Low Temperature XRF-yield XAFS of low concentration Mo in steel

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Abstract. Low temperature x-ray fluorescence yield x-ray absorption fine structure measurements have been carried out for 0.2 mass% Mo in steel and carbides extracted from a steel sample. The increase in amplitude of the extended x-ray absorption fine structure, at 8 K, was larger for Mo in bcc-Fe matrix than for Mo in carbides. This is explained by the differences in distortion of the local structure around Mo atoms between the two chemical states. The Ratio method was applied to the EXAFS, measured at 8 K, for the Fe atoms surrounding the Mo in the bcc-Fe matrix. The atomic fraction of the Mo in solution and Mo as carbides in steel was determined by this technique.

1. Introduction

Micro-alloying elements added to steel dramatically change the properties of steel products such as strength and corrosion resistance. It is important to understand the roles of these elements on the properties of the steel for designing micro-alloyed steel products of superior performance.

Nanometer-sized precipitates formed by micro-alloying elements effectively improve the strength of steel. These precipitates have been directly observed by microscopic analytical techniques such as transmission electron microscopy (TEM) [1] and atom probe (AP) microscopy. [2] XAFS is a powerful tool for clarifying the local structures of specific elements forming the nanometer-sized precipitates. [3-5] Especially, x-ray fluorescence (XRF) yield XAFS techniques have the advantages of high detectability and quantitative analysis performance for the chemical states of micro-alloying elements in steel. [6] Therefore XAFS and microscopic techniques are complementary in revealing all the added elements in steel. [3,7]

Low temperature measurements enhance the amplitude of extended x-ray absorption fine structure (EXAFS) due to the reduction of thermal fluctuations of atoms. Although this technique has been used in much basic research [8,9], there are very few studies applying it to micro-alloying elements using XRF-yield XAFS. In this study, low temperature XRF-yield XAFS measurements have been applied to Mo added to steel in order to obtain detailed information about the local structures. XAFS spectra measured for Mo in steel at low temperature and room temperature (RT) are presented and discussed in terms of the local structure of Mo and its analysis technique.

2. Experimental

The XAFS experiment was carried out at beam line BL01B1, SPring-8 (Hyogo, Japan) with a two-crystal Si (111) monochromator. The Mo-K edge XAFS spectra were recorded in the x-ray fluorescence mode with a 19-element Ge solid-state detector. The samples were cooled to 8 K using a He cryostat equipped with the beam line. The analysis of the XAFS spectra was performed with commercial software (Rex 2000, Rigaku Corp.).

Chemical composition of the base steel was 0.04mass%C-1.5mass%Mn. Ti and Mo were added as atomic ratios of Ti/C = 0.5 and Mo/C = 0.6. Two steel samples were prepared. Sample A was obtained by quenching from 900 °C to room temperature. This sample was used as a reference for Mo which is substitutional in the bcc-Fe matrix. Sample B was obtained by hot-rolling with a coiling temperature of 650 °C. The details concerning this steel were reported in ref [10]. Mo-containing carbides, with the diameter of a few nanometers, were observed by TEM for Sample B. Residue extracted from Sample B was obtained by the electrolytic extraction method and measured by XRF-yield XAFS as a reference for the carbides formed in Sample B.
3. Result and discussion

Figure 1 shows Mo-K edge x-ray absorption near edge structure (XANES) spectra measured at RT and 8 K for Sample A, Sample B, and residue extracted from Sample B. The XANES spectra measured at 8 K and at RT are indistinguishable from each other for all samples. These results show that the chemical state of Mo at RT in steel and in carbides hardly changes at 8 K. The XANES spectra for Sample B have the characteristics of those for both Sample A and Residue. This shows that the Mo atoms in Sample B are partially precipitated as carbides and the remainder are retained in the bcc-Fe matrix.

![Normalized Mo-K edge x-ray fluorescence XAFS spectra for Sample A, Sample B, and residue extracted from Sample B. The spectra measured at RT and at 8 K are denoted as broken and solid lines, respectively.](image1)

![k^3-weighted EXAFS spectra for Sample A, Sample B, and the extracted residue (carbides) from Sample B. The spectra measured at RT and at 8 K are denoted as broken and solid lines, respectively.](image2)

Figure 2 shows $k^3$-weighted EXAFS for Sample A, Sample B, and extracted carbides from Sample B. In the figure, the spectra measured at RT and 8 K are denoted as broken and solid lines, respectively. The EXAFS oscillations for Sample A originated from Fe atoms surrounding Mo atoms in the bcc-iron matrix. The EXAFS for Sample B has almost the same structure as that of Sample A except for the weaker amplitude. This is explained by the reduction of the number of Mo atoms in the bcc-Fe matrix due to the precipitation of Mo as carbides as indicated in Fig.1. The EXAFS oscillation for the carbides is very weak as shown in Fig. 2 and invisible in the EXAFS for Sample B. The difference of the EXAFS amplitude between the steel and carbide samples is caused by the difference of the Deby-Wallar factor (DW factor; $\sigma$) as well as by the differences of the scattering amplitude and the number of the neighboring atoms.

