present in the matrix of alloy *l*. Also, in the matrix of the alloys *lm1*, *lk1*, some acicular martensite was observed, but it is not visible in Fig. 2. It was noticed during sample preparation, that the resistance of the nitrided alloys against chemical etching in Marble's reagent was improved by higher Cr contents. Long time etching was necessary to reveal the duplex structure in the alloys *lm3* and *lk3*. In the nitrided alloys *lm4-m*, alloys *lk4-k* and for all alloys in the *km* series no duplex morphology was observed, not even after severe etching. The morphology of the nitrided case on the latter specimens is identical to that in AISI 304L, which is considered characteristic for expanded austenite on stainless steel. In several cross sections a thin transition "phase" in-between expanded austenite and the underlying austenite is observed (see *lk2*, *km2*, *k*, *m*, 304L). Previous investigations demonstrated that this zone is associated with an accumulation of carbon atoms originally present in the alloy and pushed ahead by the advancing nitrogen profile [32]. Thus, a thin zone of carbon-stabilized expanded austenite is formed, which led to deep etching during the metallographical preparing.

3.2. Nitrogen concentration-depth profiles

Nitrogen concentration-depth profiles over the nitrided zones for the twenty Fe-Cr-Ni alloys and AISI 304L are collected in Fig. 3. The depth axes were normalized with respect to the case-matrix transition to allow a direct comparison of the nitrogen profiles. In both *lk* and *lm* groups for increasing Cr content, a gradual change from two regions with different nitrogen contents, separated by a steep gradient (alloys *l* and *lx*) to a continuous decrease in nitrogen and a steep gradient at the case-core transition (alloys *m* and *k*) is observed. Three kinks are marked in the concentration-depth profiles. The height of the 1st kink, as observed for the alloys *lk1-k* and *lm1-m* at the case-core transition, is strongly related to Cr content in the alloys. The lower the Cr content in the alloy, the lower is the N content at the case-core transition. This nitrogen content reflects trapping of N by Cr [25]. The 2nd kink at about 1.5-2.0 μm from the surface is observable in the alloys *l-lk3* and *l-lm4* and represents the highest possible nitrogen content in the inner zone, which also increases with Cr content, in equilibrium with the outer layer. The 3rd kink closest to the surface is observed in the alloys *l-lk2* and *l-lm2* and represents the lower nitrogen concentration limit in the outer sublayer. In the alloys with the higher Cr-contents, as *lk4-k* and *lm4-m*, both the 2nd and 3rd kink vanish, and a continuous smooth nitrogen-depth profile from the surface to the 1st kink evolves. The surface concentration is the highest nitrogen concentration achieved in the outer sublayer and increases from about 20 at. % to close to 30 at. % on increasing the Cr content. The upper and lower concentration limits determine the nitrogen-concentration range of outer and inner sublayer. With the increase of Cr content in the alloys, the saturated N concentration in the inner sublayer increases faster than that of the outer sublayer with a wider saturation concentration range. In the alloys of group *km*, where the Cr-content is constant, all the concentration profiles are similar and contain only the 1st kink as for alloy *m*, alloy *k* and AISI 304L austenitic stainless steel.

3.3. X-ray diffraction analysis

X-ray diffractograms of the nitrided layers on the Fe-Cr-Ni alloys and the AISI 304L austenitic stainless steel are shown in Fig. 4. The dashed diffractograms represent the alloys before nitriding, while the drawn diffractograms were obtained after nitriding. In the

