BL-6C/2014G691

Anisotropic thermal expansion in Invar alloys

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Fe and Ni $K\alpha$ x-ray fluorescence holography measurements were employed for drawing three-dimensional atomic images of a $Fe_{66}Ni_{34}$ Invar alloy around the Fe and Ni central atoms, respectively. The obtained atomic images around the Ni central atom show the usual *fcc* atomic arrangement as predicted with x-ray diffraction. However, those around the Fe central atom exhibit a *bcc*-like atomic arrangement in the near region. This result suggests that the Invar effect shown in the $Fe_{66}Ni_{34}$ alloy would be explained by a gradual structural change in the local structure from sparse *bcc* to dense *fcc* with increasing temperature, and the spin transformation may be a phenomenon accompanied by such a structural change.

1 Introduction

In 1897, Guillaume [1] discovered an Invar alloy of $Fe_{66}Ni_{34}$, which has anomalously small thermal expansion over a wide temperature range. This effect has been utilized in various kinds of industrial products. It has been recognized for a long time that the Invar effect originates from magnetism, i.e., there are two types of electronic states in Fe, typically high-spin (HS) and low-spin (LS) states [2]. In this two-states model, the equilibrium potential energy is lower in the HS state than that in the LS one, while the atomic radius is larger in the former. These assumptions result in the competition of thermal expansion due to the increase of density in the LS state at high temperatures.

Recently, Yokoyama and Eguchi [3] discussed their XAFS results on $Fe_{64.6}Ni_{35.4}$ by comparing with those of x-ray diffraction (XD). It was found that the local bond distance around the Fe atom and the lattice constant remain almost unchanged with varying temperature as the macroscopic thermal expansion indicates, while the local bond distance around the Ni atoms shows a usual thermal expansion with increasing temperature. These experimental results imply a curious local atomic arrangement in this Invar alloy that with increasing temperature, the Ni atoms having an elongated interatomic bonds should squeeze into the same size of the crystal lattice, suggesting large lattice distortions around the minority Ni atoms and also the fundamental lattice of majority Fe atoms.

X-ray fluorescence holography (XFH) is a newly developed technique for atom-resolved structural characterizations of materials, and enables one to draw three-dimensional (3D) atomic images around a specific element emitting fluorescent x-rays [4]. Owing to an interference between direct incident x-rays and those scattered by surrounding atoms, the fluorescent x-ray intensity from the emitter slightly modulates with incident x-ray angles by about 0.1 %, from which 3D images of neighboring toms can be obtained by simple Fourier transforms without any special atomic models. This technique has, in particular, an excellent potential for investigating local structures around minority atoms [5]. Another advantage of this technique is that positional fluctuations of individual neighboring atoms can be evaluated in the radial and angular directions separately by comparing with theoretical calculation and XAFS results [5].

We have recently measured Fe and Ni $K\alpha$ XFH on $Fe_{66}Ni_{34}$ single crystal Invar alloy at room temperature, and obtained an unexpected and interesting result, which will be reported in this paper in detail.

2 Experiment

The single crystal of $Fe_{66}Ni_{34}$ Invar alloy was grown at Cooperative Research and Development Center for Advanced Materials, Institute for Materials Research, Tohoku University. The crystal was cut and polished so as to have a flat (111) surface of about 10 mmϕ. The crystallinity was examined by taking a Laue photograph, and the concentration and homogeneity were confirmed over the sample within the experimental errors by an electron-probe micro-analysis.

Fe and Ni $K\alpha$XFH measurements on $Fe_{65}Ni_{35}$ Invar alloy were carried out at room temperature at BL-6C of the Photon Factory in the High Energy Accelerator Research Organization (PF-KEK), Tsukuba, Japan. The sample was placed on a two-axes table of a diffractometer. The measurements were performed in inverse mode by changing two axes, the exit angle of $0° \leq \theta \leq 75°$ in steps of 1.00° and the azimuthal angle of $0° \leq \phi \leq 360°$ in steps of about 0.35°. Incident x-rays were focused onto the (111) surface of the sample. Fe or Ni $K\alpha$ fluorescent x-rays were collected using an avalanche photodiode detector with a toroidal graphite crystal energy analyzer. The XFH signals were recorded at eight different incident x-ray energies from 7.5 to 11.0 keV for Fe and from 8.5 to 12.0 keV for Ni in steps of 0.5 keV. Details of the experimental setup are given elsewhere [4].