The amplitude of the EXAFS measured at 8 K was higher than that measured at RT and clearer oscillations were observed, especially in the high $k$ region for Samples A and B. The Fourier transforms (FT) derived from the $k^3$-weighted EXAFS measured at 8 K show discriminating peaks from the 1st to
Fig.3 Fourier transforms of $k^3$-weighted Mo-K edge EXAFS spectra measured at 8 K for Sample A, Sample B, and extracted residue (carbides) from Sample B. The $k$ range for FT is 3 – 19.5 Å$^{-1}$ for the steel samples and 3 – 12 Å$^{-1}$ for the residue sample.

On the other hand, the increase of EXAFS amplitude at 8K for the carbides is small when compared with those for Samples A and B. (Fig.2)

The DW factor was estimated for the 1st NN Fe atoms around the Mo by the carve-fitting method, assuming that the coordination number (CN) is 8 for Sample A. The DW factor was 0.064 Å at RT and 0.041 Å at 8 K and the difference of $\sigma^2 (\Delta \sigma^2 [RT – 8 K])$ is 0.0024 Å$^2$. The latter value was also confirmed by the Ratio method.[7] The differences of $\sigma^2$ were estimated for the first shell as $\Delta \sigma^2 [300 K – 77 K] \sim 0.0047$ Å$^2$ for Cu [8] and $\Delta \sigma^2 [300 K – 40 K] \sim 0.005$ Å$^2$ for Ni [9] from the previous reports. Our datum for the Mo in the bcc-Fe matrix is about half of the previous results for pure metal. The DW factor can be divided into two parts corresponding to thermal and static fluctuations.[11] The smaller temperature dependence of the DW factor for Sample A suggests a relatively large static fluctuation compared with pure metal. This can be explained by distortion in the bcc-Fe lattice adjacent to the Mo atoms in the bcc-Fe matrix because the atomic radius of bcc- Mo (0.136 nm) is different from bcc- Fe (0.124 nm). The difference in the amplitude of the EXAFS between RT and 8 k for Mo in carbides is remarkably small. We consider that one of the reasons for this result is the large static fluctuation of the carbide structure. The nanometer-sized carbides in this type of steel have been reported as (Ti, Mo)C with a NaCl type structure.[10] The distortion caused by the coexistence of Mo and Ti in the carbide particles and the surface effects resulted from the nanometer size of the particles probably are the reasons for the large static fluctuation around the Mo atoms in the carbides.

At low temperatures, the difference in amplitude of EXAFS oscillation between Mo in the bcc-Fe matrix and in carbides increases, which would improve the quantitative analysis of the atomic fraction of Mo in the bcc-Fe matrix and in the precipitates using the curve-fitting for EXAFS.[6] However, the
estimated fraction of the former Mo from the EXAFS measured at 8K, 51 %, was almost the same as that from the EXAFS measured at RT, 50 %, for Sample B.

The Ratio method [8] can be applied to EXAFS measured at 8 K for determining the coordination number (CN) of Fe atoms around Mo atoms in the bcc Fe-matrix because the different NN Fe atoms are clearly distinguished as shown in Fig.3. This method provides relative CNs for each NN Fe atom without fitting techniques. The results are shown in Fig.4 for the 1st to the 5th NN Fe atoms around Mo for Sample B when Sample A is used as reference. The relative CN of Fe atoms for Sample B to Sample A are between 0.51 and 0.54. This is in good agreement with the values estimated by the curve-fitting methods mentioned above.

4. Conclusion

The XRF-mode XAFS measurements were carried out for low concentration Mo in steel at RT and 8 K. The difference in the DW factor between RT and 8 K for Mo in bcc-Fe was lower than those reported for pure metals. Mo in carbides showed very small differences in the EXAFS amplitude between RT and 8 K compared to Mo in the matrix. These results suggest relatively ordered and strongly distorted local structures around Mo atoms in matrix and carbides, respectively. The ratio method was successfully applied for the 1st to the 5th NN Fe atoms surrounding Mo atoms in the bcc-Fe matrix using EXAFS measured at 8K. The low temperature XRF-XAFS is useful for further investigation of the local structures of the micro-alloying elements in steel.

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