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On the crystal structure of Cr_2N precipitates in high-nitrogen austenitic stainless steel. II.¹ Orderdisorder transition of Cr_2N during electron irradiation

The crystal structure and order-disorder transition of Cr₂N were investigated utilizing transmission electron microscopy (TEM). Based on the analyses of selected-area diffraction (SAD) patterns, the crystal structure of the ordered Cr₂N superstructure was confirmed to be trigonal $(P\overline{3}1m)$, characterized by three sets of superlattice reflections (001), $(\frac{11}{22}0)$ and $\left(\frac{11}{22}1\right)$. During electron irradiation, the superlattice reflections gradually disappeared in the regular sequence (001), $(\frac{11}{23}0)$ and $(\frac{11}{23}1)$, indicating that the order-disorder phase transition of Cr₂N occurred. The convergent-beam electron diffraction (CBED) observation revealed that the space group of disordered Cr_2N is $P6_3/mmc$, which corresponds to an h.c.p. (hexagonal close packed) sublattice of metal atoms with a random distribution of N atoms in six octahedral interstices. The redistribution model of N atoms through the orderdisorder transition is discussed based on the characteristics and disappearing sequence of superlattice reflections.

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1. Introduction

It is known that the crystal structures of transition-metal carbides and nitrides are based on a face-centered cubic (f.c.c.) or hexagonal close-packed (h.c.p.) sublattice of metal atoms with interstitial atoms occupying some of the octahedral interstices (Ducastelle, 1991; Khachaturyan, 1978, 1983; Nagakura & Oketani, 1968). The ε -type ordered structure has been reported to be the most frequently observed ordering type in hexagonal interstitial compounds, and the stacking sequence of its (0001) plane along the c axis can be described as $A_M \alpha_I B_M \beta_I$... (where α_I and β_I are the two types of basal layers occupied by interstitial atoms; A_M and B_M are the h.c.p. sublattices of the metal atoms; Epicier et al., 1988; Jack, 1952; Leineweber & Jacobs, 2000). Hendricks & Kosting (1930) found a $(\frac{11}{33}1)$ -type superlattice reflection and suggested an increased $3^{1/2} \times 3^{1/2} \times 1$ -type superstructure, based on the geometrical arrangements of Fe octahedra. Jack (1952) confirmed the ε -type ordering for a wide range of Fe–N compositions and proposed a model for the continuous structural transition from ε -Fe₃N to ε -Fe₂N. Later, Leineweber & Jacobs (2000) and Leineweber et al. (2001) suggested a theoretical model for the distribution of interstitial atoms in the ε -type superstructure and investigated the ordering and magnetic properties of ε -type iron (carbo)nitrides. Recently, the present authors (Lee et al., 2005) found three sets of superlattice reflections in TEM-SAD patterns and proposed the modified occupation probability function (OPF) for describing the nitrogen distribution using the static concen-

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Table 1

Crystallographic information on the ideal Cr_2N superstructure based on the ε -type ordering model (Epicier *et al.*, 1988; Hendricks & Kosting, 1930; Jack, 1952; Leineweber & Jacobs, 2000).

For the sake of convenience in describing the superlattice reflections, the crystal coordinates $r_{\rm tris}$, $r_{\rm hep}$ are given with respect to the trigonal and h.c.p. structure, respectively.

Ordered Cr_2N superstructure (trigonal structure, space group: $P\overline{3}1m$)				
Atom position	$r_{ m tri}$	$r_{ m hcp}$	Wyckoff position	Occupancy
<i>A</i> 1	(000)	(000)	1(<i>a</i>)	1
A1	$(00\frac{1}{2})$	$(00\frac{1}{2})$	1(b)	0
<i>B</i> 1	(110)	$\left(\frac{21}{22}0\right)$	2(c)	0
<i>B</i> 2	$(11\frac{1}{2})$	$\left(\frac{211}{222}\right)$	2(d)	1
C1	(220)	$(\frac{12}{22}0)$	2(c)	0
C2	$(22\frac{1}{2})$	$ \begin{array}{c} (\frac{21}{33}0) \\ (\frac{211}{332}) \\ (\frac{12}{332}) \\ (\frac{12}{332}) \\ (\frac{121}{332}) \end{array} $	2(d)	1

tration waves (SCWs) method suggested by Landau & Lifshitz (1980) and Khachaturyan (1978, 1983).