un-nitrided alloys *l*, *lk1* and *lm1*, b.c.c. and f.c.c. phases coexist before nitriding; all other alloys contain only f.c.c. in their initial condition. The diffractograms for the nitrided alloys are significantly different from the un-nitrided alloys. In the 20 - 35° 2 θ range, the intensity scale was amplified by a factor 5 to allow the identification of superlattice reflections associated with nitrogen ordering. In alloy *l* two separate f.c.c. phases are present after nitriding. One of the two f.c.c. phases is identified as γ' -Fe₄N with 20 at. % N. Long-range order of the nitrogen atoms, as is characteristic for γ' -Fe₄N (see JCPDS 06-0627 Ref. [33]), is confirmed by the presence of 100 and 110 super-lattice reflections at 23.5 and 33.5° 2 θ . This nitride phase also contains Ni and therefore complies with γ' -(Fe,Ni)₄N, and is further referred to as γ'_N . The other f.c.c. reflections for alloy *l* were characterized as originating from a solid solution of N in f.c.c. Fe-Cr-Ni, designated as γ_N phase, with a lattice constant of 0.3639 nm. The nitrogen-containing γ_N phase has a lattice parameter that is expanded as compared to N-free f.c.c. alloys. Applying the relations given in Ref. [34], a nitrogen content of 6.0 at. % is obtained, which corresponds to the level of N that can be accommodated in the matrix for this alloy (cf. EPMA results in Fig. 3). The formation of a long-range ordered stoichiometric nitride γ' -(Fe,Ni)₄N phase and a short-range ordered solid solution, γ_N , of N in Fe-Cr-Ni is consistent with the duplex morphology on the nitrided alloy *l*, implying that γ' -(Fe,Ni)₄N is atop γ_N (cf. Figs. 2 and 3).

Apart from alloy *l*, a γ'_N phase with an LRO distribution of N atoms was also observed in the alloys *lk1-lk3* and alloys *lm1-lm3*. The intensities of the 100 and 110 super-lattice reflections decrease with increasing Cr content; for alloy *lk3* only the 100 reflection was observed (Fig. 4). The solid solution of N in f.c.c., γ_N , was observed in the alloys *lx1*, *lk1-lk3* and *lm1-lm3*. The lattice constant of the γ_N phase in the alloys *lk1-lk3* and *lm1-lm3* expanded to 0.3688-0.3733 nm, compared to that of the γ_N phase without Cr content. With an increase in Cr content, the two sets of f.c.c. diffraction patterns of the γ'_N and γ_N phases in the duplex layer on the alloys *lk1-lk3* and alloys *lm1-lm3* gradually broaden and shift to lower 2 θ . The reflections of the γ_N phase shift over larger 2 θ distance than those of the γ'_N phase, resulting in convergence and eventually overlap of the two f.c.c. patterns. The larger shifts for the Bragg peaks for the γ_N phase are consistent with a more pronounced increase in nitrogen content in

this phase (cf. Fig. 3). In the alloys *lk4-k*, alloys *lm4-m* and group *km*, with Cr contents above 12 wt. %, only one set of asymmetrically broadened f.c.c. reflections was observed, analogous to f.c.c. peaks from nitrided AISI 304L stainless steel. Such broadened f.c.c. line profiles are characteristic for traditional expanded austenite, γ_N phase [16,18]. In the light of the evolution of the diffractograms for alloys with 0-9 wt. % Cr, the asymmetrically broadened diffraction peaks in the alloys *lk4-k*, alloys *lm4-k* and group *km* can be conceived as merged Bragg peaks of γ'_N and γ_N phases. In addition, a weak diffraction peak was observed at $2\theta=43^\circ$ in the alloys *lk3-k*, alloys *k-km2* and the AISI 304L austenitic stainless steel. This peak shifted to lower 2θ angle with increasing Cr content and is identified as the $10\bar{1}1$ diffraction peak of a nitrogen-containing h.c.p. ϵ_N phase [8].

To verify the effect of ferrite in the alloys *l*, *lm1* and *lk1* on the development of the nitrided case, the alloys *lx* and *lx1* with higher Ni content were nitrided and compared in the Fig. 4. Since similar diffractograms consisting of f.c.c. peaks for γ'_N and γ_N phases were found in alloys *lx* and *lx1* as in the alloys *l*, *lm1* and *lk1*, it is concluded that the b.c.c. phase in the alloys *l*, *lm1* and *lk1* has not had an effect on the γ'_N and γ_N phase formation and that b.c.c. was transformed into f.c.c. under the influence of nitrogen dissolution.

Grazing incidence X-ray diffractograms measured at an incidence angle of 3° for the 35° - 55° 2θ range are given in Fig. 5. In the alloys *l* and *lx*, only γ'_N phase was observed on the outer sublayer of the nitrided case (cf. Fig. 2). Hence, the γ_N phase is concluded to be present underneath the γ'_N sublayer. Also, for the alloys *lm1-lm3*, *lk1-lk3* and *lx1* the γ'_N phase formed at the outer sublayer. For increasing Cr content in the alloys, the γ'_N phase is also obtained in the alloys *lm4-m*, *lk4-k* and *m-k*.

