Structural and hyperfine characterization of σ-phase Fe−Mo alloys

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ABSTRACT

A series of nine samples of σ-Fe$_{100-x}$Mo$_x$ with $44 \leq x \leq 57$ were synthesized by a sintering method. The samples were investigated experimentally and theoretically. Using X-ray diffraction techniques structural parameters such as lattice constants, atomic positions within the unit cell and populations of atoms over five different sublattices were determined. An information on charge-densities and electric field gradients at particular lattice sites was obtained by application of the Korringa−Kohn−Rostoker (KKR) method for electronic structure calculations. Hyperfine quantities calculated with KKR were successfully applied to analyze Mössbauer spectra measured at room temperature.

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1. Introduction

A σ-phase (space group P4$_2$/mnm, 30 atoms per unit cell), which belongs to a class of the so-called Frank−Kasper phases [1] characterized by a high coordination numbers (CN = 12−15, for σ) can be formed in alloy systems by a solid state reaction at elevated temperatures. About 50 examples of σ were up-to-now found in such binary systems, including the Fe−Mo one. A possibility of occurrence of the σ-phase in Fe−Mo was first revealed in 1949 by Goldschmidt [2]. Studying a ternary system of Fe−Cr−Mo, he had identified a new phase stable in the temperature interval of 1180−1540 °C. The phase had some similarities to the already-known σ-phase in Fe−Cr. Its crystallographic structure and parameters were definitely identified five years later [3]. Wilson was the first who determined the lattice parameters and distribution of atoms over the five sublattices for σ-Fe$_{50}$Mo$_{50}$ sample [4]. Further investigations depicting the structure and sites occupancy by Fe and Mo atoms were continued by other investigators, too [5,6]. Heijwegen determined borders for the existence of the σ-phase in the Fe−Mo system [7]. Finally, the phase diagram which is regarded as the most actual was proposed by Guillermet [8].

In the Fe−Mo system, the σ-phase is one of three Frank−Kasper phases that can occur in that system. The other two ones are represented by μ (16 atoms per unit cell), and R (54 atoms per unit cell).

They have different compositions and can be formed in different ranges of temperature than σ [9,10]. In the available literature, there is little information relevant to physical properties of the σ-phase in Fe−Mo. Even the data on its crystallographic structure in the whole concentration range of its occurrence is not complete. In these circumstances systematic studies aimed at filling this gap are justified, all the more so such studies have been recently carried out for this phase in Fe−Cr and Fe−V systems [11]. A comparison of corresponding data obtained for different binary alloy systems containing iron, Fe−X, where the σ-phase can be formed, is of interest *per se*, and, additionally, it may contribute to a better understanding of its formation mechanism. The knowledge of the latter is of a great importance in the light of a detrimental effect of a σ-phase presence in stainless steels used in various branches of industry as valuable construction materials. In this paper results of a systematic study of the lattice parameters, sites occupancies, Fe-site charge-densities and electric field gradients obtained using various experimental tools viz. X-ray diffraction (XRD) and Mössbauer spectroscopy (MS), as well as electronic structure calculations (KKR method) are presented in the whole concentration range of the σ-phase existence in the investigated alloys.

2. Experimental

It was not possible to obtain samples in a pure σ-FeMo alloys by using the procedure that was previously successfully applied in the case of Fe−Cr and Fe−V alloys i.e. an isothermal annealing of ingots obtained by melting constituents [11]. The Fe−Mo ingots treated in

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that way were always two-phase, the second phase being μ. Successful was, however, a procedure described by Bergman and Shoemaker [3] viz. a sintering. For that purpose, powders of elemental Fe (99.9 at%) and Mo (99.95 at%) were mixed together in adequate proportions. Next, 2 g tablets for each composition were fabricated by pressing the mixtures. The tablets were subsequently isothermally annealed at 1430 °C during 6 h, and afterward quenched into liquid nitrogen. For XRD and Mössbauer spectroscopic measurements, both carried out at room temperature (RT = 294 K), the pellets were attrited into powder in an agate mortar. Altogether nine samples with the following nominal concentration of Mo: 44, 45, 47, 48, 49, 51, 53, 55 and 57 at% were prepared. Based on the XRD patterns, an example of which is shown in Fig. 1, it was found that all samples except two with the lowest Mo content, and one with the highest content of Mo were single-phase, namely σ. The samples containing nominally 44 and 45 at% Mo had some admixture of μ-phase (Fig. 1a), and the most Mo-concentrated sample contained ~4.2 wt% of undissolved Mo-rich, bcc Fe−Mo phase. In the latter case the content of Mo in the σ-phase was estimated as equal to 56.7 at%.