The order-disorder transition of an ε -type ordered structure has been studied mainly using neutron diffraction analyses (Epicier et al., 1988; Hiraga & Hirabayashi, 1980; Hashimoto et al., 1974; Hirabayashi et al., 1974; Leineweber et al., 2001). Epicier et al. (1988) studied the crystal structures and order-disorder transitions of Mo_2C_{1-x} and W_2C_{1-x} . The disordering ($\varepsilon \rightarrow L'3$) of both hemicarbides occurred through the second-order transition in the temperature range from 1898 to 2233 K, depending on their chemical compositions. Hashimoto et al. (1974) and Hirabayashi et al. (1974) investigated the order-disorder transition of non-stoichiometric ZrO_x (0.3 < x < 0.5), with trigonal structure (space group: P312). They also suggested that the occupation probability of the O atoms, even in a perfect ordered state, was found to be different depending on the coordinate of interstitial sites, resulting in the peculiar behaviour of both the change in stacking sequence of O-atom layers and the order-disorder transition. However, there are still disagreements on the mechanism for interstitial atom redistribution during the order-disorder transition in an ε -type ordered structure, for most of the previous studies (Epicier et al., 1988; Hendricks & Kosting, 1930; Jack, 1952) have failed to detect the (001) superlattice reflection characterizing the M_2X -type superstructure, leading to discrepancies in the distribution of interstitial atoms within six octahedral sites. Moreover, no study on the order-disorder transition of the Cr2N system has been carried out because the crystal structure of Cr₂N has been controversial from a crystallographic point of view (Andrews et al., 1971; Kim et al., 1990; Lee et al., 2004a, 2005; The Bristol Group, 1984).

The objectives of the present study, therefore, are

(i) to clarify the crystal structure of $\mathrm{Cr}_2 N$ in both ordered and disordered states,

(ii) to investigate the order–disorder transition of Cr_2N during electron irradiation and

(iii) to elucidate the redistribution model of N atoms through the order-disorder transition based on the characteristics of superlattice reflections.

2. Experimental

The investigated material was a commercial, high-nitrogen austenitic P900NMo alloy (manufactured by VSG, Germany) with the following composition in wt %: 17.94 Cr, 18.60 Mn, 2.09 Mo, 0.89 N, 0.04 C, balance Fe. A detailed description of the heat treatment and specimen preparation has been previously reported (Lee *et al.*, 2004*a,b*; Lee *et al.*, 2005). Thin foils for TEM were prepared in a twin-jet electrolytic polishing apparatus using a solution containing 15% perchloric acid and 85% methanol. The samples were examined in a JEM 2010 transmission electron microscope at 200 kV. Detailed analyses of SADPs were carried out using Desktop Microscopist V2.2 software (Lucuna Laboratory, USA).

3. Results

3.1. Brief description of the ordered structure of Cr_2N (Lee et al., 2005)

The crystal structure system of ordered $\operatorname{Cr}_2 N$ ($P\overline{3}1m$), based on the ε -type occupational ordering model, was suggested in our previous paper (Lee *et al.*, 2005). The unit cell based on the h.c.p. arrangement of Cr atoms consists of six Cr atoms and six interstitial sites for N atoms and vacancies. One N atom occupies the A1 site [Wyckoff position (1*a*)] in the α_I plane and then the other two N atoms, due to the repulsive interactions between them, occupy B2 and C2 sites [Wyckoff position 2(*d*)] in the β_I plane in the Cr₂N superstructure. The new crystal-coordinate system based on the location of the N atom at the origin corresponds to a trigonal structure with the space group $P\overline{3}1m$. This ε -type occupational ordering of nitrogen leads to an increased $3^{1/2} \times 3^{1/2} \times 1$ superstructure. The crystallographic information on the ideal Cr₂N superstructure is summarized in Table 1.

