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Quantitative Chemical State Analysis of Ti and Mo in a High Strength Steel Using X-Ray Absorption Fine Structure (XAFS)[†]

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Abstract:

An X-ray absorption fine structure (XAFS) technique with the X-ray fluorescence yield mode was applied to a non-destructive chemical state analysis of Ti and Mo in a Ti-Mo added high-strength steel. The Ti-K and Mo-K edge XAFS spectra clearly showed a transition of Ti and Mo from in solution form in the α-Fe matrix to a carbide form with heat treatments. The authors propose this XAFS analysis for the quantification of the fraction of the precipitation of micro-alloy elements. The analysis revealed a significant difference between the precipitation kinetics of Ti and Mo in the steel.

1. Introduction

There recently has been an increasing demand for improved high-strength steel sheets to achieve lighter-weight designs for automobiles without sacrificing safety. Steelmakers have extensively developed high-strength steel sheets with highly controlled steel and precipitate microstructures. JFE Steel released a new hot-rolled high-strength steel with 780 MPa grade tensile strength and outstanding stretch flange formability. The key technology behind the outstanding mechanical properties of this steel is based on the very fine Ti-Mo carbides in the ferrite matrix[1–3]. To succeed in the design of high-strength steel sheets strengthened by nanometer-sized precipitates, steelmakers will need to clarify the sizes and amounts of the precipitates used.

Analysis methods are used in combination with analytical electron microscopy (AEM) and the electrolytic extraction method to investigate the precipitates in steel. Investigators can now directly observe precipitates as small as a few nanometers in diameter and analyze their chemical compositions and crystal structures by AEM[3]. As of this writing, however, limitations of the areas analyzed make it difficult to ascertain the total amounts of precipitates. The electrolytic extraction methods tend to underestimate the amounts of very fine precipitates, as small precipitates readily dissolve into solutions or leak through filters during extraction.

In earlier studies we investigated the chemical states of micro-alloy elements using X-ray absorption fine structure (XAFS) spectroscopy[4–7]. XAFS is widely used to study the short-range structures of specific elements applied as catalysts, amorphous materials, and nanometer-sized materials[8,9]. Very few studies, however, have focused on crystalline materials such as steel. In this paper the authors report the application of XAFS to an investigation of the chemical states of micro-alloying elements and a quantification of the atomic fractions of the elements in precipitates. We present and discuss the results for a Ti-Mo added steel.

2. Experimental

2.1 Sample Preparation

The experiments were performed using hot-rolled steel sheets coiled at 530°C, 575°C, and 675°C. The

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steel had a chemical composition of 0.04%C-1.3%Mn-0.1%Ti-0.2%Mo. A reference specimen with Ti and Mo atoms residing almost exclusively in solution form in the α-Fe matrix was prepared by soaking a piece of steel with the same composition at 1 250°C and then quenching it from 900°C. An extraction residue was taken from the steel sheet coiled at 675°C by the electrolytic extraction method as a reference for the Ti-Mo complex carbide[1–3)]. To simulate the hot-rolling process, a piece of steel with a chemical composition similar to that mentioned above was quenched from 625°C after a holding period of 0 min to 60 min. The cross sections of the steel specimens were mirror-polished for the XAFS measurement.

2.2 XAFS Measurements

XAFS is fine structures appearing on the X-ray absorption spectra obtained by measuring the change of the X-ray absorption coefficient as a function of X-ray energy around the absorption edge of the element of interest. XAFS provides important information about chemical bonding states of specific elements and short-range order structures around the atoms. Conventional XAFS measurements are carried out by a transmission mode in which the X-ray intensities are measured before and after transmission onto a thin specimen. The X-ray fluorescence mode, a technique for monitoring the intensity of fluorescence X-rays emitted from specimens by X-ray absorption, has excellent sensitivity. The authors used the latter technique because of the low Ti and Mo concentrations in the specimens in the present study.

The XAFS measurements were carried out using a station BL27B at the Photon Factory, High Energy Accelerator Research Organization (2.5 GeV; Tsukuba, Ibaraki, Japan) with a two-crystal Si (111) monochromator. The directions of the incident X-ray and the detected X-ray were 45° to the normal direction of the sample surfaces and on the polarized light plane of the incident X-ray. Ti-K edge and Mo-K edge XAFS spectra were measured using a Lytle-type detector or multi-element solid-state detector. The XAFS data provided averaged information from a sample surface measuring 1 mm × 6 mm–10 mm, an area which corresponds to the irradiation area of the incident X-ray.

3. Results and Discussions

3.1 Change of XAFS Spectra with Coiling Temperature

Figure 1 shows the Mo-K edge XAFS spectra for specimens of Ti-Mo added steel coiled at 530°C (b), 575°C (c), and 675°C (d). Spectra for the specimen quenched from 900°C (a) and carbides extracted from the steel (e) are also presented.