To analyze the phase constitution immediately below the surface, approximately $1\ \mu\text{m}$ was removed by mechanical polishing. The X-ray diffractograms after removal of $1\ \mu\text{m}$ are shown in Fig. 6. In alloy *l*, the diffraction peaks of γ_N phase have become stronger and those of the γ'_N phase are weakened, as compared to the diffractogram in Fig. 4. This confirms that the γ_N zone is only present as the inner subzone and the γ'_N phase only the outer sublayer. Similar observations apply for the alloys *lk1-lk3* and *lm1-lm3*, after polishing off $1\ \mu\text{m}$. The smaller shift of the diffraction peaks of the γ'_N phase as compared to the γ_N peaks, leads to

1 increasing overlap of the peaks of γ_N and γ'_N phases in the alloys **lm** and **lk**. No ϵ_N phase was
2 observed after polishing, which indicates that the ϵ_N phase is mainly formed in the outer part
3 of the nitrided zone.
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6 Summarizing, the serial diffractograms in Figs. 4-6 show that the outer sublayer consists
7 of γ'_N phase and the γ_N phase resides underneath the γ'_N phase. For relatively low Ni contents
8 combined with high Cr contents also the ϵ_N phase can be present, albeit in very small
9 quantities. The isostructural evolution of the nitrided layers formed on the Fe-Cr-Ni austenitic
10 alloys and AISI 304L austenitic stainless steel suggests that both phases with an f.c.c.
11 sublattice of metal atoms are present in all diffraction patterns in this work. The broadened
12 f.c.c. diffraction patterns in the austenitic alloys (and steel) with high Cr-content, can be
13 considered as the overlapping of peaks of the γ_N and γ'_N phases.
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23 3.4. TEM characterization of surface adjacent cross sections

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25 A detailed investigation of the first 3 μm below the surfaces of nitrided alloys **k** and **m**
26 and austenitic stainless steel AISI 304 was performed with (high resolution-) transmission
27 electron microscopy ((HR-)TEM) and selected area electron diffraction (SAED) on cross
28 sections. The results are collected in Figs. 7-1 to 7-3. A schematic diagram of the SAED
29 patterns for the f.c.c. $\langle 011 \rangle$ zone axis with and without nitrogen ordering (γ_N and γ'_N ,
30 respectively) and h.c.p. (ϵ_N) for the $\langle 11\bar{2}0 \rangle$ zone axis is given in Fig. 7-4 to assist in the
31 interpretation of the SAEDs.
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42 In alloy **m** (Fig. 7-1), the SAED pattern (a) is constituted of a set of strong f.c.c.
43 diffraction spots formed by the f.c.c. lattice of substitutional Fe, Cr and Ni atoms arrangement
44 and weak spots representative for long-range ordering of N in γ'_N . The intensity of the
45 super-lattice reflections diminishes with depth at locations (b) and (c). At location (d),
46 corresponding to a depth of 3 μm , they are no longer observed, indicating that the content of
47 γ_N phase increases with depth until it is the only phase in the nitrided zone. This convincingly
48 shows the duplex structure with γ'_N phase present in the outer region and γ_N phase underneath,
49 consistent with the XRD results. The HR-TEM image shows domains with a super-lattice
50 (marked as SL) due to nitrogen ordering in γ'_N , adjacent to unordered domains. Clearly,
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(nano-)twinning is observed in-between the twin boundaries marked by the thin white lines (TB). The occurrence of nano-twins is a consequence of plastic accommodation of the large lattice expansion in expanded austenite.

In alloy *k* (Fig. 7-2), the Fe₄N-like diffraction spots associated with nitrogen ordering are observed at locations (a)-(b). Apart from the (ordered) f.c.c. spots also h.c.p. diffraction spots are visible at locations (a)-(c) (cf. Fig. 7-4). The HR-TEM image shows that the h.c.p. arrangement is associated with continuous stacking faults, analogous to work in [8]. Similar observations are often observed in deformed f.c.c. alloys with a low stacking faulty energy[35-37]. The super-lattice is not clearly resolved in this HR-TEM image.