3. Results

The powder XRD patterns were collected at RT with a D5000 Siemens diffractometer (using Cu K-α radiation and a graphite secondary monochromator) from 10° to 140° in steps of 0.02° in 2θ. Data were analyzed by the Rietveld method as implemented in the FULLPROF program [12] with 22 free parameters: 6 of them were related to a background and positions of lines, 10 parameters represented sites occupancies and atomic positions in the unit cell. Remaining 6 parameters described line widths, lattice constants and Debye−Waller factors. The analysis yielded values of the lattice constants, a and c (Fig. 2, Table 1), atomic positions (Table 2), as well as occupancies of the sublattices (Fig. 3). Concerning the lattice constants, as clearly evidenced in Fig. 2, they exhibit a linear dependence on the Mo content, x. Yet, the ratio $c/a = 0.52233(2)$ is
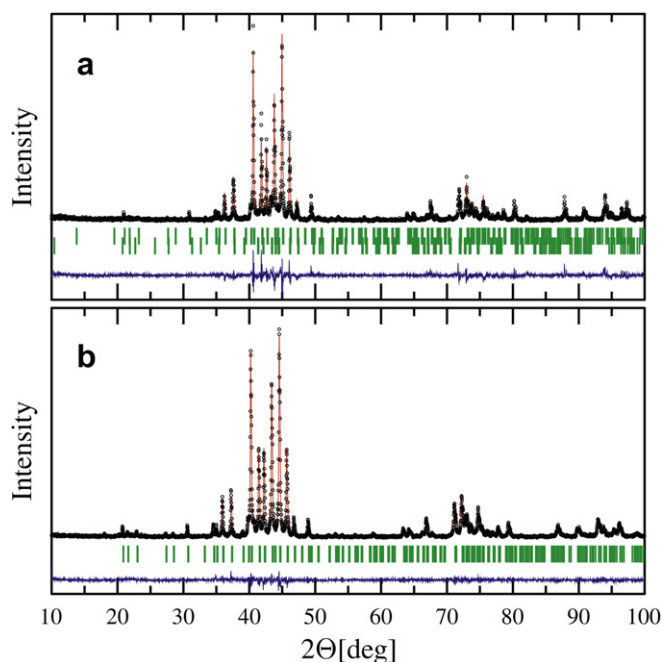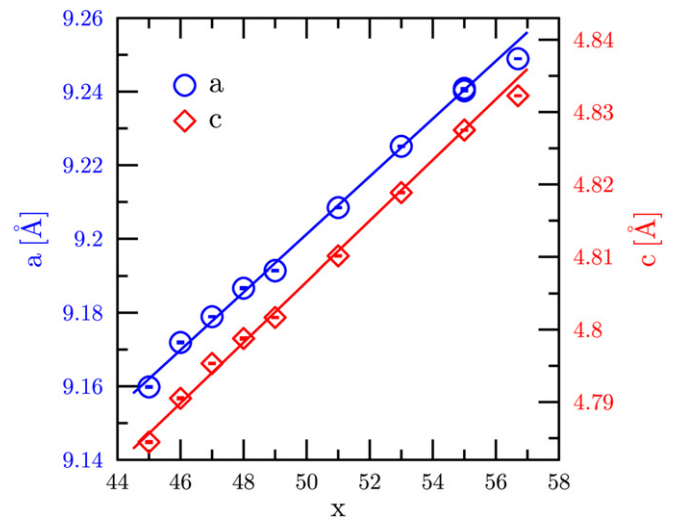

Fig. 2. Dependence of the lattice parameters a (circles, blue) and c (diamonds, red) on Mo-content, x, as determined from the X-ray diffractograms recorded at 294 K. Error bars indicated in the figure are smaller than marker size. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

rather x-independent. For comparison, Bergman found the value of 0.5237 for this ratio [3]. The values of the lattice constants given in the literature [3,4,13] are in line with ours. This can be taken as indication that the nominal compositions of our samples can be regarded as very close to the real ones. Also the atomic positions found in our analysis agree within error limits with those known from the literature [3,13]. As far as the occupancy of the lattice sites is concerned, the analysis of the XRD patterns gave evidence that sites A and D were exclusively populated by Fe atoms, which is slightly different than in the case of the σ-phase in Fe−Cr and Fe−V systems where the population of Fe atoms at these sites was lying within 80−90% range [14]. The remaining three sites were found to be occupied by both Fe and Mo atoms, the former being in minority. However, the actual occupancy is concentration dependent and it decreases linearly with x at a rate characteristic of a given site. These results agree qualitatively with those reported earlier [4,13].

[57]Fe-site Mössbauer spectra, shown in Fig. 4a, were recorded in a transmission geometry using a standard equipment and Co/Rh source for the 14.4 keV gamma-radiation. No traces of magnetism were found in all the spectra recorded at RT. Despite it is known from the XRD experiments that Fe atoms are present at all five sublattices, which means that each spectrum should be composed of at least five subspectra. However, a unique analysis of the measured spectra in terms of five components that could be associated with the five sublattices is not possible due to a lack of a well-defined structure of them. Instead, one can analyze them in terms of an isomer shift distribution, ISD, as explained elsewhere [15,16].

Fig. 1. Selected fitted X-ray diffractograms recorded at 294 K on the σ-phase sample of (a) Fe$_{55}$Mo$_{45}$ and (b) Fe$_{45}$Mo$_{55}$. The solid line stays for the best-fit obtained with the procedure described in the text. Peak positions for μ and σ (a) as well as for pure σ-phase (b) are indicated. A difference diffractograms are shown, too.

Table 1
Lattice constants (in Å), a and c as well as the average isomer shift $\langle IS \rangle$, (in mm/s, relative to the Co/Rh source), for all investigated σ-Fe$_{100-x}$Mo$_x$ samples.

x	a	c	$\langle IS \rangle$
45	9.1598(2)	4.7844(1)	−0.242
46	9.1719(2)	4.7905(1)	−0.235
47	9.1789(1)	4.7953(1)	−0.234
48	9.1866(2)	4.7987(1)	−0.236
49	9.1913(1)	4.8016(1)	−0.236
51	9.2084(1)	4.8101(1)	−0.240
53	9.2251(1)	4.8188(1)	−0.242
55	9.2402(1)	4.8275(1)	−0.248
56.7	9.2489(1)	4.8322(1)	−0.252