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**A simple model for nitrogen-induced lattice expansion of γ'_N and γ_N
phases in Fe-Cr-Ni alloys with different chromium contents**

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A recent publication on low-temperature nitriding of Fe-Cr-Ni alloys with various combinations of Cr and Ni contents showed experimentally the co-existence of γ_N and γ'_N phases. An important result of the investigations was that with increasing Cr-content in the alloy, the lattice expansion induced by nitrogen dissolution in short-range ordered (SRO) γ_N is more pronounced than in the long-range ordered (LRO) γ'_N phase. Eventually, for Cr contents beyond about 12 wt.%, the lattice expansions of the two co-existing phases become inseparable with X-ray diffraction investigation. The present contribution gives a simplified visualization and prediction of the lattice expansion to explain this phenomenon. It is demonstrated that 25 % of the N atoms trapped by Cr resides in LRO positions of γ'_N -Me₄N (Me = Fe,Cr,Ni).

Keywords: Stainless steel; solid solutions; modelling; Fe-Cr-Ni alloys; order–disorder phenomena; nitriding

1. Introduction

Since the first report by Zhang and Bell[1], it is generally regarded that during low-temperature nitriding of austenitic stainless steel (AUSS) a metastable supersaturated interstitial solid solution of nitrogen in austenite, referred to as expanded austenite, γ_N , develops [1-4]. Thus treated AUSS surfaces possess an excellent combination of wear and (localized) corrosion resistance performance, provided that the precipitation of CrN is prevented [5, 6]. Various interpretations have been given of the nitrogen-expanded austenite phase: i) an interstitial solid-solution phase wherein N is short-range ordered with Cr [7-11]; ii) a phase containing both Fe₄N-like long-range ordering (LRO) and Cr-N short-range ordering (SRO) [12, 13]; iii) a mixture of various phases, including γ' -Me₄N (Me = Fe,Cr,Ni) and/or ϵ -Me₂₋₃N phases and nano-scale CrN precipitates

dispersed in nitrogen solid solution [1, 14, 15].

Recent experimental work on plasma-based low-energy ion implantation of nitrogen into a series of Fe-Cr-Ni alloys with a wide variation in Fe, Cr and Ni contents, showed that essentially two phases develop in the nitrified case: γ_N without LRO among the nitrogen atoms, and γ'_N , a γ' -Fe₄N like phase, wherein LRO does occur among the N atoms [16]. For relatively low Cr contents (< 12 wt.%) these phases develop as separate layers, with the nitrogen-rich γ'_N closest to the surface. The two phases diffract X-rays independently, have different compositions and can be distinguished metallographically. For high Cr contents the phases are mixed as (tiny) domains and can only be distinguished with high-resolution transmission electron microscopy, while Bragg peaks of γ_N and γ'_N , as observed with X-ray diffraction (XRD), merge.

The lattice parameters for γ_N and γ'_N were observed to increase with Cr content owing to the increase in nitrogen content (see Fig.8 in ref [16]). The recently first-principle calculation about expanded austenite provides a study on the SRO of Cr-N, but includes no information on the LRO [17]. In the present contribution, a simplified model is given to rationalize and estimate the evolution of the lattice parameters for γ_N and γ'_N in relation to the Cr content and to gain a phenomenological understanding of the structure for the γ'_N phase to clearly clarify the N-induced lattice expansion mechanism of the γ'_N and γ_N phases.

2. The Model

The basic assumptions of the distributions of atoms over the available sites,

which can be confirmed by experiments and corresponding theory, are as follows:

- (i) Cr atoms are randomly distributed over the sites of the f.c.c. lattice of the alloys [18, 19];
- (ii) N atoms reside on the f.c.c. sub-lattice formed by the octahedral interstices of the f.c.c. metal lattice [19, 20];
- (iii) γ'_N phase contains long-range ordered (LRO) arrangements of N atoms similar to Fe_4N [16];
- (iv) Ni behaves as Fe in the alloys, which is consistent with Ni stabilizing $(\text{Fe,Ni})_4\text{N}$ [16];
- (v) Cr atoms can have (trap) one N atom in a neighbouring interstice, irrespective of the phase involved, i.e. γ_N or γ'_N , which is a simplified constraint referenced from a trapping-detrapping model [9, 21];
- (vi) N neighbouring Cr is either in an LRO position of γ'_N , or in a disorder site with respect to LRO.

Assumptions (i)-(iv) are realistic for low-temperature nitriding processing. This is a simplified crystallographic model that does not involve thermodynamic and kinetic processes, but only considers the distribution of nitrogen atoms over available sites and their interaction with chromium atoms in order to arrive at an estimate for the solubility of nitrogen in relation to the chromium content. Assumption (vi) is the most important part of the model and implies that the γ'_N phase can have an over-stoichiometric composition with respect to $\text{Me:N} = 4:1$ (Me represents a metal atom). If no Cr atoms

are present, the maximum N content in γ'_N is Me:N = 4:1, as for Fe_4N [22] and $(\text{Fe,Ni})_4\text{N}$ [16]. The implications of assumption (vi) are graphically illustrated in Fig. 1.

Based on the above assumptions, the N contents in the γ_N and γ'_N phases can be estimated as follows. Assume that y_{Cr} is the atomic fraction of Cr and that $y_N(\gamma)$ is the fraction of interstices occupied by N atoms in phase γ . Then, the fractions of N atoms in the γ_N and γ' phases in Fig. 1 are:

$$y_N(\gamma_N) = y_N(\gamma) + y_{\text{Cr}} \quad (1)$$

$$y_N(\gamma') = \frac{1}{4} \quad (2)$$

with $y_N(\gamma)$ the solubility of nitrogen in austenite without chromium. To arrive at an estimate for the lattice expansion of austenite by nitrogen in dependence of the Cr-content, an assumption concerning the nitrogen solubility in austenite without Cr, $y_N(\gamma)$, is necessary. From the Fe-N phase diagram, an estimate for the maximum solubility of N in γ -Fe in equilibrium with γ' - Fe_4N at the eutectoid temperature (865 K) is 2.4 wt.%, which corresponds to $y_N(\gamma) = 0.089$.