In AISI 304 (Fig. 7-3), SAED patterns similar to those in alloy *k* are observed; the (N-ordered) f.c.c. and (faint) h.c.p. diffraction spots can be observed near the surface. The N-ordering and h.c.p. lattice disappear with increasing depth. Near the surface, continuous stacking faults can be observed similar as in alloy *k*. The HR-TEM image was taken deeper than the locations (a)-(d). Here a single layer stacking fault corresponding to a local single layer h.c.p. (sl-h.c.p.) is observed.

Summarizing, the (HR-)TEM and SAED observations confirm that the nitrated case formed on the high Cr austenitic alloys show similar features as the AISI 304L austenitic stainless steel, and the case consists of the outer Fe₄N-like ordered γ'_N phase and the inner disordered γ_N phase.

4. Discussion

4.1. Co-existence of γ_N and γ'_N phases in the nitrated case

Based on the experimental results, the γ'_N phase contains both Fe₄N-like LRO and Cr-N SRO among the N atoms. The LRO gives rise to superlattice diffraction peaks as observed with XRD (for relatively low Cr contents) and superlattice diffraction spots for SAED (for all investigated high Cr contents). The total interstitial content in the γ'_N phase varies from near stoichiometric with respect to M:N=4:1 (M=Fe,Cr,Ni) to over-stoichiometric, depending on the Cr content. The over-stoichiometry with respect to M:N=4:1 can be understood as follows:

The LRO nitrogen atoms are preferentially located in the central octahedral interstice of a f.c.c. unit cell that so-called order sites, which corresponds to 1 out of 4 octahedral interstices occupied by N. Because of Cr-N trap interaction, the SRO nitrogen prefer to occupancy of interstitial sites neighbored by Cr atoms. Since Cr is distributed more or less randomly in the host lattice, some of these N trapped by Cr may be in the LRO coincidentally, but most of the N neighbored by Cr atoms are stay out of the LRO configuration. Hence, nitrogen contents beyond 20 at. % can be reached in γ'_N . While, in the γ_N phase, it only content the SRO nitrogen that trapped by Cr in the neighbored interstitial sites.

All investigated nitrided austenitic Fe-Cr-Ni alloys and the austenitic stainless steel AISI 304L showed a nitrided case that contains γ'_N phase close to the surface and γ_N phase at larger depth (Figs. 4-7). For the Cr-lean alloys, a clear subdivision is observed with light optical microscopy (Fig. 2), a discontinuity occurs in the nitrogen concentration-depth profile at the γ'_N/γ_N interface (Fig. 3) and separate Bragg peaks are identified for γ_N and γ'_N phases (Fig. 4). An increase of the Cr-content in the Fe-Cr-Ni alloy affects the solubility of N in both γ_N and γ'_N phases. This is reflected by an increase in the N-content in the EPMA profiles (Fig. 3) and shifts of the γ_N and γ'_N Bragg peaks to lower 2θ angles (Fig. 4). The results show that the enhanced solubility of N is more pronounced in the γ_N than in the γ'_N phase. Eventually, this leads to the disappearance of the interface between γ_N and γ'_N phases in the micrographs in Fig. 2 and the discontinuity in the EPMA profiles (Fig. 3), while overlap of Bragg peaks for γ_N and γ'_N phases (Fig. 4) is observed. For the nitrided Cr-lean Fe-Cr-Ni alloys the clear super-lattice reflections associated with long-range ordering of N atoms were observed with XRD. For higher Cr-contents, these super-lattice reflections disappear in the X-ray diffractograms, but can still be observed with electron diffraction (Fig. 7-1 to Fig. 7-3). The absence of super-lattice reflections in the X-ray diffractograms is explained from the limited size of LRO domains. Indeed, the HREM results in Fig. 7 show that the ordered domains are very small and are separated by anti-phase boundaries, which obscures their detection with X-ray diffraction.

