DETERMINATION OF DIFFUSION AND SEGREGATION CHARACTERISTICS OF $^{32}$P IN POLYCRYSTALLINE Fe – 2.2 wt.% Si

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Abstract
The grain boundary diffusion of phosphorus in polycrystalline Fe – 2.2 wt.% Si was measured using serial sectioning method with radioisotope $^{32}$P. The measurements were carried out under the conditions of the B-regime (845 – 1173 K) and the C-regime (735 – 830 K). The diffusivity $P = s \delta D_{gb}$ ($s$ denotes the segregation factor, $\delta$ the grain boundary width and $D_{gb}$ the grain boundary diffusion coefficient) was obtained from the penetration profiles measured in B regime. The pre-exponential factor $P_0$ and the activation enthalpy $Q_{gb}$ were calculated from the temperature dependence of $P$. The initial part of the penetration profiles measured in B-regime was used to calculate the volume diffusion coefficients $D_v$ and together the relevant Arrhenius parameters were also calculated. The grain boundary diffusion coefficient $D_{gb}$ was directly measured under the condition of the C-regime. Combining both sets of measurements, the segregation coefficient $s$, the segregation enthalpy $H_s$ and the pre-exponential factor $s_0$ were determined. The obtained results were compared with segregation data of phosphorus measured by Auger Electron Spectroscopy in alpha-Fe.

1. INTRODUCTION
Iron-based materials, for example low-alloy steels, are the most used construction materials in many industrial applications. The knowledge of their mechanical and other physical properties is very important for understanding their behaviour under specific conditions. Especially, the chemical composition and the structure of the grain boundaries (GB) in these materials have strong effect on their behaviour. The study of GB diffusion and segregation give us important information about impurity behaviour hence this phenomenon is the subject of many investigations.

The Fe-Si alloys as a model system have been intensive studied in many investigations. They have included: studies of diffusion of various elements such as Fe in polycrystalline $\alpha$-Fe(Si) in the concentration range 1.48 – 12.1 at.% Si [1-3] or in Fe – 1.28 wt.% Si bicrystals [4]; studies of the interdiffusion of Si [5] and phosphorus volume and GB diffusion in iron and iron alloys [6]; studies of the segregation phenomena mostly in bicrystals with a exactly defined GB [7-10]; and studies of GB corrosion [11]. In steels the GB brittleness strongly depends on the presence of impurities. Among a lot of elements (IVB - VIB group of the periodic table) presented as impurities in low-alloyed steels, phosphorus is the most harmful element that promotes a temper embrittlement of these materials [12]. This phenomenon depends, among others factors, on an amount of P at GBs [13].

The Auger Electron Spectroscopy (AES) is usually used to direct measure the segregation at GBs. This method is most successfully applied in the case of brittle materials, such as intermetallics. The specimens are fractured in situ in high vacuum and the Auger spectra are measured. Unfortunately, the many metals and metallic alloys are ductile and this method
cannot be used. In these cases, the indirect methods such as GB diffusion measurements are used.

The trace diffusion measurements are carried out usually in the so-called B-regime [14]. The diffusivity $P = s \delta D_{gb}$ ($s$ denotes the segregation factor, $\delta$ the grain boundary width and $D_{gb}$ the grain boundary diffusion coefficient), so-called triple product, is obtained from the measured penetration profiles. The value of $\delta$ is usually supposed equal to $5 \times 10^{-10}$ m. In this case, the parameters $s$ and $D_{gb}$ cannot be separated. A separation of both parameters is possible using combination of the measurements in the B- and C- regime as have been successfully demonstrated in many studies, see e.g. in [15-18]. The diffusion in C-regime may be considered as taking place only within the GB with negligible out-diffusion to the adjoining grains. It possible only at lower temperatures and the GB diffusion coefficient $D_{gb}$ is direct obtained from the penetration profiles. The segregation factor $s$ can be calculated using the $P$ value (extrapolated from higher temperatures) and the $D_{gb}$ value (measured at lower temperatures) by

$$s = \frac{[P]_B}{\delta [D_{gb}]_C}, \quad (1)$$

where the experimentally measured values are in the brackets and indexes indicate the diffusion regime.

In the present work, the grain boundary diffusion of $^{32}$P isotope was studied in polycrystalline Fe - 2.2 wt.% Si. The measurements were carried out under the conditions of the B- and C- regimes.

