MEASUREMENT OF CARBON DIFFUSION COEFFICIENT – CALIBRATION OF SPUTTER DEPTH

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Abstract

Depth profiling mode of MiniSIMS device was applied to diffusion measurement. Calibration of crater depth was done using shearing interference microscope Zeiss Epival Interphako (ZEI) and confocal mikroskope Olympus LEXT OLS3100 with atomic force microscopy (AFM) modul. The ZEI uses one of the classical interferometric measuring methods. Generally this method leads to results with considerable experimental error. AFM is a very high-resolution type of scanning probe microscopy, with typical resolution of the order of fractions of nanometers, which is more than 1000 times better than the optical diffraction limit. However, the results taken by ZEI were in agreement with much more precise results of surface profiling achieved by AFM. It was found, at given experimental conditions (Fe-rich matrix, Ga\textsuperscript{+} primary ions, 5 kV/3nA, DWT=1), that the sputter rate is some 0.3 nm per a single sputter scan of the crater area (50x50 µm).

This depth calibration with SIMS technique can be applied to the study of carbon diffusion in BCC iron as an example. Special technique was developed, which avoids radio-tracer measurements with C\textsuperscript{14}. Obtained results are lower than the extrapolated values, which may be due to limited solubility of carbon in iron.

Keywords: SIMS, carbon diffusion, ferrite, carbides

1. INTRODUCTION

Secondary ion mass spectrometry (SIMS) is a technique used in materials and surface science to analyze the composition of solid surfaces and thin films by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing ejected secondary ions. SIMS is the most sensitive surface analysis technique, being able to detect elements present in the parts per billion range. The experimental SIMS technique, which enables to measure shallow concentration depth profiles, is dynamic SIMS (secondary ion mass spectroscopy) \cite{1}. Every material is characterized by a different sputter rate and depth calibration per one sputter scan is very important.

The measurement of the crater depth can be carried out by optical interferometry (OI). This method involves superposition of two spatially- and time coherent beams. If OI is applied to a measurement of very fine surface profiles, it leads to a considerable experimental error.

The atomic force microscopy (AFM) is another way how to measure the crater depth. AFM is a very high-resolution type of scanning probe microscopy.

In this paper these methods were used for measurement of crater depth. The SIMS technique was applied to estimation of diffusion behavior of carbon close to the free surface at two temperatures in α-Fe region in Fe-C as binary alloy model system. It is characterized above all by extreme difference in diffusion coefficients of the both components and, moreover, it shows a strong tendency to phase separation (carbon solubility in α-Fe is very low \cite{2}). Experimental conditions were arranged in a way enabling to study penetration profiles with mean diffusion path $\sqrt[3]{Dt} \sim 10^8$ m ($D$ – carbon diffusion coefficient, $t$ – diffusion time).
2. EXPERIMENTAL DETAILS

2.1 Samples
Diffusion samples were machined from zone refined iron (purity in at. ppm - C: 42, S: 80, P: 54, Bi: <0.08, Al: 85, Pb: 24, Cd: 4, Sb: <0.14, Zn: 80, Cu: 21). The starting material was remelted in induction furnace in Ar atmosphere and cast in copper mould. Ingot was spark cut into individual samples with diameter 10 mm and height 4 mm and the cut planes were ground on metallographic papers to remove surface impurities. After that, the samples were relaxed for 5 h in vacuum $2 \times 10^{-5}$ mbar at temperature 1073 K. Grain size of relaxed samples was $102 \text{–} 103 \mu m$. One plane surface was finally polished with diamond paste of grain size 2 µm.

2.2 Anneals
Both relaxation and diffusion anneals were done in a special vacuum furnace MILA-5000 Ulvac-Riko with infrared heating, which enabled extremely rapid heating (hundreds of Kelvins can be reached in several seconds). Such a rapid heating made it possible to carry on very short anneals in isothermal regime. Typical air rest pressure was about $2 \times 10^{-5}$ mbar. The diffusion anneals were done at two chosen temperatures $T_1 = 609$ K and $T_2 = 1130$ K.