Based on the analyses of SAD patterns and the ε -type ordering model, the crystal structure of ordered Cr₂N could be deduced (Lee *et al.*, 2005):

(i) the h.c.p.-type reflections with strong intensity correspond to the disordered state of Cr_2N ($P6_3/mmc$), namely, the h.c.p. sublattice of Cr atoms with a random distribution of N atoms;

(ii) the superlattice reflections that are absent in the h.c.p. structure originate from the occupational ordering of N atoms in three out of six octahedral interstices within the h.c.p. arrangement of Cr atoms;

(iii) consequently, the trigonal structure $(P\overline{3}1m)$, characterized by three sets of superlattice reflections (001), $(\frac{11}{33}0)$ and $(\frac{11}{13}1)$, can be considered as the ordered h.c.p. structure.

Based on the careful examinations in TEM, it should be noted that that the (001) superlattice reflection did not originate from the multiple scattering but from the main characteristics of Cr_2N precipitates, which was also confirmed by the intensity calculation of the M_2X -type ordered structure (Epicier *et al.*, 1988; Jack, 1952) and several experimental results using neutron diffraction analyses (Hashimoto *et al.*, 1974; Hirabayashi *et al.*, 1974).

Table 2

Summary of crystal structure data for both the trigonal (ordered) and h.c.p. (disordered) structures of Cr_2N .

	Trigonal	H.c.p.
Point group Space group Lattice parameters (Å)	$\overline{\overline{3}1m}$ $P\overline{\overline{3}1m}$ $a = 4.796$ $c = 4.470$	6/mmm $P6_3/mmc$ a = 2.748 c = 4.438

References: Kim et al. (1990); Vallas & Calvert (1985); Andrews et al. (1971); The Bristol Group (1984).

3.2. Order-disorder transition of Cr_2N during electron irradiation

In the present study, the irradiation-induced disordering of the Cr_2N superstructure was observed for the first time in TEM analyses, where the superlattice reflections characterizing the ordered Cr_2N superstructure disappeared in regular sequence with increasing irradiation time. The electron irradiation in TEM was carried out in parallel-beam mode, since the order–disorder phase transition in convergent-beam mode including microbeam diffraction was difficult to observe owing to the fast extinction of superlattice reflections. The crystal structure data for the ordered and disordered Cr_2N are given in Table 2.

Fig. 1 shows a series of SAD patterns with a [100]_{tri} zone axis showing the order-disorder transition of Cr₂N during electron irradiation at 200 kV. At an early stage of irradiation, the (001) superlattice reflection started to disappear and eventually was observed to vanish after electron irradiation for 10 min (Fig. 1b). On prolonged irradiation up to 20 min, the $\left(\frac{12}{33}\right)$ superlattice reflection with lower scattering intensity compared with the $\left(\frac{12}{12}0\right)$ reflection disappeared first, followed by the extinction of the $(\frac{11}{33}0)$ superlattice reflection (Fig. 1c). The $\left(\frac{11}{33}\right)$ superlattice reflection was stable for up to 30 min and then disappeared gradually with irradiation time. After electron irradiation for 60 min none of the superlattice reflections were visible, indicating that the order-disorder transition of Cr_2N was complete. Fig. 1(d) shows the SAD pattern corresponding to the disordered structure of Cr2N after the order-disorder transition was complete and is the same as that of calculated Cr₂N based on h.c.p. structure (Figs. 3e and f in Lee et al., 2005).