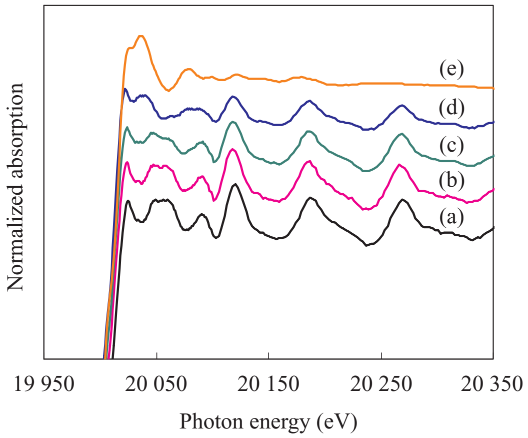

Fig. 1 Mo-K edge XAFS spectra for Ti-Mo bearing steel (900°C-quenched (a), coiled at 530°C(b), 575°C(c), 675°C(d), and carbides extracted electrolytically from the steel(e). The spectrum for the steel gradually changed as the coiling temperature rose ((b)-(d)).)

The XAFS spectra are usually divided into two parts by the photon energy region. The X-ray absorption near-edge structure (XANES) in the energy region from the absorption edge up to about 50 eV (20 020 eV–20 080 eV in Fig. 1) is used to estimate the chemical states of elements by comparison with measured or calculated spectra for reference materials. The extended X-ray absorption fine structure (EXAFS) is the intensity oscillation in the energy region higher than XANES (higher than about 20 080 eV in Fig. 1). EXAFS is used to analyze short-range structures such as the bonding length and coordination number.

The XAFS spectrum (b) for steel coiled at 530°C is indistinguishable from that for the specimen quenched from 900°C (a). This indicates that almost all of the Mo atoms in this specimen existed in solution form in the Fe matrix. A peak at about 20 030 eV appeared in the spectra (c) and (d) for the steel sheets coiled at 575°C and 675°C, respectively. This strongly suggests that some of the Mo atoms formed carbides in these specimens, as the position of the peak was close to that for the carbides shown in the spectrum (e).

The amplitude of the EXAFS oscillation (peaks at 20 120 eV, 20 190 eV, and 20 270 eV are clearly seen) dropped as the coiling temperature rose. The Fourier transforms (FTs) of the k^3-weighted EXAFS spectra were obtained from the spectra shown in Fig. 1 and are shown in **Fig. 2**. The FT relates to the radial distribution function of the nearest neighbor atoms around the Mo atoms. The FT for the specimen quenched from 900°C had a typical pattern for the bcc-metal, although the k range used for the FT was too narrow to separate peaks of the 1st and 2nd (also 4th and 5th) nearest neighbors. This tells that the Mo atoms substituted for the Fe atoms in the bcc-Fe matrix. The peaks in the FT dropped as the

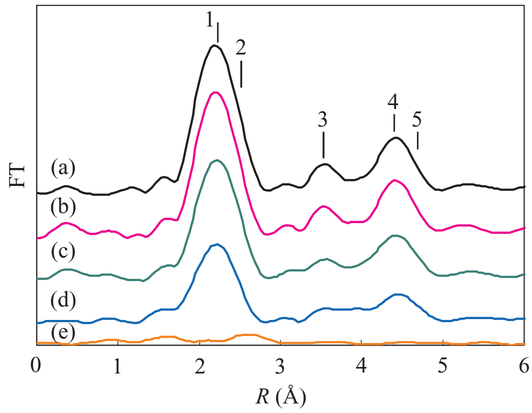

Fig. 2 Fourier transformation (FT) of Mo-K EXAFS for Ti-Mo bearing steel (900°C-quenched(a), coiled at 530°C(b), 575°C(c), 675°C(d), and carbides electrically extracted from the steel (e). FTs of (a)–(d) show typical patterns of a bcc structure, including evidence of Mo in solution form in the bcc-Fe matrix. The positions of the 1st–5th nearest neighboring Fe atoms are denoted by italic numbers.)

coiling temperature rose, while the FT pattern hardly changed. The reduction of the FT peak intensity can be attributed to the decreased number of Mo atoms substituting for the Fe atoms in the matrix due to the precipitation of the carbides.

The XANES and EXAFS spectra changed corresponding to the transition from Mo in solution form in α-Fe matrix to Mo of a carbide form as the coiling temperature rose.

3.2 Method for Quantifying Atomic Fraction of Precipitates

The authors have proposed a method for determining the atomic fractions of micro-alloying elements in an α-Fe matrix and in precipitates by XANES and EXAFS[4–6]. This paper presents and discusses the use of the EXAFS method. The Mo atoms in solution form in the α-Fe matrix dominated the EXAFS signal intensity, while the precipitated carbides showed only a weak EXAFS amplitude (Fig. 1, 2). The ratio of the FT intensity of the 1st and 2nd nearest neighboring Fe atoms (the strongest peak of FT in Fig. 2) of the specimens to the FT intensity of the reference specimen quenched from 900°C was calculated as the relative number of Mo atoms in solution form. For the specimens in which large numbers of interest atoms are in carbide form, the reference spectrum for the carbide was also used to extract the EXAFS signals of the atoms in solution form from the EXAFS data.

