Particle size dependence in thermal disorder/order transformation of FeCo alloy

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Abstract. FeCo alloy particles synthesized by liquid phase reduction are disorder distribution of the alloying elements in bcc crystalline lattice. The particle size dependence of thermally ordering behavior during heating was investigated. Superlattice lines such indices as 100, 111 etc., which appear in the x-ray diffraction pattern when the atomic arrangement is ordered, are difficult to detect due to quite small difference between Fe and Co in the atomic x-ray scattering factor. In this study, the energy near to Fe K absorption edge for incident x-ray was used in order to apply the anomalous x-ray dispersion effect. From results of the in situ heated x-ray diffraction experiments using the Synchrotron radiation source, different ordering-onset temperature was observed for the two samples with different particle size. This is considered due to a difference on the lattice distortion and its elimination during heating.

1. Introduction
FeCo alloys are known to be a fundamental material for many applications due to their soft magnetic properties [1]. Bulk Fe50Co50 alloy exhibits a body-centered cubic (bcc) structure below 983 °C, the temperature of transformation to a face-centered cubic (fcc) structure. And the alloy undergoes a crystalline phase transformation from disordered bcc structure (namely A2 phase) to ordered CsCl-type structure (namely B2 phase) at 730 °C [2]. Such order/disorder phase transformation has been studied using their change of physical properties such as the electrical resistivity, specific heat and the magnetization [3-6], structural change applying x-ray [3, 7], electron [8] and neutron [9, 10] diffraction techniques, or theoretical approach [11]. On the other hand, several nanometer to sub-micrometer sized particles of FeCo alloy system have been successfully synthesized by using a liquid phase reduction method namely polyol process in recent [12, 13]. In the synthesis process, poly alcohol such as ethylene glycol (EG) or tetraethyl glycol (TEG) is used as solvent. The poly alcohol (so called polyol) also act as reductant and dispersant during the precipitation of alloy particles. The particle size and the alloy composition can be controlled easily by tuning the reaction conditions such as kind of salt for metal precursor and its concentration, kind of polyol, reaction temperature, additives, etc. Degree of ordering in FeCo alloy system is important parameter relating with the magnetic properties. To determine directly the long range order parameter S using observed intensity of diffraction so called superlattice line is useful to investigate the process of thermal disorder/order and order/disorder transformation. For bulk FeCo relating alloys, such investigations by determination of S using neutron or electron diffraction have been studied. On the other hand, there had been almost no report using x-ray diffraction due to the marginal difference between Fe and Co in the amplitude of the atomic x-ray scattering factors when ordinary x-ray source such as Cu Kα radiation. Recently, the ordering degree...
in the FeCo alloy particles was investigated by using Co Kα radiation to apply the anomalous x-ray dispersion effect on Fe to enhance the difference between the atomic scattering factors of Fe and Co [14].

The atomic x-ray scattering factor \( f \) is described by the following equation,

\[
f(\sin \theta / \lambda, E) = f_0 (\sin \theta / \lambda) + f' (E) + i f'' (E) \quad (1)
\]

where, \( f' \) and \( f'' \) are the real and imaginary parts of the anomalous dispersion terms. The diffracted intensity of the \( hkl \) indices reflection \( I_{hkl} \) is related to the structure factor \( F_{hkl} \), multiplicity factor \( p \) and Lorentz-polarization factor \( LP \) as follows:

\[
I_{hkl} = |F_{hkl}|^2 \cdot p \cdot LP \quad (2)
\]

\( F_{hkl} \) of (110) fundamental line is represented by the sum of \( f \) for Fe and Co and independent of the degree of ordering. On the other hand, \( F_{hkl} \) of (100) superlattice line is described by \( F_{hkl} = S (f_{Co} - f_{Fe}) \) (0 < \( S < 1 \)) as a function of \( S \). The value of \( S \) can be obtained from the observed diffraction intensity ratio between (110) fundamental and (100) superlattice lines by the following equation,

\[
S^2 = (I_{100} / I_{110})_{observed} / (I_{100} / I_{110})_{calc} \quad (3)
\]

\( (I_{100} / I_{110})_{calc} \) is the ratio calculated on the assumption of perfectly ordered, \( S = 1 \). The plot of \( |F_{100}|^2 \) variation in consideration of the anomalous dispersion terms vs. the incident x-ray energy around the Fe K (7111 eV) and Co K (7709 eV) absorption edges is shown in Fig. 1. \( I_{100} \) is almost zero even in perfectly ordered structure at the energy of Cu Kα radiation. The (100) superlattice line is detectable when Co Kα radiation is used, and it was found that the atomic distribution in the crystalline lattice of as-synthesized FeCo alloy particles is random [14]. This feature of atomic arrangement in the liquid phase synthesized particles is not found in bulk FeCo alloys. The arrangement was ordered gradually with increase of temperature at above approximately 400 °C. Such thermal “disorder/order” transition behavior is unique in the liquid phase synthesized FeCo alloy particles. Although its size-dependence can be easily predicted, the detection of weak peak intensity and accurate determination of \( S \) in the initial ordering stage are quite difficult. In this study, the XRD measurements were carried out at just below the Fe K absorption edge of 7086 eV using a synchrotron radiation to make more effective in enhancement of superlattice diffraction intensity than using Co Kα radiation.