Therefore, it can be concluded that:

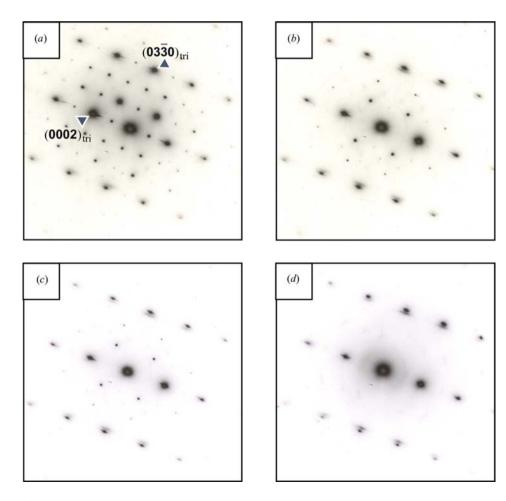


Figure 1

SAD patterns with a $[100]_{tri}$ zone axis showing the order-disorder transition of Cr₂N after electron irradiation for (*a*) 0 min (the perfect ordered state), (*b*) 20 min, (3) 40 min and (*d*) 60 min (the disordered state).

(i) the superlattice reflections characterizing the trigonal-type Cr_2N superstructure gradually disappeared in a regular sequence: (001), ($\frac{11}{33}$ 0) and ($\frac{11}{33}$ 1), and

(ii) the resulting disordered structure shown in Fig. 1(d) originates from the redistribution of N atoms in six octahedral interstices during electron irradiation, corresponding to the h.c.p. sublattice of metal atoms with a random distribution of N atoms.

3.3. CBED study on the disordered structure of Cr₂N

Due to the rapid disappearance of superlattice reflections, especially in the case of the (001) reflection, it is difficult to study the ordered Cr_2N superstructure using CBED which is one of the most accurate techniques for determination of crystal symmetries. The CBED observations, therefore, were restricted only to the disordered structure of Cr₂N after the order-disorder transition was complete. Tables 3 and 4 (Buxton et al., 1976; Loretto, 1984) show the possible symmetries shown by the WP (whole pattern), including high-order information **Table 3** Symmetries observed in CBED from the 6/mmm and $\overline{3}$ 1*m* point groups depending on the zone axis (Buxton *et al.*, 1976; Loretto, 1984).

Zone axis	Point group		
	6/mmm	$\overline{3}1m$	
[0001]	$6mm1_R$	$6_R m m_R$	
<2110>	$2mm1_R$	21 _R	
<1100>	$2mm1_{R}^{n}$	_	
<i><uvt< i="">0></uvt<></i>	$2_{R}mm_{R}$	-	
<uutw></uutw>	$2_{R}^{n}m_{R}^{n}$	-	
$\langle u\overline{u}0w \rangle$	$2_{R}^{n}m_{R}^{n}$	$2_{R}mm_{R}$	
<uvtw></uvtw>	2_R^{n}	2_R	

and by the BF (bright field) containing HOLZ (high-order Laue zone) lines in the zero-order disc depending on the zone axes related to the h.c.p. (disordered) and trigonal (ordered) structure. From Table 3, it is worth noting that the distinction between 6/mmm (h.c.p.) and $\overline{3}m$ (trigonal) point-group symmetries can be possible only in two ([001] and $[1\overline{10}]_{hcp}$ zone axes, *i.e.* the symmetries of both WP and BF corresponding to the disordered Cr₂N structure should be the

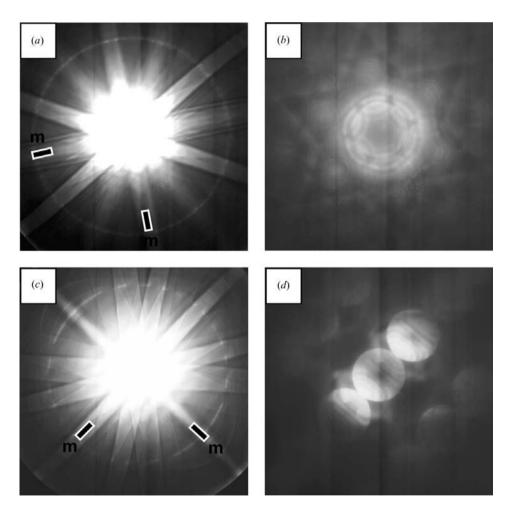


Figure 2

CBED patterns of Cr₂N after electron irradiation; (a) [001] whole pattern symmetry, (b) [001] zero-order disc pattern, (c) $[100]_{tri}$ whole pattern symmetry and (d) $[100]_{tri}$ zero-order disc pattern, respectively.

sixfold symmetric from [001] and have the mirror symmetry as well as the twofold symmetry from the $[1\overline{10}]_{hcp}$ zone axis, respectively.