2. EXPERIMENTAL

2.1 Sample preparation

The Fe-Si polycrystalline was prepared from Fe (3N6) and Si (5N) by melting in the induction coil furnace under vacuum atmosphere. The molten alloy was cast into a copper mould. The final ingots were a cylindrical form, 13 mm in diameter and 150 mm in length. There were reduced in diameter to 8 mm. The diffusion specimens with thickness 2 mm were cut from ingots using the disk saw. The planar surfaces of specimens were metallographically polished. Thus prepared samples were wrapped into Ta foil, sealed in the quartz tube under the Ar protective atmosphere and annealed at 1173 K for 2 days in order to stabilise the grain size and GB segregation of impurities. The final mean grain size was about 900 $\mu$m. The samples were than pre-annealed at the temperature and for at least the time of the intended diffusion anneal. The samples prepared in such way were suitable to diffusion measurements in the B-regime. Electron microprobe analysis yielded a mean concentration of 2.2 wt.% Si, which guaranteed the body-centred cubic structure of our samples in the whole temperature range.

For the measurements under the condition of the C-regime, the specimens were prepared by following procedure. Each ingot was repeatedly cold-rolled until its size was reduced by 20 %. To prevent the possibility of impurity contamination, after each rolling the ingot was shortly etched with the solution of 100 cm$^3$ ethanol and 1 cm$^3$ HNO$^3$. The ingot was then sealed in a silica tube under an Ar atmosphere and annealed in four steps. The first step was at 677 K for 4 days to induce stress relaxation. A second step was at 873 K for 1 h plus a third step at 1023 K for 1 h induced recrystallization. The fourth step at 873 K for 6 days allowed stabilisation of the grain size. The final grain size was 13 $\mu$m and the sample diameter $\sim 10$ mm. Specimens were cut and polished using the same preparation procedure as above.
2.2 Radiotracer measurements
The radiotracer was used in form of an aqueous solution of orthophosphoric acid containing $^{32}\text{P}$ with specific activity 10.6 TBq$\cdot$mg$^{-1}$. The radioisotope was dropped on the polished surface of the specimens and dried. The specimens were sealed in the quartz tube under the Ar atmosphere and annealed at selected temperatures in interval from 854 to 1173 K. The annealing temperature was controlled by Pt-PtRh or Ni-NiCr thermocouple with accuracy $\pm$ 1 K.

After the diffusion treatment, the specimens were reduced in diameter about 1.5 mm to eliminate possible effects of radial and surface diffusion. The penetrations profiles were obtained by usual serial sectioning method. Thin layers of specimens were removed using a precision grinding device with special abrasive mylar foil. The thickness of each section was calculated from the mass difference, measured with a microbalance, the diameter and the density of Fe-Si specimens. Each abrasive mylar foil containing the removed layer of the sample was inserted into 20 cm$^3$ liquid scintillation vials filled with scintillation cocktail. In contrast to usually used residual-activity method [19], the activity $\sigma(x,t)$ of each layer was measured directly with high efficiency by liquid scintillation counter TRI CARB 2500 TR equipped with an automatic sample chamber [20].

3. RESULTS

3.1 Diffusion measurements in B-regime
Eight temperatures in the interval 854 - 1173 K were selected. The examples of penetration profile in the co-ordinates $\ln(\xi)$ vs. $y^{6/5}$ (where $y$ is the penetration depth) is shown in the Fig. 1a. The initial conditions corresponded to the diffusion from a thin layer to the half-space. Therefore, the slope $\partial \ln(\xi) / \partial y^{6/5}$ of the linear parts of the penetration profiles at deeper penetrations was used to calculate the triple product $P$, according to the Suzuoka solution [21]. The following equations were applied:

for $\beta < 10^2$

$$P = 0.2585 D_v^{0.4601} t^{-0.5309} \left( \frac{\partial \log(\xi)}{\partial y^{6/5}} \right)^{-1.7182}$$  \hspace{1cm} (2)

and for $10^2 < \beta < 10^4$

$$P = 0.2968 D_v^{0.4916} t^{-0.5084} \left( \frac{\partial \log(\xi)}{\partial y^{6/5}} \right)^{-1.6807}$$  \hspace{1cm} (3)

where $D_v$ is the volume diffusion coefficient, $t$ is the annealing time and $\beta = P / 2D_v \sqrt{D_v t}$. As can be seen, the volume diffusion coefficient $D_v$ is necessary for calculating the triple product $P$. Since there is the lack of literature data on $^{32}\text{P}$ volume diffusion in Fe(Si) alloys, the $D_v$ values were determined from the initial parts of the measured diffusion profiles, for detail see in [21]. The temperature dependencies of the volume coefficient $D_v$ and the triple product $P$ are shown in Figs. 2 and 3, respectively.

