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Surface magneto-optical and Mössbauer observations of Fe–Al

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ABSTRACT

The paper is devoted to detailed surface studies of the $Fe_{82}Al_{18}$ alloy prepared from high purity Fe and Al by arc melting. The results summarize observations of the surface sensitive methods – high resolution scanning electron microscopy (HRSEM), slow energy electron microscopy (SLEEM), magneto-optical Kerr effect (MOKE), and conversion electron Mössbauer spectrometry (CEMS). Morphology of grains and grain boundaries obtained by HRSEM is observed in more detail by SLEEM. The CEMS results analyzed using free components with characteristic hyperfine parameters and by theoretical model, give evidence for *A*2 order of the as-prepared and as-quenched $Fe_{82}Al_{18}$ sample surfaces. A small contribution of the oxide layer influences the shape of hysteresis loops and domain structure of the sample surface above all in the as-quenched state.

1. Introduction

Iron aluminides represent a class of materials under unremitting research efforts because of their excellent corrosion and oxidation resistance, good combination of mechanical properties, such as high specific strength/weight ratio, and low raw material costs [1–3]. Likewise, they are object of studies from the viewpoint of magnetic properties [4–6], defects and their formation in various substructures [7–9], possibilities to be alloyed with other elements, e.g. Ni, Ta, Ti, [10,11] with the aim to influence their mechanical and/or magnetic properties and further extend facilities for their high-temperature applications like aircraft turbines [12,13].

The Fe–Al system has a complex equilibrium phase diagram and exhibits a large variety of metastable non-equilibrium phases [14]. The reason for this is a large difference in atomic radii and different crystal structures of Fe and Al. Whereas iron has flexible bcc lattice, aluminum forms a dense packed fcc structure. Alloying of both elements leads then to solution of high amount of Al in Fe but only several at.% Fe in Al [15]. Consequently, two phases, Fe_3Al and FeAl, exist on the iron-rich side, while several phases, e.g. $FeAl_3$, $FeAl_2$, Fe_2Al_5, exist on the aluminum-rich side. From the magnetic viewpoint, the iron-rich Fe–Al alloys, namely Fe_3Al, as soft magnetic materials, are highly promising. They are ferromagnetic and show a variety of structural phase transitions between the low-temperature ordered $D0_3$ structure, the partially disordered *B*2 structure, the disordered high-temperature *A*2 structure, and two-phase regions at intermediate temperatures.

The extensive applied research has also stimulated more fundamental work in the field of surface science. It was realized that understanding of the surface structure, composition and physical properties is essential for insight into macroscopic properties like corrosion resistance and ductility. From this viewpoint the most investigated system is the Ni-based aluminide, namely NiAl with the bcc CsCl structure. The results obtained by various experimental techniques (e.g. low energy electron diffraction or low energy ion scattering) indicate that the surface can be either slightly enriched by Al [16] or slightly lower Al concentration can be detected in the topmost layer compared to the nominal composition [17]. Less information is available on the surface properties of Fe–Al alloys despite the fact that they are also important structural materials. LEED-I-V analysis was used to show that the (1 0 0) surface of the ordered intermetallic FeAl compound is Al terminated and determined the relaxation for the top surface layers [18]. Auger electron spectroscopy (AES) and LEED were used for composition and ordering behavior of the (1 0 0) and (1 1 0) surfaces of $Fe_{53}Al_{47}$ binary alloy [19].

In this paper we investigate the alloy of $Fe_{82}Al_{18}$ composition that occurs at the boundary between the highly disordered bcc

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Fe–Al solid solution of $A2$ structure and the $D0_3$ structure [14]. Our work is focused on the connection between surface magnetic properties, surface microstructure, and phase composition that are studied in detail using methods sensitive to the surface like high resolution scanning electron microscopy (HRSEM) and slow energy electron microscopy (SLEEM). These methods are completed by measurements of the surface magnetic characteristics using magneto-optical Kerr effect (MOKE) and by conversion electron Mössbauer spectrometry (CEMS) yielding properties on atomic scale [20]. MOKE has emerged into a powerful surface-sensitive instrumentation for investigation of magnetic materials due to its sensitivity to the magnetization within the skin depth region, typically 10–20 nm in most metals [21]. By focusing the laser beam into different places on the sample the local measurements can be performed. CEMS embodies slightly higher depth sensitivity yielding information on structural properties on atomic scale from the surface of approximately 200 nm thick. The surface sensitive methods are supplemented by the X-ray diffraction technique.

2. Experimental

2.1. Materials

Fe–Al alloy was prepared from high purity Fe (99.99%) and Al (99.99%) by arc melting in Ti-gettered Ar atmosphere. The samples were cut from the as-cast ingots into a form of approximately 500 μm thick discs of 20 mm diameter. Their surfaces were polished and etched in a 30% Nital solution to remove oxides and to visualize grains and grain boundaries. The sample in the as-prepared state is denoted "AP". The other sample, denoted "AQ", was sealed in the evacuated quartz ampoule, annealed at 1000 °C for 1 h and finally quenched into water at room temperature.

