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Investigation of ordered structures in oxidation-synthesized  $\alpha$ -FeO nanowhiskers with Cs-corrected HR-TEM and monochromated core-loss EELS( Digest\_要約)

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# 学位論文の要約

題目 Investigation of ordered structures in oxidation-synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowhiskers with C<sub>s</sub>-corrected HR-TEM and monochromated core-loss EELS

(球面収差補正高分解能透過電子顕微鏡法と単色化内殻電子励起エネルギー損失分光法による酸化合成された $\alpha$ -酸化鉄ナノウィスカー中の規則構造の研究)

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## Chapter 1 Research background and motivation

Ordered structures are found in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowhiskers (NWs) synthesized via oxidation of iron-based substrates. (3 $\bar{3}$ 0)-related and (1 $\bar{1}$ 2)-related ordered structures have been observed to exist in NWs with the basal faces respectively perpendicular to the [001] direction and to the [ $\bar{1}$ 11] direction. They are believed to be related to oxygen vacancy ordering. Their formation reasons, however, were long unclear.

HR-TEM observations with spherical-aberration (C<sub>s</sub>) correction are available to have an information limit of 1 Å or better and much reduced image delocalization. The monochromated core-loss EELS technique enables the sensitive detection of crystal structure variations from the microchemical aspect. An integration of these two microscopic advancements brings an opportunity to ascertain the microstructural characteristics of the (3 $\bar{3}$ 0)-related and (1 $\bar{1}$ 2)-related ordered structures and thus their formation reasons.

## Chapter 2 Experimental method and detail

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NWs were synthesized via atmospheric thermal oxidation on 45 Permalloy at 550 °C. Analyses of the NWs were performed by using a monochromator-equipped double-C<sub>s</sub>-corrector TEM/STEM operated at an acceleration voltage of 200 kV. The C<sub>s</sub> value for HR-TEM observations of the ordered structures was tuned to be about -14  $\mu$ m. Both wide-range STEM-EELS acquisitions and monochromated O K-edge and Fe L<sub>2,3</sub>-edge STEM-EELS acquisitions were done.

## Chapter 3 Results and discussion

### 1. Ascertainment of the (3 $\bar{3}$ 0)-related ordered structure:

A negative-C<sub>s</sub>-imaging (NCSI)-based HR-TEM observation revealed that the crystallographic position of the (3 $\bar{3}$ 0)-related ordered structure was at interplanar gaps each between two adjacent (3 $\bar{3}$ 0) planes, designated as (3 $\bar{3}$ 0) gaps. By using atomic-column position analysis, the (3 $\bar{3}$ 0) gaps corresponding to the (3 $\bar{3}$ 0)-related ordered structure were found to exhibit positive width jumps. A further atomic-column arrangement inspection then helped identify that the (3 $\bar{3}$ 0)-related ordered structure was periodic local lattice expansions induced by oxygen vacancy accumulations.

Through comparing monochromated O K-edge EELS spectra of an as-synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NW with the basal faces perpendicular to the [001] direction and a stoichiometric  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> reference sample, it was observed that the average Fe-O and O-O interatomic distances in the NW were larger than in pristine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, for which the volume-averaged lattice expansion degree was evaluated to be ~0.8%. A following monochromated Fe L<sub>2,3</sub>-edge EELS study, together with an EELS-based quantitative comparison, provided evidence of oxygen deficiency in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NWs containing the (3 $\bar{3}$ 0)-related ordered structure.

The surface termination of the investigated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NWs was verified to be in accordance with the stoichiometric predictions, meaning their oxygen deficiency is a consequence of tensile strain that roots from their growth mechanism. Since the interaction energy of oxygen vacancies is reduced through aggregation, the emergence of the oxygen vacancy-induced ordered (3 $\bar{3}$ 0) gap expansions for strain accommodation is thermodynamically reasonable.

## 2. Ascertainment of the (1 $\bar{1}$ 2)-related ordered structure:

An HR-TEM FFT-based microstructure diagnosis revealed that the (1 $\bar{1}$ 2)-related ordered structure occurred in the [ $\bar{1}$ 11]-oriented grains of oxidation-synthesized [ $\bar{1}$ 11] || [001] bicrystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NWs. The formation of such  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NWs was subsequently deduced to be based on [001]-oriented matrix grains containing the (3 $\bar{3}$ 0)-related ordered structure, indicating the (1 $\bar{1}$ 2)-related ordered structure originates in the (3 $\bar{3}$ 0)-related ordered structure. This deduction was verified in a site-specific microstructural study of a partly overlapped [ $\bar{1}$ 11] || [001] bicrystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NW segment.

A detailed C<sub>s</sub>-corrected HR-TEM investigation pointed out that the (1 $\bar{1}$ 2)-related ordered structure was essentially periodic atomic-column displacements serving as tensile strain accommodation. The corresponding displacement scenario was suggested to be the splitting of neighboring atomic columns.

An O K-edge EELS fine-structure comparison similar to that above showed that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NWs hosting the (1 $\bar{1}$ 2)-related ordered structure had larger average O–O and Fe–O interatomic distances relative to pristine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Moreover, through a monochromated Fe L<sub>2,3</sub>-edge EELS study and an EELS-based quantitative comparison, it was identified that the (1 $\bar{1}$ 2)-related ordered structure was less oxygen-deficient than the (3 $\bar{3}$ 0)-related ordered structure.

## **Chapter 4 Conclusions**

The microstructural characteristic of the (3 $\bar{3}$ 0)-related ordered structure was revealed to be periodic (3 $\bar{3}$ 0) gap expansions induced by oxygen vacancy accumulations, forming to create a thermodynamically preferred route for accommodating the host NWs' internal tensile strain. The (1 $\bar{1}$ 2)-related ordered structure was identified to be essentially periodic atomic-column displacements serving as tensile strain accommodation, which originates in the (3 $\bar{3}$ 0)-related ordered structure.