In Fig. 2, the obtained diffusion coefficients $D_v$ are compared with the data on self-diffusion in $\alpha$-Fe [22] and on P diffusion in $\alpha$-Fe [6]. The temperature dependence obtained from the fitted straight line of the experimental points in the ferromagnetic state gives the following Arrhenius parameters: pre-exponential factor $D_0 = 10^{12600} \text{ m}^2 \text{ s}^{-1}$ and activation enthalpy $Q_v = 320 \pm 45 \text{ kJ mol}^{-1}$. 
Fig. 1 Examples of GB diffusion penetration profile measured in the B-regime (a) and C-regime (b)

Fig. 2 Arrhenius plot of volume diffusion coefficients $D_v$ of $^{32}$P in Fe-2.2 wt.% Si (triangles) compared with volume diffusion data of $^{32}$P in $\alpha$-Fe [6] (red lines) and $^{59}$Fe in $\alpha$-Fe [22] (blue line).

Fig. 3 Arrhenius plot of GB diffusion in the B-regime and in the C-regime (full symbols) and in the transition range (open symbols).

Fig. 3 shows the temperature dependence of the triple products $P$ for GB diffusion of $^{32}$P in the polycrystalline Fe - 2.2 wt.% Si concerning the B-regime measurements. We observed two deviations from the standard Arrhenius behaviour. At higher temperatures, the deviation is probably influenced by the magnetic transformation in the material. This effect has been observed in many GB diffusion measurements, e.g., in $\alpha$-Fe in [22] or Fe-Si alloys in [2]. The dotted vertical line in Fig. 2 and 3 indicates the Curie temperature $T_C = 1043$ K [23]. A second deviation is observed at the lowest temperatures (open circles in Fig. 3). This behaviour is characteristic for measurements performed in the intermediate range between the B and C regimes.
The linear fit of the experimental points in the temperature interval from 925 - 1020 K is expressed by following Arrhenius parameters: pre-exponential factor $P_0 = (1.8^{+1.2}_{-1.1}) \cdot 10^{-10} \text{ m}^3 \text{ s}^{-1}$ and activation enthalpy $Q^B_{gb} = 171.3 \pm 8.3 \text{ kJ mol}^{-1}$.

This Arrhenius dependence is also shown in Fig. 4 by the straight line, which is extrapolated to lower temperatures. This is important for calculating the segregation factor $s$ (see below).

### 3.2 Diffusion measurements in the C-regime

The measurements of the GB diffusion of the $^{32}$P in the polycrystalline Fe-Si in the type C-regime were carried out in the interval from 735 - 830 K. The penetration profiles are shown in Fig. 1b in the co-ordinates $\ln \bar{c}$ vs. $y^2$. The GB diffusion coefficient $D_{gb}$ was calculated from the linear part of the profiles using the following relation:

$$D_{gb} = -\frac{1}{4t} \frac{\partial \ln \bar{c}}{\partial x^2}$$ (4)

Fig. 3 represents the temperature dependence of the results (squares) evaluated from the measurements in the C regime. For comparison with the measured $P$ values the GB diffusion coefficient $D_{gb}$ was multiplied by the GB width $\delta = 5 \cdot 10^{-10} \text{ m}$. A good linearity is observed in the temperature interval from 735 - 830 K. The Arrhenius fit of $D_{gb}$ within this interval is represented by parameters: pre-exponential factor $D^0_{gb} = (7.9^{+28.2}_{-6.2}) \cdot 10^{-3} \text{ m}^2 \text{ s}^{-1}$ and activation enthalpy $Q^C_{gb} = 201.5 \pm 9.9 \text{ kJ mol}^{-1}$.

### 3.3 Determination of the segregation factors

The measured diffusion coefficient $D_{gb}$ and the triple product $P$ can now be combined for the calculation of the segregation factor $s$, see Fig. 3. When the values of $P$ are extrapolated to lower temperatures, the product $\delta D_{gb}$ turns out to be very much smaller than $P$. This observation corresponds to a strong segregation of $P$ in Fe-Si, i.e., $s>>1$. The segregation increases as the temperature decreases and the Arrhenius parameters are: pre-exponential factor $s_0 = 47^{+159}_{-35}$ and activation enthalpy $H_s = 30 \pm 10 \text{ kJ mol}^{-1}$.

The temperature dependence of the segregation factor $s$ is shown in Fig. 4. Since there are no available data of the segregation factor in the studied system in literature, the obtained segregation factor $s$ was compared with the enrichment factor $b$. The enrichment factor $b$ was taken from the AES measurements of 4 elements in pure iron [24-27]. The relation between $b$ and $s$ will be discussed below.
4. DISCUSSION

In the present work, the GB diffusion of $^{32}$P in Fe - 2.2 wt.% Si was measured under the conditions of the B regime. The calculations of segregation factor $s$ (Fig. 4) allowed us to establish the temperature limits and to determine reliably the Arrhenius parameters.