4.2 Development of epsilon phase

The occurrence of a diffraction peak associated with the h.c.p. ϵ phase is discussed as follows. It has the orientation relationship $\{1\bar{1}1\}_{\gamma} // \{0001\}_{\epsilon}$ and $\langle 110 \rangle_{\gamma} // \langle 11\bar{2}0 \rangle_{\epsilon}$ with f.c.c. structure as shown in HR-TEM and SAED of alloy *k* and 304L in Fig. 7-2 to Fig. 7-4. The h.c.p. ϵ phase could be regarded as a nitride phase with stoichiometry M_2N_{1-z} ($M=Fe, Cr, Ni$), having the same Fe, Cr and Ni composition ratio as the matrix, because no diffusion of metal atoms occurs during low temperature nitriding. Alternatively, the h.c.p. ϵ phase can be formed by strain-induced plastic deformation, which can develop in f.c.c. Fe-Cr-Ni steels from plastic straining, provided that the alloy has a relatively low stacking fault energy [35-38]. The h.c.p. ϵ phase is mainly observed at the surface of the as-nitrided alloys *lk3-k* and *k-km2*, with relatively high Cr- and low Ni-contents, which promotes a low stacking fault energy[39]. Also the dissolution of N in f.c.c. steels has been demonstrated to decrease the stacking fault energy [40]. The plastic straining causing the strain-induced ϵ phase formation is a consequence of the enormous nitrogen-induced lattice expansion [41], which becomes particularly pronounced for high Cr contents and for the highest nitrogen contents. The TEM observations for alloy *k* in Fig. 7 show that ϵ phase has a thin lamella morphology and is relatively thick at the surface and thinner in the deeper zone. These observations would be consistent with strain-induced ϵ phase formation rather than nucleation and growth of a nitride phase. Thus, the occurrence of ϵ phase is concluded to be the outcome of high plastic straining combined with low stacking fault energy, both of which are maximized close to the surface where the highest nitrogen content is present.

4.3 Evolution of lattice parameters in γ_N and γ'_N

The evolutions of the lattice parameters calculated based on the 111 and 200 peak positions in XRD and GI-XRD are given in relation the Cr content in Fig. 8. For a Cr content over 12 wt. % Cr, the merged γ_N and γ'_N peaks in the diffractograms can be separated by deconvolution for some alloys, in particular those with a relatively high Ni content (alloy *m* and *km5-km3*). This may be caused by the weak Ni-N repulsion with slightly decreases the solubility of N in γ_N (see in this respect [42-44], where it is observed that a high Ni content

limits the N solubility in the alloys²). These lattice parameter values are affected by both the composition and the occurrence of compressive residual stresses [45]. The lattice parameter of original alloys is also plotted in the Fig. 8 as comparison. All the lattice parameter of the f.c.c. original alloys are closed to 0.36 nm with a small difference, because of the variation of Fe-Cr-Ni composition.

For the γ'_N phase, the lattice parameter values obtained from the peak positions of 111 and 200 reflections are consistent with each other. The values for these lattice parameters increase from below 0.38 nm to about 0.39 nm when the Cr content changes from 0 to about 18 wt.%. The lowest values reflect under-stoichiometry as compared to Fe₄N (for $y_N=0.25$ $a=0.37988$ nm)[46], while the values for high Cr contents correspond to approximately $y_N=0.37$. These results are in very good agreement with the EPMA measurements in Fig. 3. The observation that the lattice parameter obtained from 111 is systematically higher than for 200 can be discussed as follows. The γ'_N phase is elastically anisotropic, such that a load in the 111 direction is leading to a larger strain than in the 100 direction [47]; note that this is opposite to f.c.c. iron or austenitic stainless steel (see below). Consequently, a larger shift of the 111 reflection in an X-ray diffractogram due to larger lattice strain is expected for the 111 reflection than for the 200 reflection. Accordingly, the systematically larger lattice parameter obtained from the 111 reflection can be interpreted as the consequence of a compressive residual stress in the γ'_N phase. This is exactly what is expected.

On the other hand, for the γ_N phase, the value for the lattice parameter obtained from the 200 reflection is systematically higher than for the 111 reflection. For the γ_N phase the elastic anisotropy is such that 200 would experience a larger strain (by a factor 3) than 111 for the same applied load along the normal vector. Even though this may appear consistent with the observed discrepancy between 111 and 200 for γ_N phase, a substantially larger shift of 200 is generally reported for expanded austenite and has been debated for many years [2,13,48-50]. The larger increase of the lattice parameters in 200 directions than in the 111 directions were discussed in relation to anisotropic elastic and plastic effects by Wu et al. [51]. Later, Brink et