When the γ'_N phase has formed, nitrogen atoms can be either located at order sites, for which LRO occurs, or disorder sites, for which only SRO with Cr occurs. Over-stoichiometry with respect to the LRO configuration Me:N = 4:1 is realized by the enhanced solubility associated with the presence of Cr atoms in the γ'_N phase and N at disorder sites. Since the ratio of order to disorder sites is 1:3, the probability that an N atom in an SRO configuration with Cr is located at a disorder site is 3/4. Note that N atoms at order sites and in SRO configuration with Cr are already included in the atomic

fraction 1/4. Accordingly, the content of N atoms in γ'_N , accounting for LRO and SRO, is:

$$y_N(\gamma'_N) = \frac{1}{4} + \frac{3}{4}y_{Cr} \quad (3)$$

The lattice parameter of strain-free expanded austenite increases with interstitial content by $0.060 \times y_N$ (nm) [23, 24] and an additional increase in lattice parameter of 0.0043 nm occurs, because of a transition from paramagnetism to ferromagnetism [23], which occurs for the γ'_N phase. Using this data, the increase in lattice parameter, as a consequence of dissolving nitrogen atoms in γ_N and γ'_N , can be estimated.

3. Results and discussion

The results are shown by the dashed lines in Fig. 2 and compare favourably with the experimental lattice-parameter data, in particular for the lattice expansion of γ'_N [16]. The strikingly good correlation found between the estimated and experimental lattice parameter values for γ'_N suggests that the set of assumptions provides a satisfactory approach for the actual distribution of nitrogen atoms in this phase, which essentially is an LRO configuration of N atoms commensurate with Fe_4N and additional N atoms at disorder sites adjacent to a Cr atoms, leading to over-stoichiometry as compared to $Me:N = 4:1$. For the γ_N phase the lattice parameter increase for Cr-free austenite is a fair prediction, despite the simplifications of leaving out the role of nickel and taking the eutectoid temperature in the Fe-N phase diagram rather than the nitriding temperature (for which no data is available). On the other hand, the dependence on the Cr content is

underestimated by about 40%, implying that assumption (v) is too rigid and indicating that more than one of the Cr neighbouring sites are occupied simultaneously.

Previous work experimental work showed that the nitrogen content can be as high as corresponding to Cr:N = 1:3 for commercial austenitic stainless steels with 18-19 wt.% Cr, while the Cr atoms have a coordination number larger than five [11, 25]. The experimental lattice parameter data reproduced in the Fig. 2 demonstrate that higher N contents than predicted by the proposed model have been achieved experimentally. How much nitrogen will be dissolved depends on the balance between the flux of nitrogen atoms provided at the surface and the flux of nitrogen atoms diffusing into the interior. This was also observed for lattice-parameter data in dependence of the nitrogen content at constant Cr content, where the equilibrium nitrogen content depends on the applied chemical potential of nitrogen by the nitriding medium [11, 23]. These values cannot be reproduced under the present set of assumptions owing to the limitations of the model. A more realistic description of the Cr-N interaction should take into consideration that octahedral interstices can be surrounded by 0-6 Cr atoms and that N atoms prefer to reside in the interstices that are surrounded by more Cr atoms[26]. Furthermore, a statistical distribution of interstices with 0-6 neighbouring Cr atoms occurs. These sites have different probabilities for occupancy by nitrogen and will therefore be occupied in order of decreasing number of Cr atoms, thus providing a range of nitrogen solubility for a particular Cr content (see in this respect also the probabilities for occupancy in [23]). Furthermore, a more realistic model should, in addition to the

Cr-N SRO, also take into account the N-N repulsion leading to LRO. This will be the subject of future research.

4. Conclusions

The present work presents a simple model that can rationalize the nitrogen-dissolution-induced expansion of an f.c.c. lattice in dependence of the Cr content. In the light of the simplistic assumptions on which the model is built, satisfactory agreement is obtained between the lattice parameter dependence for co-existing γ_N and γ'_N phases in Fe-Cr-Ni alloys with different Cr contents. The reason that a more pronounced lattice expansion by nitrogen in dependence of the Cr content occurs for short-range ordered (SRO) γ_N as compared to the long-range ordered (LRO) γ'_N phase, is that 1/4 of the N atoms trapped by Cr resides in LRO positions in γ'_N . The model is considered to yield a minimum lattice expansion, mainly on account of the assumption that Cr atoms can only bind 1 N atom. In particular for the γ'_N phase the model predicts a surprisingly accurate expansion of the lattice and convincingly proves the occurrence of over-stoichiometry with respect to Me:N = 4:1.

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Fig.1. 2D representation of the γ'_N phase developing in the case of nitrided AUSS. (1) γ_N with a random distribution of Cr atoms and one trapped N atom in a neighboring interstice. (2) γ' -Fe₄N with LRO of N atoms. (3) γ'_N phase having both LRO of N and Cr-N SRO. N atoms in LRO position and trapped by Cr are identified by a red circle.

Fig. 2. Estimated change in lattice parameter for γ'_N and γ_N (dash lines), relative to the original Fe-Cr-Ni alloys. The experimental data were reproduced from Fig. 8 in the authors' previous experimental results [16] after subtracting of the appropriate reference lattice of the original alloy.