2.2. X-ray diffraction

X-ray diffraction (XRD) measurements were performed on the diffractometer X'Pert-PRO (Panalytical) in the symmetric Bragg–Brentano geometry. It was used as a supplemental method to check the structure of both samples. The samples (AP, AQ) exhibit relatively large size grains and the orientation of crystallographic planes is not random like in powder samples. Therefore only very limited number of grains contribute to the diffraction pattern. For these reasons the classical Θ–2Θ scan was supported by the rotation around the axis normal to the surface, so-called ω scan.

2.3. Electron microscopy

High resolution TESCAN LYRA 3XMU FEG/SEM × FIB scanning electron microscope (HRSEM) was used to follow the surface morphology and microstructure. The details of the grain interiors and grain boundaries were examined using the SEM Vega TS 5130MM at standard vacuum conditions, equipped with a cathode lens (CL) [22]. This arrangement enables to collect both secondary electrons (SE) and back-scattered electrons (BSE). At energies down to 3 keV, the SE escapes through the central bore of the detector. The BSE, which are emitted at high polar angles with respect to the surface normal, carry information about the surface topography.

2.4. Conversion electron Mössbauer spectrometry

^{57}Fe Mössbauer spectra of samples were taken at room temperature (RT) in scattering geometry by detecting 7.3 keV conversion electrons with the penetration depth about 200 nm. ^{57}Co(Rh) was used as a source and calibration of velocity scale was done by α-iron at RT. In the first step the measured spectra were analyzed using CONFIT program package based on a non-linear least-squares procedure with the Fast Fourier Transform technique. A combination with improved matrix formalism can create various physical models to analyze the measured experimental data in a proper way [23]. The procedure yields following parameters of individual sextets: hyperfine induction B [T], isomer shift δ [mm/s], and quadrupole splitting Δ [mm/s] characterized in measured spectra also by their intensities I [%]. These components relate to a specific atomic coordination in the nearest neighboring shells of resonating iron atoms. Moreover, the experimental data were analyzed also by special software, where models of structure atomic order were fitted. The individual superstructures were divided into sublattices, for which the content of non-iron atoms was controlled by ordering constants. The distribution of "impurity" atoms within individual sublattices was supposed to be random. For probability p quantification, the binomial distribution was used:

$$p_i(j,x) = \binom{i}{j} \cdot x^j (1-x)^{i-j}$$

Here i is number of atoms in the given coordination sphere and the probability depends on the appropriate number of impurity atoms j and on the impurity concentration x within the particular sublattice. In our case the calculations were limited to two coordination spheres. Besides the disordered structure $A2$, a combination of $A2$ and $D0_3$ order (four sublattices and two parameters) was supposed [24]. As for the individual components of Mössbauer spectra, the reduction of hyperfine induction with increasing number of impurity Al atoms was supposed to be quadratic in the first coordination sphere and linear in the second one. Analogous influence on the isomer shift was set to be linear in both cases. Principally, the effect of all atoms on both the hyperfine field and isomer shift is additive from the physical point of view. However, the restriction of the calculations to first two coordination spheres and the neglect of volume effects make it necessary to approximate empirically the influence of nearest neighbors on the hyperfine field – where the effect is the strongest – with a slightly bent curve instead of a straight line [25]. This effect is yet more pronounced for higher Al atomic concentrations. Presence of quadrupole splitting as well as correlation effects was neglected. Intensity of Mössbauer sextets belonging to individual configuration was fitted as linearly dependent on the computed probability. So besides this intensity/probability coefficient, ordering parameters can be directly fitted together with coefficients describing hyperfine induction and isomer shift dependences.

2.5. Surface magneto-optical methods

Magneto-optical Kerr effect (MOKE) was used for the hysteresis loops measurements and domain structure observations. The experimental setup for hysteresis loops measurement uses a red semiconductor laser working at wavelength of 670 nm, Frank-Ritter polarizer and photo-elastic modulator ensuring that the laser beam is linearly polarized (s or p polarization) and modulated at frequency of 50 kHz. The angle of linearly polarized light incident on the sample surface is 50°. After reflection from the sample, the light is elliptically polarized and propagates through the Wollaston prism, where two mutually orthogonal laser beams are obtained. Each of them is detected by PIN photodiode and their differential signal is proportional to the magneto-optical angle of Kerr rotation.

The hysteresis loop investigations were supported by magneto-optical Kerr microscopy method. Specially designed polarization microscope allows direct surface magnetic domains observation. The white light from arc Xe lamp comes through the system composed of the aperture diaphragm, polarizer and polarization