2.3 Experimental arrangement
Two modes of carbonizing were used: (i) at $T_1$ carbon diffused into iron from surface layer vacuum deposited in the same way usually used for making conducting covers for electron microscopy and (ii) at $T_2$ carbon diffused from a gas mixture CH$_4$+Ar (1:9 by volume) under total gas pressure 1 bar. Flow regime of carbonizing assured that partial pressure of hydrogen was low enough and, therefore, carbon activity in the gas mixture was very high. The two modes of carbonizing were chosen to test both experimental possibilities.

2.4 SIMS
SIMS is an extremely sensitive technique of surface analysis [1, 3]. It is principle consists in bombardment of the surface by accelerated primary ions. Secondary ions (fragments emitted from the target material having both polarity and/or neutrals) are continually analyzed in a mass spectrometer. In the present work, MiniSIMS MILLBROOK was used that enables surface sputtering-off the material from the target and hence, concentration-depth profiling. The apparatus is equipped with a liquid metal ion source emitting Ga$^+$ primary ions and with a quadrupole mass spectrometer. Ions of both polarities (but not neutrals) could be registered.

2.5 Measurement of crater depth

2.5.1. Optical measurement
Calibration of rectangular crater depth was done using shearing interference microscope Zeiss Epival Interphako (ZEI) and confocal microscope Olympus LEXT OLS3100 with AFM modul.

A schematic of the ZEI microscope used for depth calibration in light transmitted by the studied sputtered crater in sample is shown in Fig. 1. Monochromatic light from a tungsten lamp with a filter for $\lambda = 578$ nm, 1, is transmitted through the beamsplitter prism, 2, to the sample, 3, to the objective lens, 4, and an auxiliary rightangled prism, 5. Light is using this right-angle prism into a two-beam interferometer - a Mach-Zehnder-type interferometer. This interferometer is constructed from two
beamsplitters, 6, 11 and wedges, 7, 9 and 10 with compensator 8 connected with micrometer. The value of the wedge angle of wedge 7 can be changed.

By using appropriate operations with wedges 7, 8, 9, 10 we can obtain two waves corresponding to two beams whose wave fronts are tilted and translated mutually so that a certain lateral shear originates between these waves. These waves interfere and interference fringes can be observed in ocular.

These two wave-planes interfered, which can be observed in ocular. In the edge area these wave-planes are shifted by \( z + 2t \) (Fig.2) therefore, this area has other intensity than surroundings.

We can set surroundings on the smallest intensity and determine \( a \) value from micrometer. After that set the same intensity in the edge of the crater and determine \( b \) value from micrometer.

The evaluation of the crater depth \( t \) is based on the equation:

\[
t = \frac{K}{2}(b - a)
\]

Where \( K \) is constant of compensator (for \( \lambda = 546 \text{nm} \) is \( K = 5.17 \text{nm/segment of the micrometer} \)).

### 2.5.2. AFM measurement

The confocal microscope Olympus LEXT OLS3100 with AFM module is fully controlled by computer. The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically a silicon holder with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, atomic forces between the tip and the sample lead to a deflection of the cantilever according to Hooke’s law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (see magnetic force microscope, MFM), Casimir forces, solvation forces, etc. The resolution of this device is in the order of fractions of nanometers, more than 1000 times better than the optical diffraction limit.

**Fig.2** Schema of interfered two wave-planes observed in ocular

- **a** – sample with crater,
- **b** – wave planes.

