

Nitrogen atom shift and the structural change in chromium nitride



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ABSTRACT

The atomic configurations and structural evolution of disordered Cr₂N have been investigated by C_s-corrected high-resolution transmission electron microscopy (HRTEM) imaging, electron diffraction analysis, electron energy loss spectroscopy (EELS) and *ab initio* calculations. The atomic structure of the disordered Cr₂N is experimentally confirmed by C_s-corrected atomic resolution imaging. Both diffraction and HRTEM image analysis revealed that the disordered Cr₂N structure possesses a hexagonal (*hcp*) arrangement of Cr atoms with N atom random distributions, particularly, N atoms shift away from octahedral interstices at (001) plane. The nitrogen atom shifts result in a clear reduction of the relative intensity ratio of (030) to (002) reflection. It has also been found that the disordered Cr₂N can transform into a face-centered cubic (*fcc*) phase at the specimen surface while chemically retaining a Cr/N atomic ratio close to 2:1. Structurally, such cubic phase is similar to sub-stoichiometric *fcc* CrN. The analysis corroborated that the structural transformation could be achieved by shearing motion of Cr atoms in (001) planes. Based on the experimental observations and theoretical calculations, the effects of nitrogen atom redistribution on the structure and the stability of various Cr₂N phases are addressed in detail.

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1. Introduction

Many binary nitride and carbide interstitial compounds may adopt hexagonal or face-centered cubic structure of metal atoms with interstitial atoms occupying the octahedral interstices. The crystal structure typically changes with the content of interstitial non-metal atoms, as exhibited by e.g. Cr-N, Ti-N, Fe-N, V-N and Nb-C systems [1–9]. When the occupancy of octahedral interstices is relatively low (for example, less than 50%), the metal atoms tend to form a hexagonal structure [4,7–8,10]. If the occupancy increases, the structure of metal atoms changes from hexagonal to face-centered cubic [5–6,8–9]. It is therefore obvious that the contents of non-metal atoms play an essential role in the *hcp*–*fcc* structure change. However, this relation between interstitial atoms and structure of metal atoms has not yet been experimentally investigated.

Chromium nitride is a typical example of such an interstitial compound. It exhibits different crystal structures for different Cr/N atomic ratios. It is well known that CrN has an *fcc* lattice structure [3] while Cr₂N possesses an *hcp* structure (Cr atomic arrangements) [11–13]. Lee et al. identified the structure of

ordered Cr₂N in the high-nitrogen austenitic alloy as an *hcp* Cr arrangement with ordered N atoms located exactly at the octahedral interstices [11].

In an *hcp* structure, distances between two adjacent octahedral interstices are smaller along the [001] direction (*a trigonal coordinate notation is used throughout the paper*) than those within the (001) plane. The interaction between nitrogen atoms has been reported to be repulsive in the study of ordered and disordered Cr₂N [14]. Therefore, nitrogen atoms do not occupy neighboring interstices along the [001] direction in an ordered structure. Only in this way, the distances between two adjacent N atoms are kept as large as possible, and the repulsive interaction can be minimized. This structure has been successfully confirmed by neutron diffraction [1]. A recent first-principles study on the ordered Cr₂N also indicated that a large distance between two adjacent N atoms, originating from the repulsive interaction, could make the structure more stable [15].

The ordered N atoms in Cr₂N may redistribute randomly under electron irradiation, triggering an order–disorder transition of Cr₂N and further forming a disordered Cr₂N structure with N atoms randomly distributed in the octahedral interstices [2]. As a consequence, the average repulsive interaction between two adjacent N atoms certainly increases [14]. Therefore, the order–disorder transformation provides an opportunity to investigate the

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influence of the repulsive interaction between interstitial atoms on the crystal structure in a TEM. However, so far, the detailed atomic configuration of the disordered Cr₂N remains unknown.

The structure of the ordered Cr₂N reported by Lee et al. actually results from such repulsive interaction. However, the authors have not considered the case of an *hcp*–*fcc* structure transition. The *hcp*–*fcc* transition in chromium nitride was mostly seen as a thermally induced transformation from CrN (*fcc*) to Cr₂N (*hcp*) [16–17]. Moreover, the previous studies were mainly based on an XRD analysis, which is unable to reveal local atomic structure changes, mechanisms of the structural transformation, and the Cr₂N–CrN interface structure.

Hexagonal phase Cr₂N, an important member of the Cr–N compounds, exhibit significantly higher hardness values compared to that of the *fcc* phases [18], and comparable corrosion and wear resistance [19]. From the basic research point of view, hexagonal phase Cr₂N possess the structure complexity, i.e. sub-stoichiometric and ordering among the anion sites can influence the crystal symmetry etc [20]. The study of the electronic and atomic structure of this hexagonal nitride is of particular interest in order to establish significant bases in relation with their specific properties, and further reveal the structural peculiarity of Cr₂N.

Here, we closely investigate the atomic structure of the disordered Cr₂N films and the structural transition from *hcp* to *fcc* at the specimen surface, using modern spherical aberration-corrected (C_s-corrected) high-resolution transmission electron microscopy (HRTEM), electron diffraction, electron energy loss spectroscopy (EELS), and theoretical calculations. The objectives are as follows: (i) to elucidate the atomic structure of disordered Cr₂N and understand the N atom distributions in Cr₂N; (ii) to identify the mechanism of the structural transformation from *hcp* to *fcc*, and (iii) to further reveal the importance of N atom distribution in the *hcp* to *fcc* structural transition.