Fig. 2 shows a series of CBED patterns with [001] and $[1\overline{10}]_{hcp}$ zone axes taken from the disordered Cr₂N after electron irradiation for 60 min. Since the position and distribution of intensities in the HOLZ reflection (Fig. 2a) show sixfold rotation together with 'two-types' mirror symmetry, the projection symmetry is described by 6mm. Although no HOLZ line detail in the zero-layer disc is visible, the examination of BF in Fig. 2(b) clearly shows the 6mm symmetry again. Thus, the symmetry of the CBED pattern taken in the [001] zone axis is confirmed to be 6mm, in accordance with the findings of The Bristol Group (1984). The WP and BF patterns taken from the $[1\overline{10}]_{hep}$ zone axis are shown in Figs. 2(c) and (d). In Fig. 2(c) the HOLZ reflection disc, whose position shows twofold rotation and mirror symmetry, is described by 2mm. The BF in Fig. 2(d) again confirms the existence of two types of mirror symmetries. Therefore, the CBED observation shows that the point group of the disordered Cr₂N structure after electron irradiation is 6/mmm rather than $\overline{3}1m$, meaning that the N atoms are redistributed through the order-disorder

> transition during electron irradiation.

4. Discussion

The crystallographic information on three sets of superlattice reflections (001), $(\frac{11}{33}0)$ and $(\frac{11}{33}1)$ obtained in our previous study (Lee et al., 2005) is summarized in Table 5. In this study the superlattice reflections characterizing the ordered Cr₂N superstructure were observed to vanish during electron irradiation in the regular sequence: (001), $(\frac{11}{33}0)$ and $(\frac{11}{33}1)$, indicating that the order-disorder phase transition has occurred. The redistribution model of the N atoms during the order-disorder transition is thus discussed on the basis of the characteristics and disappearing sequence of the superlattice reflections.

The (001) superlattice reflection disappeared first during the order-disorder transition. As discussed in a previous study (Lee *et al.*, 2005), the (001) superlattice reflection characterizes the modulation of the interstitial contents between α_I and β_I layers (Fig. 3*a*). The extinction of this reflection means that the interstitial contents in these two layers

Table 4

Relation between the observed symmetries and the diffraction group related to the 6/mmm and $\overline{3}1m$ point groups (Buxton *et al.*, 1976; Loretto, 1984).

Observed symmetry	Projection diffraction groups	Possible diffraction groups	Symmetries of high-order information	
in zero-order zone			Whole pattern	Zero-order disc
6 <i>mm</i>	$6mm1_R$	$6m_Rm_R$	6	6 <i>mm</i>
	i.	6mm	6mm	6 <i>mm</i>
		$6_R m m_R$	3 <i>m</i>	3 <i>m</i>
		$6mm1_R$	6mm	6mm
2	21_{R}	2	2	2
		2_R	1	1
		21_R	2	2
2mm	$2mm1_R$	$2m_Rm_R$	2	2mm
	K	2mm	2mm	2mm
		$2_{R}mm_{R}$	m	m
		$2mm1_R$	2mm	2mm

become equal through the redistribution of N atoms. From Fig. 3(*a*), in a perfectly ordered state, the nitrogen concentration in the β_I layer is twice that in the α_I layer. Therefore, in order to equilibrate the nitrogen contents between these layers, the N atoms in B2 and C2 [Wyckoff position 2(*d*)]