Table 1 shows the atomic fractions of the precipitated Mo estimated by this method for the Ti and Mo added steel. The results obtained by the conventional electrolytic extraction method are also shown for the steel specimens coiled at 575°C and 675°C. The EXAFS analysis provides a value about 70% higher than the value provided by the electrolytic extraction method for the steel coiled at 575°C. Small precipitates probably dissolved into the solution or leaked through the filter during the extraction in the conventional method. These results show the promise of XAFS as a powerful tool for estimating the fractions of even nanometer-sized precipitates. The proposed method is based on the reduction in the number of carbide-forming elements substituting the Fe sites in the bcc matrix. Thus, the technique will be applicable to precipitates smaller than a few-nanometers in the early stages of precipitation.

Table 1 Fraction of precipitated Mo determined by EXAFS analysis for Ti-Mo bearing steel coiled at 530°C, 575°C, and 675°C (The results obtained by the typical extraction method (Res.) and the differences from the XAFS (▲) are also presented.)

T (°C)	Fraction of segregation (%)		
	EXAFS	Res.	▲ (%)
530	4	—	—
575	18	5	70
675	49	41	15

3.3 Precipitation of Ti and Mo during Hot-Rolling Process

Ti-K and Mo-K XAFS spectra were measured for specimens quenched from 625°C after a holding period of 0 to 60 min at 625°C, in order to clarify the precipitation kinetics of Ti and Mo. **Figure 3** shows the atomic fraction of precipitated Ti and Mo as a function of holding time, determined by the methods mentioned in the previous section. The atomic fraction of Ti in the precipitates rose rapidly from the outset of the holding period at 625°C, reaching a constant level in 10 min. In contrast, the atomic fraction of Mo in the precipitates increased gradually even after the saturation of the Ti

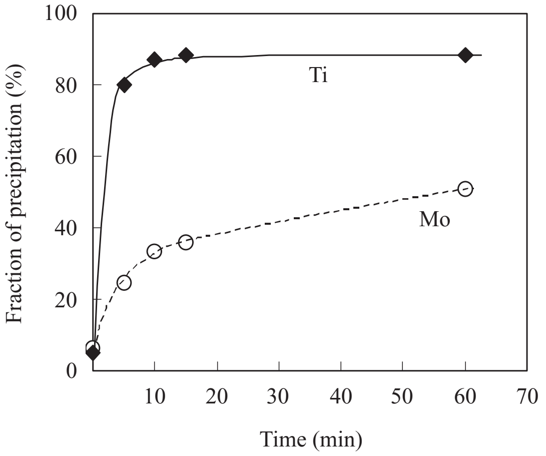

Fig. 3 Changes of the atomic fraction of precipitation determined by EXAFS analysis as a function of annealing time at 625°C for Ti and Mo in Ti-Mo bearing steel

precipitation. These results demonstrate a significant difference between the precipitation kinetics of the Ti and Mo in the steel: Ti precipitated much faster than Mo during the annealing. This difference may relate to the mechanisms by which nanometer-sized Ti-Mo complex carbides are formed in Ti-Mo added high-strength steel.

4. Summary

The paper of the authors demonstrates the considerable power of the fluorescence mode XAFS as a tool for the chemical state analysis of micro alloying elements in steel. The atomic fraction of precipitates and elements in solution form was successfully quantified for Ti and Mo in a Ti-Mo added high-strength steel. This technique can be applied even when the size of the precipitates is on the order of a single nanometer. The spatially averaged quantitative information on chemical states provided by the XAFS technique complements the data from direct imaging techniques such as AEM. This and future studies on micro-alloying elements will certainly contribute to the design of high-strength steels with excellent properties based on precipitation-strengthening strategies.

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References

1) Tomita, T.; Funakawa, M.; Shiozaki, T.; Maeda, E.; Yamamoto, T. Materia. vol. 42, 2003, p. 70–72. (Japanese)
2) Funakawa, Y.; Shiozaki, T.; Tomita, K.; Yamamoto, T.; Maeda, E. ISIJ Int. vol. 44, 2004, p. 1945–1951.
3) Sato, K.; Nakamichi, H.; Yamada, K. Kenbikyou. vol. 40, 2005, p. 183. (Japanese)
4) Nagoshi, M.; Kawano, T.; Sato, K.; Funakawa, Y.; Shiozaki, T. CAMP-ISIJ. vol. 15, 2002, p. 1368. (Japanese)
5) Nagoshi, M.; Kawano, T.; Sato, K.; Funakawa, Y.; Shiozaki, T.; Kobayashi, K. User Experiment Report SPring-8 (2003A). no. 11, 2003, p. 12.
6) Nagoshi, M.; Kawano, T.; Sato, K.; Funakawa, Y.; Shiozaki, T.; Kobayashi, K. Physica Scripta. T115, 2005, p. 480–482.
7) Kawano, T.; Nagoshi, N.; Sato, K.; Funakawa, Y.; Shiozaki, T. CAMP-ISIJ. vol. 19, 2006, p. 586. (Japanese)
8) Udagawa, Y., ed. X-Ray Absorption Fine Structure. Gakkai-shuppan Center, 1993. (Japanese)
9) Ohta, T., ed. “X-ray Absorption Spectroscopy—XAFS and Application”. ICP, 2002. (Japanese)