Holographic oscillation data were obtained by subtracting the background from the fluorescent x-ray intensities. An extension of the hologram data was carried out using the crystal symmetries of the *fcc* structure [3] and the measured x-ray standing wave lines. From the hologram patterns, 3D atomic configuration images were reconstructed using Barton's algorithm [6] by superimposing the holograms with eight different incident x-ray energies, which can highly suppress the appearance of twin images.

3 Results and Discussion

Figure 1(a) shows atomic images around the Ni central atom on the (001) plane obtained from Ni *Kα*XFH measurement. The dashed lines indicate unit cells of the *fcc* structure for the $Fe_{66}Ni_{34}$ Invar alloy obtained from XD measurement [3]. The characteristic image for the *fcc* structure is located at the center of the squares in addition to those at the intersections of the unit cells. Although large lattice distortions were expected from previous XAFS and XD measurements [3], such distortions are hardly seen in the XFH images.

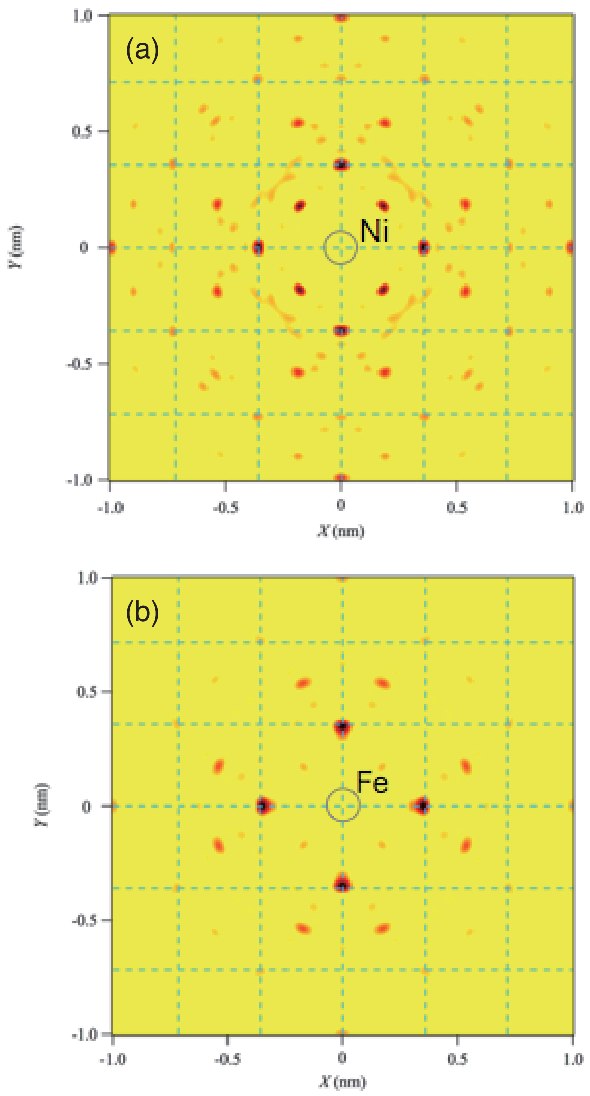

Fig. 1: Atomic images of $Fe_{66}Ni_{34}$ Invar alloy around the (a) Ni and (b) Fe central atoms on the (001) plane obtained from Ni and Fe *Kα*XFH measurements, respectively.

Figure 1(b) shows atomic images around the Fe central atom on the (001) plane obtained from Fe *Kα*XFH measurement. The dashed lines also indicate unit cells. A feature very different from Fig. 1(a) is that the images at the center of the squares are very weak, indicating that the local atomic configurations around the Fe atom would be a *bcc*-like structure, the same as that in pure Fe crystal. Note that such a *bcc*-like structure is limited in the first cell, and the *fcc*-like structures look to be recovered in the distant unit cells.

From the present XFH experiments, a new idea is suggested for the Invar effect in the $Fe_{66}Ni_{34}$ Invar alloy that with increasing temperature, local structures around the Fe atoms gradually change from sparse *bcc*-like to dense *fcc*-like, and the change of the HS-LS spin states may be accompanied by the gradual structural change with temperature. Detailed discussion is necessary by obtaining further structural investigations using Mössbauer spectroscopy and XAFS measurements, which are now in progress.

Acknowledgement

The authors thank Professor S. Sasaki and Dr. M. Okube for the support of the XFH experiments. The experiments were performed at BL-6C (No. 2014G691). This work was supported by Grant-in-Aid for Scientific Research on Innovative Areas "3D Active-Site Science" (No. 26105006).

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