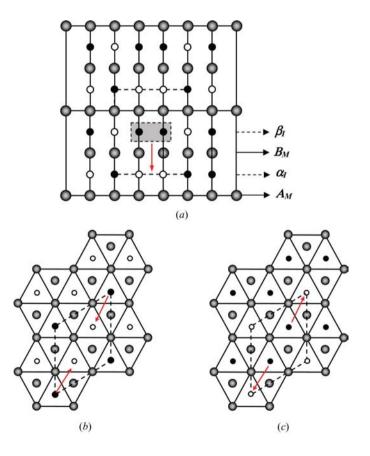


Figure 3

The redistribution model of N atoms through the order-disorder transition; (a) N atoms move from the B2 and C2 (β_I layer) to the B1 and C1 (α_I layer) Wyckoff sites along the *c* axis, and N atoms redistribute along the α_I (b) and β_I (c) layers, respectively. The arrows indicate the partial transfer of N atoms during the order-disorder transition.

should partially move onto *B*1 and *C*1 [Wyckoff position 2(c)] octahedral sites along the *c* axis. When the occupancies of n(B2) and n(C2) reached 0.75, namely, n(A1) + n(B1) + n(C1) = n(A2) + n(B2) + n(C2) = 1.5, the (001) superlattice reflection eventually vanishes through the redistribution of N atoms along the *c* axis.

Epicier et al. (1988) studied the phase transition of Mo₂C using in situ neutron diffraction analyses and found a successive transformation from the ξ -Fe₂N type (orthorhombic) to the ε -Fe₂N type (trigonal), and finally disordered L'3 (h.c.p.). They suggested that the carbon contents were almost identical at 0.5 in each layer, irrespective of the layer structure; the evidence for this equal distribution of carbon was the lack of (001) superlattice reflections. Epicier & Esnouf (1984) carried out an irradiation experiment of the ordered ε -W₂C with an electron microscope. They reported that the C atoms were more easily displaced when the electron beam is perpendicular to the c axis rather than parallel, indicating that the carbon diffusion across the basal planes of the metal atoms is more difficult. Leineweber et al. (2001) studied the magnetic structure and the disorder of nitrogen in ε -Fe₃N and suggested that the disorder occurred through the nitrogen redistribution perpendicular to the c axis from the Wyckoff positions 2(c) to 2(b) above 450 K. They also explained that the nitrogen redistribution along the c axis was difficult because the occupancy for the 2(d) Wyckoff position was not changed during the order-disorder transition.

Contrary to these previous studies, in the case of Cr₂N the order-disorder transition was initiated through the partial transfer of N atoms along the c axis rather than perpendicular to the c axis, which was supported by the disappearance of the (001) superlattice reflection. As indicated earlier, most previous studies (Epicier et al., 1988; Hendricks & Kosting, 1930; Jack, 1952) concerning the ε -Fe₂N-type superstructure failed to detect the (001) superlattice reflection, which presumably led to a misunderstanding of the redistribution of interstitial atoms during the order-disorder transition. Moreover, different types of superlattice reflection were found in SAD patterns depending on the zone axis. Whereas $(\frac{11}{33}0)$ is the only superlattice reflection in the [001] zone axis which is parallel to the c axis (Fig. 3c in a previous paper; Lee et al., 2005), there are three classes of superlattice reflections in $[100]_{tri}$ perpendicular to the *c* axis. In addition, the most stable $\left(\frac{11}{22}\right)$ superlattice reflection does not appear in the [001] zone axis. Therefore, it is unreasonable to say that the redistribution of interstitial atoms along the c axis is difficult due to the preferential crystallographic direction. Furthermore, the diffusion distance of interstitial atoms along the c axis is shorter than that perpendicular to the c axis: the distance vector between two octahedral sites in the planes α_I and β_I is $c_0/2 \simeq 0.816a_0$, whereas that for two octahedral sites in the same plane is a_0 (a_0 and c_0 are the lattice parameters of the h.c.p. sublattice of the Cr atoms).