The penetration profiles were detected over 2 decades in the concentration in the coordinates $\ln{\bar{\tau}}$ vs. $y^{6/5}$. Most penetration profiles consist of two parts. The first part was used for the calculation of the volume diffusion coefficients. The obtained Arrhenius parameters for $^{32}$P volume diffusion differ slightly from the parameters $D_0 = 13.8 \text{ m}^2 \text{ s}^{-1}$ and $Q_v = 332.0 \text{ kJ mol}^{-1}$ obtained by Matsuyama et al. [6] for P volume diffusion in pure $\alpha$-Fe. The amount of Si in the present alloy has only a small enhancement effect on $^{32}$P volume diffusion. The activation enthalpy of the $^{32}$P volume diffusion is somewhat larger than the value for self-diffusion in pure $\alpha$-Fe ($Q_v = 284.6 \text{ kJ mol}^{-1}$) measured by Lübbehusen and Mehrer [22] in the ferromagnetic state. The ratio $Q_{gb}/Q_v$ of $^{32}$P diffusion equals to about 0.54. This value is very well in line with the results in other systems and is characteristic for a vacancy diffusion mechanism [21].

The segregation factor $s$ was estimated using the combination of GB diffusion measurements in the B and C regimes. The relation $\alpha > 10$ (where $\alpha = (s \delta)/2\sqrt{D_0}$), which characterises the diffusion in the C regime, was fulfilled in most cases. The linear part of the penetration profiles in the co-ordinates $\ln{\bar{\tau}}$ vs. $y^2$ was fitted over about one decade in the concentration to estimate reliably the GB diffusion coefficient $D_{gb}$.

The segregation factor $s$ is defined by the relation

$$s = \frac{c_{gb}}{c_v} \quad (5)$$

where $c_{gb}$ and $c_v$ are the GB and volume concentration at the GB, respectively. In AES measurements of the segregation the McLean segregation isotherm is frequently used. In terms of concentrations it can be presented as:

$$\frac{c_{gb}}{c_{gb}^0 - c_{gb}} = b \frac{c_v}{1 - c_v} \quad (6)$$

In this equation, $c_{gb}^0$ is the fraction of GB positions in a monolayer allowed for the segregating atoms at saturation. Eq.(6) define the enrichment factor $b$ of solute segregation as the initial slope of the segregation isotherm. In the dilute limit the enhancement factor $b$ can be written as:

$$b = \frac{1}{c_{gb}^0} \frac{c_{gb}}{c_v} \quad (7)$$

The comparison between Eqs.(5) and (7) yields the relation between the segregation factors $s$ and the enrichment factor $b$:

$$s = c_{gb}^0 b. \quad (9)$$
Thus $s$ and $b$ are identical only in the case of $c_{gb}^0 = 1$. In general, this condition is not fulfilled and $c_{gb}^0 < 1$ has to be expected [28] as was recently demonstrated experimentally in the case of Ag segregation at Cu GBs [18].

An overview on segregation data obtained from AES measurements was presented e.g. in [7]. Our experimental results of the P segregation (Fig. 5) are within the limit of errors in fairly good agreement with the data of the enrichment factor $b$ measured for the segregation of P in Fe by Erhart and Grabke [24] with the AES technique. These authors report a segregation enthalpy $H_s = -34.3$ kJ mol$^{-1}$, which is in reasonable agreement with our experimental result. This allows the conclusion that $c_{gb}^0$ is close to unity in the case of segregation of P in Fe and Fe-Si, i.e., the saturation limit amounts to about one monolayer.

5. SUMMARY

1. GB diffusion measurements in the B-regime were carried out in the interval 854 - 1173 K. The initial parts of the penetration profiles were used to calculate the volume diffusion coefficients $D_v$. The relevant Arrhenius parameters were obtained for both the volume diffusion ($D_v = 10$ m$^2$ s$^{-1}$ and $Q_v = 320$ kJ mol$^{-1}$) and for the GB diffusion ($D_{gb} = 18 \cdot 10^{-10}$ m$^2$ s$^{-1}$ and $Q_{gb} = 171.3$ kJ mol$^{-1}$).

2. The GB diffusion experiments under the condition of the C-regime were carried out in the temperature interval 735 - 830 K and the GB diffusion coefficient $D_{gb}$ was directly measured, resulting in an activation enthalpy $Q = 201.5$ kJ mol$^{-1}$.

3. The segregation coefficient $s$ was estimated, using a combination of the GB diffusion measurements in the B- and C-regime, respectively. The phosphorus segregation in Fe-Si alloys is very strong, resulting in a segregation enthalpy $H_s = -30 \pm 10$ kJ mol$^{-1}$.

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REFERENCES