![Figure 1. The square of structure factor for (100) superlattice line.](image)

2. Sample preparation

The FeCo alloy samples with different particle size were synthesized by using the polyl process. The procedure is as follows: Iron chloride tetrahydrate (FeCl\(_2\) \cdot 4H\(_2\)O), cobalt acetate tetrahydrate (Co(CH\(_3\)COO)\(_2\) \cdot 4H\(_2\)O), polyvinylpyrrolidone (PVP) as dispersant and sodium hydroxide (NaOH) were dissolved in EG. The total concentration of metal salts and amount of PVP were 0.03 mol/L and
50 g/L, and 0.05 mol/L and 5 g/L for the large and the small particle samples, respectively. The concentration of NaOH was 0.2 mol/L for both. The solution was heated up to the reaction temperature of 130 °C, and refluxed for 1 hour. After the precipitation reaction the suspension was cooled to room temperature, and the formed particles were centrifuged, washed with ethanol several times. The chemical composition of Fe : Co analyzed by EPMA and average particle size are listed in Table 1. The morphology of the as-synthesized particles is shown in Fig. 2.

### Table 1. Chemical composition and average particle size of as-synthesized particles.

| Sample  | Fe : Co | Particle size |
|---------|---------|---------------|
| A (large) | 50.7 : 49.3 | 170 nm |
| B (small) | 51.5 : 48.5 | 80 nm |

3. X-ray diffraction measurements

*In situ* x-ray diffraction (XRD) measurements to analyze the thermal variation of $S$ were performed at BL19B2 in SPring-8 (proposal No. 2009A1777). The Debye-Scherrer camera with imaging plate mounted at the position at camera length of 286.5 mm as media for detecting the diffraction intensity profiles was used. The FeCo alloy powder samples were sealed in a glass capillary of 0.5 mm in diameter under an oxidation-free atmosphere. In the *in situ* XRD experiments, the sample was heated with a N$_2$ gas flow system with a conical nozzle at temperature between RT and 770 °C. At each measuring temperature, two exposures for 30 min were carried out after 30 min interval. Achieving equilibrium in the ordering degree was confirmed by comparison of the two diffraction patterns.

4. Results

Any oxide or other crystalline phases were not detected even after the high-temperature *in situ* XRD experiments, as shown in Fig. 3(a). After heating up to 770 °C, (100) and (111) superlattice lines were clearly observed. Fig. 4 shows variation of $S$ calculated from the intensity ratio of (100) superlattice line shown in Fig. 3(b) and (110) fundamental line. The random structure in as-synthesized sample was ordered with increasing the temperature above 300 °C, and disordered again immediately after exceeding the order/disorder transition point of 730 °C. The ordering-onset temperature of sample B was higher than that of sample A.

![Figure 2. SEM images of as-synthesized samples A (left) and B (right).](image)

![Figure 3. Observed XRD patterns of the samples as-synthesized and after in situ experiments (a), (100) superlattice line profiles during heating (b) for sample A.](image)
Fig. 5 shows the Williamson-Hall plot using the three fundamental lines of (110), (200) and (211) for the samples A and B as-synthesized and after 400 °C annealing. The XRD measurements were carried out using Cu Kα at room temperature. The two as-synthesized samples were similar in both the size component from the intercept and the strain component from the slope. On the other hand, although the crystallite size of the annealed samples is not change, the strain in the smaller sample B is still large in comparison with that in another sample. This difference of strain is considered relating with the degree of ordering. The fraction of surface in sample B is larger than A. Therefore, a resistance to thermally reduction of the lattice strain in sample B is larger probably due to presence of a resist layer on the surface of particles. The surface layer will be lattice defect, surface oxidation, or deviation of the surface alloy composition from the average. The authors found an alloy compositional gradation in the surface layer on the FeCo particles synthesized by the polyol process [15].

5. Conclusion
The thermal ordering behavior was investigated by in situ XRD measurements applying anomalous x-ray dispersion effect. Particle size dependence in the ordering-onset temperature was indicated. Such difference in the transformation behavior is considered due to higher resistance to reduction of strain by defect, oxide layer or composition gradation in the surface of particles.

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