Hashimoto *et al.* (1974) and Hirabayashi *et al.* (1974) studied the ordered superstructure and order–disorder transition of ZrO_x (0.30 $\leq x \leq$ 0.41) and found that the stepwise disordering occurred in a different temperature range (T_1 and

 Table 5

 Crystallographic information on the superlattice reflections obtained in this study.

Superlattice reflections	hkl	Characteristics
(001)	h-k=3n	(i) Characteristics of ε - M_2 N
	l = 2n + 1	(ii) Modulation between α_I and β_I layer
$(\frac{1}{2},\frac{1}{2},0)$	$h - k \neq 3n$	(i) Characteristics of ε - M_3 N
557	$l = 2n^{\prime}$	(ii) Modulation among A, B and C channel
		(iii) Deviation from ideal h.c.p. arrangement of metal atoms
$(\frac{1}{3}\frac{1}{3}1)$	$h - k \neq 3n$ $l = 2n + 1$	(i) Characteristics of all ε -type ordering

 T_2) in ZrO_{0.41} (Fe₃N_{1 + x} type, P312). This is similar to the ideal ε -Fe₂N-type superstructure, except that one octahedral site such as C2 (Fig. 3a) is partially occupied by interstitial atoms (Jack, 1952). Jack suggested that the transition at T'_1 is regarded as the rearrangement of O atoms along the c axis (intra-layer redistribution) on the grounds of the disappearance of the (001) superlattice reflection. The random distribution in each interstitial layer (inter-layer redistribution) was also obtained at T_2 , which is explained by the gradual extinction of the $(\frac{11}{33}1)$ superlattice reflection. Apart from the existence of $(\frac{11}{33}0)$ due to the involvement of other alloying elements (Lee *et al.*, 2005) this stepwise disordering was also a probable process, as is the case in this study.

Contrary to the case for the (001) reflection, the gradual disappearance of $\left(\frac{11}{33}0\right)$ and $\left(\frac{11}{33}1\right)$ can be explained by the redistribution of interstitial atoms perpendicular to the c axis, *i.e.* along each interstitial α_I and β_I layer. Suppose that the disordered structure consists of a random distribution of interstitial atoms within six octahedral sites, for example, the N atom may occupy every octahedral site uniformly [n(A1) = $n(A2) = \ldots = n(C2) = 0.5$]. Then, the redistribution of N atoms should occur along the α_I and β_I interstitial planes. Thus, the partial transfer of N atoms occur simultaneously from Wyckoff sites 2(d) (B2 and C2) and 1(a) (A1) to 1(b)(A2) and 2(c) (B1 and C1), respectively. The resultant crystal structure of disordered Cr₂N corresponds to the h.c.p. sublattice of metal atoms with a random distribution of N atoms, as confirmed from the SADP and CBED analyses. This redistribution model perpendicular to the c axis was suggested on numerous occasions in various ε -type superstructures irrespective of their structure or composition (Epicier et al., 1988; Hiraga & Hirabayashi, 1980; Hashimoto et al., 1974; Hirabayashi et al., 1974; Leineweber et al., 2001). The redistribution model based on the characteristics of superlattice reflections is shown in Fig. 3 and can be summarized as follows.

The electron-irradiation-induced disordering of the Cr_2N superstructure can be explained in a two-step process:

(i) Redistribution of N atoms along the *c* axis: The (001) superlattice reflection characterizes the modulation of the interstitial contents between α_I and β_I layers (Fig. 1*b*). The extinction of this reflection means that the interstitial contents in these two layers become equal through the redistribution of N atoms.

(ii) Redistribution of N atoms perpendicular to the *c* axis: The $(\frac{11}{33}0)$ and $(\frac{11}{33}1)$ superlattice reflections disappeared with increasing irradiation time, which means that the redistribution of N atoms occurs along each interstitial planes until the configurations of the N atoms are attained to be the disordered structure.

5. Conclusions

The TEM study of the crystal structure and order–disorder transition of Cr_2N precipitates in high-nitrogen austenitic Fe-18Cr-18Mn-2Mo-0.9N steel is summarized as follows.