² This is not further considered here, because the Ni content in the alloys in this work is relatively low as compared to [42-44] and is obscured by the effects of actual importance.

al. [49] suggested that the combination of elastic and plastic anisotropy and in particular the anomalies for various reflections hkl arising upon the introduction of plastic deformation in γ_N phase, is responsible for an incommensurately larger shift of the 200 than the 111 reflection. Hence, the larger shift of the 200 reflection and the associated larger lattice parameter calculated from the reflection is ascribed compressive stress and large plastic deformation in γ_N phase to accommodate the lattice expansion due to nitrogen dissolution. Clearly, this “anomalous” shift of the 200 reflection is not so pronounced for 0 % Cr (alloy I), because the additional solubility of N due to SRO of Cr and N is absent.

Another clear observation in Fig. 8 is that the lattice parameters for the γ_N phase increase faster than that for the γ'_N phase, i.e. the peaks for the two phases get closer and finally merge. This is mainly caused by the N atom sharing in both LRO and SRO in γ'_N phase. It could be simply discussed as followed: with the N concentration increase, N atom should first be trapped by Cr to form γ_N , and then form LRO in γ'_N . When the LRO formed, some N atoms that trapped by Cr should be in the LRO, and some are out of the LRO. However, when we compared with the Fe_4N , only the N atoms that trapped by Cr and stay out of the LRO is the addition part. In the ideal random condition, 75% of trapped N will locate out of the LRO, because of the N occupancy in the f.c.c. Fe matrix is 25% in LRO- Fe_4N . Therefore, the N increasing with Cr in γ'_N is only 75% compared with γ_N . Here is just a simplified explanation, the more detailed discussion will be given in the theoretical part of this study (paper II: theory). Otherwise, with the increase of Cr content in the alloys, the diffraction peaks in Fig. 4 not only move to lower degrees, but also get broader. This is another important reason for the two peaks get merged, which is consistent with concentration evolution. The reason of this phenomenon will also be detailed discussed in the following paper II: theory.

4.4 Comparison of the present results to literature observations on duplex structures

The formation of a duplex layer composed of γ'_N phase and γ_N phase sublayers may explain experimental phenomena reported in previous studies. The occurrence of long range ordering of nitrogen atoms in γ_N phase as reported in [27,28] should be ascribed to the local presence of γ'_N phase. Previous studies [26-28] mentioned that ordered γ'_N phase may be

misinterpreted as Fe_4N precipitation, because the N supersaturated austenite is metastable. However, as demonstrated in the present work the ordered γ'_N phase is actually an independent phase, most likely with a better thermodynamic stability than the γ_N phase with only SRO. The only XRD work that reports evidence for the presence of LRO in homogeneously nitrided powder of stainless steel AISI 316 was reported by Brink et al. [12] for a nitrogen content of approx. 35 at.% N ($y_\text{N}=0.56$). This nitrogen content for the stabilization of γ'_N phase with 18 wt.% Cr is higher than for the results presented in Figs. 3. Further, Brink, et al. [29] investigated the decomposition of expanded austenite powders with high and low nitrogen content. For the high nitrogen-containing powder (γ'_N) they reported the development of an f.c.c. phase with a lattice parameter close to Fe_4N along with the precipitation of CrN for a temperature higher than 750 K, and this f.c.c. phase was reported to be more stable against nitrogen loss than γ_N phase with a lower nitrogen content than corresponding to M_4N . On the basis of the present results it is suggested that this intermediate f.c.c. phase is $(\text{Fe,Ni})_4\text{N}$, as developing in the low Cr-containing alloys investigated (cf. Fig. 2-4).

Duplex layer structures formed on f.c.c. alloys and steels by low-temperature plasma-based nitriding or nitrogen implantation processes were reported earlier. Williamson et al. [42] reported an outer γ_{N1} phase layer and inner γ_{N2} phase layer structure in Fe-rich alloys after low-energy, high-flux, nitrogen ion beam implantation of commercial austenitic alloy and steel at 400° C for 15 min. With the exception of the nitrogen implanted Cr-free Invar alloy (containing Fe and 34 at. % Ni) which is analogous to the alloy *1x* in the present work, for the cases investigated in Ref. [42] the duplex layer structure is not compatible with an outer γ'_N phase sublayer and inner γ_N phase as reported in this work. Also, Czerwiec, et al. [52] observed a γ_{N2} phase and attributed it to the cooling speed after nitriding. Later, Ahmadi and Czerwiec [53] revisited the subject. The composition-depth profiles presented in Ref. [53] clearly demonstrate an accumulation of carbon atoms underneath the nitrogen-stabilized expanded austenite. It is suggested that the f.c.c. peak associated with a low interstitial content and “identified” as γ_{N2} in Ref. [42,52,53] can be ascribed to a carbon accumulation, similar to observations for nitrocarburizing or nitriding preceded by carburizing[32,54].