**Fig.3** Crater edge measured by ASM device.

**Fig.4** Profile of crater edge measured by ASM device. (values of 127 profiles).
3. RESULTS

3.1 Depth calibration

The OI and AFM devices were used for measurement of the crater depth. Measurement by OI leads to results with considerable experimental error. However, they are with agreement with much more precise result of surface profiling by AFM (Fig.3, 4). In Fig. 4, the profile of the sputter edge measured by AFM device is shown. It can be seen that at given experimental conditions (Fe-rich matrix, Ga\(^+\) primary ions, 5 kV/3nA, DWT=1), the sputter rate is some 0.3 nm per one sputter scan of the crater area 50x50µm. This sputter rate is very important for obtain depth profiles measured by SIMS technique.

3.2 Depth profiles

The example of measured depth profiles obtained with samples annealed in CH\(_4\)+Ar atmosphere is shown in Fig.5. The sputter rate was used for evaluation of the depth of the measurement. The chemical composition of carbon in the vicinity of the surface is well scaled by depth profile taken for peak m/e = 24 (C\(_2\)). This profile is not too much influenced by oxygen and at the same time, the peak C\(_2\) is sufficiently high to achieve acceptable accuracy of results at reasonable counting time. Therefore, profiles were taken with C\(_2\) only.

4. EVALUATION OF DATA

The depth of profile was calculated using the previously obtained sputter rate. For the sake of simplicity, we assume here that \(D\) is a constant at high carbon concentration by the surface and another constant at low carbon concentrations at concentration tails. Hence, carbon concentration at low values of \(C\) can be described by analytic solution relevant to the diffusion from carbon surface layer into half-space and at high \(C\) (small \(x\) and diffusion from gas mixture) it can be described by solution for the diffusion from the constant source into half-space [4]. After simple derivation of known solutions, one can obtain relations for \(D\)'s at \(x = 0\). Resulting values of \(D\) together with that obtained by fitting the concentration tail to the penetration profile measured at 609 K are shown in Fig.6 together with literature data.

5. SUMMARY

It was shown in the present work that SIMS technique could be applied for diffusion measurement.

It was very important to known the sputter rate – the depth of sputtered layer per one sputter scan. This sputter rate was evaluated from measurement of sputtered crater by optical interferometry and by AFM methods. It was found that these methods give for the crater area 50x50µm the same results. At given
experimental conditions (Fe-rich matrix, Ga⁺ primary ions, 5 kV/3nA, DWT=1), the sputter rate is some 0.3 nm per one sputter scan.

This value of sputter rate was used for obtain the diffusion profile of carbon in Fe – rich matrix in dependence of counts on x.

In carbon-rich area (near the surface of the sample), the values of D are much lower than it could be expected for carbon diffusion in ferrite. Possible explanation can be found in the presence of carbide clusters and/or coherent transition carbides in supersaturated ferrite [5-8]. As the activation energy associated with this process was found value 89.5 ± 12 kJ/mol. This value, added to that for diffusion motion of carbon in ferrite (84.12 kJ/mol [9]) leads to calculated carbon diffusion coefficients $D(336 \text{ K}) = 2.6 \times 10^{-21} \text{ m}^2/\text{s}$ and $D(1130 \text{ K}) = 1.9 \times 10^{-14} \text{ m}^2/\text{s}$ that are reasonably close to present experimental values $D(336 \text{ K}) = 9.8 \times 10^{-21} \text{ m}^2/\text{s}$ and $D(1130 \text{ K}) = 6.2 \times 10^{-14} \text{ m}^2/\text{s}$ respectively (Fig. 6). It can be expected that value of D would approach value of tracer diffusion coefficient $D^*$ in stable structures (ferrite, austenite) with decreasing C_C marked with dashed arrows in Fig.6.

Present data deepen the knowledge of kinetics of very early stages of carbon diffusion under extreme high carbon concentration gradient. Optimum experimental mode is to register intensity of C²⁻ ions, which is not sensitive to heterogeneous distribution of oxygen impurities in the sample. It was found that diffusion rate of carbon in supersaturated solid solution of C in α-Fe is similar to that in carbide phase Fe₃C, Fe₅C₂ and/or in Fe₄Cₙ (n ~ 1).

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