During electron irradiation, the superlattice reflections gradually disappeared in the regular sequence: (001), $(\frac{11}{33}0)$ and $(\frac{11}{33}1)$, indicating that the order-disorder phase transition of Cr₂N occurred.

The CBED observation revealed that the space group of disordered Cr_2N was $P6_3/mmc$ and corresponded to the h.c.p. sublattice of metal atoms with a random distribution of N atoms in six octahedral interstices.

The electron irradiation-induced disordering of the Cr_2N superstructure was explained by a two-step process: N atoms redistributed first (i) along the *c* axis, followed by (ii) perpendicular to the *c* axis.

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References

- Andrews, K. W., Dyson, D. J. & Keown, S. R. (1971). Interpretation of Electron Diffraction Patterns, p. 203. London: Hilger.
- Buxton, B. F., Eades, J. A., Steeds, J. W. & Rackham, G. M. (1976). *Philos. Trans. R. Soc.* 281, 171–194.
- Ducastelle, F. (1991). Order and Phase Stability in Alloys, p. 162. North-Holland: Elesevier Science Publishers BV.
- Epicier, T., Dubois, J., Esnouf, C., Fantozzi, G. & Convert, P. (1988). *Acta Metall.* **36**, 1903–1921.
- Epicier, T. & Esnouf, C. (1984). J. Microsc. Spectrosc. Electron. 9, 17–28.
- Hashimoto, S., Iwasaki, H., Ogawa, S., Yamaguchi, S. & Hirabayashi, M. (1974). J. Appl. Cryst. 7, 67–73.
- Hendricks, S. B. & Kosting, P. B. (1930). Z. Kristallogr. 74, 511-533.
- Hirabayashi, M., Yamaguchi, S., Arai, T., Asano, H. & Hashimoto, S. (1974). *Phys. Status Solidus*, **23**, 331–339.
- Hiraga, K. & Hirabayashi, M. (1980). J. Appl. Cryst. 13, 17-23.
- Jack, K. H. (1952). Acta Cryst. 5, 404-411.
- Khachaturyan, A. G. (1978). J. Prog. Mater. Sci. 22, 1-150.

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- Khachaturyan, A. G. (1983). *Theory of Structural Transformations in Solids*. pp. 39–95. New York: John Wiley.
- Kim, S. J., Marquart, T. & Franzen, H. F. (1990). J. Less-Common Met. 158, L9–L10.
- Landau, L. D. & Lifshitz, E. M. (1980). *Statistical Physics Part I*, pp. 401–516. Oxford: Pergamon Press.
- Lee, T. H., Oh, C. S., Lee, C. G., Kim, S. J. & Setsuo, T. (2004a). Met. Mater. Int. 10, 231–236.
- Lee, T. H., Oh, C. S., Lee, C. G., Kim, S. J. & Setsuo, T. (2004b). Scr. Mater. 50, 1325–1328.
- Lee, T. H., Oh, C. S., Han, H. N., Lee, C. G., Kim, S. J. & Setsuo, T. (2005). Acta Cryst. B61, 137–144.

- Leineweber, A. & Jacobs, H. (2000). J. Alloys Comput. 308, 178–188. Leineweber, A., Jacobs, H., Hüning, F., Lueken, H. & Kockelmann,
- W. (2001). J. Alloys Comput. **316**, 21–38. Loretto, M. H. (1984). Electron Beam Analysis of Materials, p. 88.
- London: Chapman and Hall.
- Nagakura, S. & Oketani, S. (1968). *Trans. ISIJ*, **8**, 265–294.
- The Bristol Group (1984). *Convergent Beam Electron Diffraction of Alloy Phases*, p. 61. Bristol and Boston: Adam Hilger.
- Vallas, P. & Calvert, L. D. (1985). Pearson's Handbook of Crystallographic Data for Intermediate Phases, Vol. 2, p. 1877. Ohio: ASM Metals Park.