Lutz et al. [55] also reported an outer γ_{N1} phase layer and inner γ_{N2} phase layer structure by plasma immersion ion implantation of Co-Cr-Ni HS188 alloys varied at 673 K and 853 K for 2 h, and the authors attributed this unexpected behavior to a chemical effect due to the Co matrix. Since Co_4N phase [56] can exist, isomorphous with Fe_4N , it may have a similar mechanism of formation as the outer γ'_N and inner γ_N reported in this work.

5. Conclusions

- (1) A duplex morphology, consisting of a Fe_4N -like γ'_N phase at the surface and γ_N phase underneath, develops on model Fe-Cr-Ni austenitic alloys and AISI 304L austenitic stainless-steel during plasma based low energy ion implantation at a temperature around 653 K. The γ'_N phase is characterized by long-range ordering (LRO) of nitrogen atoms, as evidenced by super-lattice reflections in XRD and/or SAED; the γ_N phase is a solid solution of N in austenite and shows short-range order (SRO) of Cr and N atoms. For Cr contents higher than 12 wt. %, the γ'_N phase becomes indistinguishable as a separate layer at the surface, XRD diffractograms for both phases overlap and do no longer show evidence of LRO, irrespective of the Fe and Ni contents. Nevertheless, SAED and HR-TEM still allows to identify domains of LRO γ'_N phase along with the γ_N phase for the highest nitrogen contents at the outer part, and only the SRO γ_N phase for the lower nitrogen content at the inner part, indicating that both phases co-exist on nitrided austenitic Fe-Cr-Ni alloys.
- (2) The solubility of N in both γ_N and γ'_N phase increases with the Cr content, because Cr has a stronger affinity to N than Fe and Ni. Hence, the occurrence of short-range ordering between Cr and N. The γ'_N phases have a nitrogen content exceeding the metal:nitrogen=4:1 ratio, which for (Cr-free) Fe_4N reflects the maximum N content. The nitrogen content in excess of $y_N=0.25$ is explained from the Cr-N SRO in addition to LRO in γ'_N . All the γ'_N phases on the twenty designed Fe-Cr-Ni austenitic alloys are isostructural that varied by short-range Cr-N order related to the Cr content in the alloys, and the case of γ_N phase is the same.
- (3) The lattice parameters of γ'_N phase and γ_N phase both increase with Cr content, because of

the associated enhanced nitrogen solubility in both phases. This increase is more pronounced for γ_N phase than for γ'_N phase, which leads to the XRD peaks merge and the interface disappearance in the higher Cr-content alloys. It can be explained qualitatively with an octahedral interstice site sharing occupancy model considering both LRO and SRO.

- (4) For alloys with a combination of a relatively low Ni and relatively high Cr content, i.e. alloys with a low stacking fault energy, the ϵ nitride phase forms by a strain-induced transformation for the region with the highest nitrogen content. This observation can be consistently explained from the plastic accommodation of lattice expansion and reduction of the stacking fault energy associated with nitrogen dissolution.

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Figure.1

Fig. 1. Schaeffler-diagram containing the compositions of the model alloys and AISI 304 L austenitic stainless steel.

Figure.2

Fig. 2. Micrographs of cross-sections over the nitrided zone of twenty model Fe-Cr-Ni alloys and AISI 304L austenitic stainless steel. Nitriding by plasma-based low energy nitrogen ion implantation at 653 K for 4 h.

Figure.3

Fig. 3. Nitrogen content (in at. %) vs. depth for the investigated nitrided Fe-Cr-Ni alloys and AISI 304L austenitic stainless steel. For each alloy two profiles are given. The lines keynoted 1st-3rd kink are explained in the text.