2. Methods

Cr₂N films were deposited on a single crystal Si substrate by means of magnetron sputtering deposition in an Ar + N₂ discharge at 350 °C using a constant target power of 6 kW (The target has 145 mm in diameter), a total pressure of 1 Pa, a nitrogen partial pressure $p_{N_2} = 0.1$ Pa, and an applied substrate bias voltage of –40 V. The resulting overall thickness of the film was 1 μm. An XRD phase analysis was performed on the Rigaku SmartLab diffractometer system.

The TEM specimen was prepared by a standard approach including polishing, grinding, and a final ion milling at an energy of 4.0 keV for a few minutes. A 200 kV field emission TEM/STEM (JEOL 2100F) equipped with an image-side C_s-corrector was used in this study, which demonstrates a 1.2 Å resolution at 200 kV. The alignment of the C_s-corrector was performed using the CEOS software based on the aberration measurements deduced from Zemlin tableaus. All HRTEM images shown here were recorded on a 2 k × 4 k pixel CCD camera at a magnification of 800 k× using an acquisition time of 1.0 s and a negative C_s imaging condition (NCSI) [21], under which all atoms are imaged as bright dots. Multi-slice method in JEMS software [22] was used for image simulations, with the parameters set to 200 kV, a focus spread of 3.8 nm, and a chromatic aberration of 1.10 mm.

Atomic structure of disordered Cr₂N was studied by selected area diffraction (SAD) patterns analysis and the C_s-corrected HRTEM imaging. HRTEM and SAD simulations were used to confirm the atom positions. During the SAD analysis, a quantitative evaluation of reflection intensity, developed by Gammer et al., was used [23]. SAD patterns and HRTEM images were also used

to analyze the structure changes during the *hcp* to *fcc* structural transformation. Electron energy-loss spectroscopy (EELS) analyses were conducted to evaluate the N content change and possible fine structure variations during the structural evaluation.

Quantum mechanical first principles calculations were carried out within the framework of Density Functional Theory (DFT) as implemented in pseudopotential plane-wave Vienna *Ab initio* Simulation Package (VASP) [24–25]. Projector augmented-wave method potentials were used for Cr and N [26]. The exchange–correlation effects were treated within the generalized gradient approximation as formulated by Perdew et al. [27]. Plane wave cut-off energy of 500 eV and ~3500 k-points atoms were applied [28]. Spin-polarization of Cr atoms was considered. The assumed paramagnetic state was modeled using disordered collinear magnetic moments [28] distributed according to the special quasi-random structures approach [29–30].

3. Results

3.1. Phase composition

XRD phase analysis (Fig. 1) was conducted to clarify phases present in the as-deposited film. The diffraction peaks, labeled with trigonal coordinate notation (corresponding to the ordered Cr₂N, ICSD 240393 [1]), reveal that the film was composed mainly of the Cr₂N phase with a small amount of pure *bcc*-Cr (ICSD 64711 [31]). The growth direction of the Cr₂N film is usually perpendicular to the (1 1 1) plane [32]. Thus, the (1 1 0) and (0 0 2) peaks may be invisible in the XRD spectrum.

3.2. Atomic structure of disordered Cr₂N

3.2.1. Electron diffraction and HRTEM

Disordered Cr₂N was reported as a hexagonal structure, which corresponds to an *hcp* arrangement of Cr atoms with N atoms randomly distributed in octahedral interstices [11]. In general, electron diffraction pattern along the [210] direction illustrate the distribution of N atoms within the hexagonal structure. (0 0 1) and ($\frac{1}{3} \frac{1}{3} 1$) diffraction spots should be present in the case of the ordered Cr₂N (Note: in the ordered structure the Cr atoms are arranged with ordered N atoms exactly at the octahedral

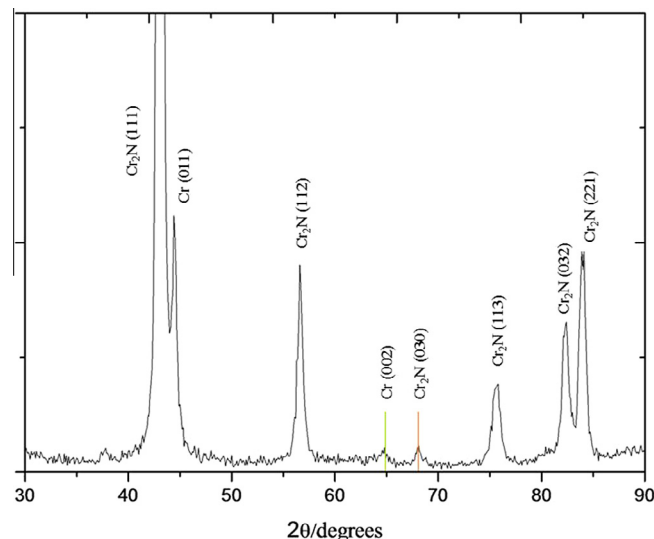


Fig. 1. XRD pattern of the Cr₂N film before an exposure to electron irradiation, and peaks are labeled by trigonal coordinates.

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