Fig.4. XRD patterns of the nitrogen-modified layers on the designed Fe-Cr-Ni alloys in group *lk*, group *lm*, group *km* and the alloys that not fully austenized.

Figure.5

Fig.5. Grazing incidence XRD patterns of the nitrogen-modified layers on the designed Fe-Cr-Ni alloys in group *lk*, group *lm*, group *km*.

Figure.6

Fig.6. XRD patterns of the nitrogen-modified layers polished off about 1 μm -thick on the designed Fe-Cr-Ni alloys in group *lk*, group *lm*, group *km*.

Fig. 7-1. TEM cross-sectional (top left) and HR-TEM (top right) images of the nitrogen-modified layer on alloy *m*. SAED patterns (bottom) of the nitrogen-modified layer at depths up to 3 μm corresponding to the locations marked (a) - (d) in the TEM image. The HR-TEM image was taken at a depth of about 1 μm (see black arrow). Twin boundaries are marked as TB and the super-lattice for the ordered regions is marked as SL by parallel white lines. The enlarged white boxes in the HR-TEM image show the f.c.c. (110) arrangement in the two side of the twin boundaries.

Figure.7-2

Fig.7-2 TEM cross-sectional (top left) and HR-TEM (top right) images of the nitrogen-modified layer on the alloy *k*. SAED patterns (bottom) of the nitrogen-modified layer at depths up to 3 μm corresponding to the locations marked (a) - (d) in the TEM image. The HR-TEM image was taken at a depth of 1 μm (see black arrow) and illustrates a region corresponding the shear bands in the TEM image. The enlarged white boxes in the HR-TEM image show the (110) arrangement of f.c.c. and the (11-20) arrangement of h.c.p. lattices.

Figure.7-3

Fig. 7-3. TEM cross-sectional (top left) and HR-TEM (top right) images of the nitrogen-modified layer on AISI 304L. SAED patterns (bottom) of the nitrogen-modified layer at depths up to 3 μm corresponding to the locations marked (a) - (d) in the TEM image. The HR-TEM image was taken at a depth of about 3 μm (see black arrow). The enlarged white box in the HR-TEM image shows a single layer stacking fault.

Figure.7-4

Fig. 7-4. Schematic diagram of SAED patterns for the locations of f.c.c. with and without nitrogen ordering (γ_N and γ'_N , respectively) in the $\langle 011 \rangle_{\gamma/\gamma'}$ zone axis and h.c.p. (ϵ_N) in the $\langle 11\bar{2}0 \rangle_\epsilon$ zone axis is indicated.

Figure.8

Fig. 8. Lattice parameters calculated from the 111 and 200 peak positions of γ_N and γ'_N phase in XRD and GI-XRD. Lattice parameters calculated from the XRD of the original alloys are also plotted as comparison. The dot line gives the lattice parameter of Fe_4N [46].

Table.1

Table. 1 The weighed Fe, Cr and Ni compositions for melting the model alloys

(wt. %)	<i>l</i>	<i>lm1</i>	<i>lm2</i>	<i>lm3</i>	<i>lm4</i>	<i>lm5</i>	<i>m</i>
Fe	73	70	67	64	61	58	55.34
Cr	0	3	6	9	12	15	17.66
Ni	27	27	27	27	27	27	27

(wt. %)	<i>l</i>	<i>lk1</i>	<i>lk2</i>	<i>lk3</i>	<i>lk4</i>	<i>lk5</i>	<i>k</i>
Fe	73	72.46	71.86	71.38	70.78	70.24	69.74
Cr	0	3	6	9	12	15	17.66
Ni	27	24.54	22.14	19.62	17.22	14.76	12.6

(wt. %)	<i>k</i>	<i>km1</i>	<i>km2</i>	<i>km3</i>	<i>km4</i>	<i>km5</i>	<i>m</i>
Fe	69.74	67.58	65.12	62.72	60.2	57.8	55.34
Cr	17.66	17.66	17.66	17.66	17.66	17.66	17.66
Ni	12.6	14.76	17.22	19.62	22.14	24.54	27

(wt. %)	<i>lx</i>	<i>lx1</i>
Fe	66	68.46
Cr	34	28.54
Ni	0	3

Supplementary Material

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