Determining the bulk concentration of S in Fe-S: a Auger electron spectroscopy study

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Abstract. Auger electron spectroscopy constant temperature segregation runs have been performed on Fe-S-C for the temperatures 823 K – 1073 K in 50 K increments. At temperatures 823 K – 973 K, the segregation of C is initially observed, but soon replaced by S which dominates the Fe surface once it start segregating. At temperatures 1023 K and 1073 K only the segregation of S was observed on the surface. Fitting of the adapted $t^{\frac{1}{2}}$ equation to the segregation profile of S for each of the temperatures delivered an average bulk concentration of 14.065 ± 0.1946 ppm S in the Fe sample. The results show the ability of S to segregate and dominate the surface of Fe, even for a low bulk concentration.

1. Introduction

Fe having such a vast amount of applications, has captured the attention of both scientist and engineers alike. The mechanical properties of Fe make it a useful element in the manufacturing of machinery and tools. Fe is also used in the Fischer-Tropsch process, whereby it acts as a catalyst to convert syn gas into hydrocarbons which is used in the petrochemical industry. The presence of S in the Fe, however causes a weakening of these properties. The presence of S in machinery operated at high temperatures leads to grain boundary segregation, causing grain boundary embrittlement which ultimately leads to failure of the machinery. S in the Fe catalyst used in the Fischer-Tropsch process, segregates to the surface and occupies surface positions. This causes a decreased conversion rate of the syn gas into hydrocarbons and ultimately leads to the deactivation of the catalyst.

The application of Fe in the above mentioned cases, where Fe is operated at high temperatures, calls for a study of Fe-S under high temperatures in order to investigate the diffusion properties of the system. Such studies have been performed on polycrystalline Fe by Reichl *et al*. [1] and also on the Fe(100), Fe(110) and Fe(111) surfaces [2]. Using the models of Fick, Reichl *et al*. was able to determine the diffusion parameters, D_0 and Q, as well as the segregation energies for C and S in Fe.

As mentioned above the fitting of Fick`s model to experimental data delivers the diffusion parameters for a sample of known concentration. The study discussed here made use of Fick`s adapted $t^{\frac{1}{2}}$ equation [3] to extract values for the bulk concentration of S in the a polycrystalline sample of Fe by making use of diffusion parameters from literature. A similar study has been performed by Terblans *et al.* [4] on a Cu(Bi,S) system in order to determine the bulk concentration of S in the sample.

2. Theory

The surface segregation of elements, including the changes that occur to the bulk concentration during sputtering, has been shown by du Plessis *et al.*[3] to be described by equation 1.

$$C^{\phi} = C_0^{\phi} + C^B \left[1 + \frac{2}{d} \left(\frac{D(t+t_0)}{\pi} \right)^{\frac{1}{2}} \right] - C^B \left[\frac{2}{d} \left(\frac{Dt_0}{\pi} \right)^{\frac{1}{2}} \right] \tag{1}$$

where C^{ϕ} is the surface concentration of the segregated species, C_0^{ϕ} is the concentration of the segregated species that was not sputter in time t_0 and remained on the surface, C^B is the bulk concentration of the sample, d is the interlattice spacing of the sample, D is the diffusion coefficient, t_0 is the time the sample was sputter cleaned and, t is the time in which the segregation measurements were performed.

Equation 1 can be fitted to experimental data in order to extract important parameters such as the diffusion parameters or as was done in this study the bulk concentration. In order to extract the bulk concentration values, equation 1 was written in the linear form given by equation 2, where the concentration, C_0^{ϕ} was considered negligible.

$$C^{\phi} = \frac{2C^B}{d} \left(\frac{D}{\pi} \right)^{\frac{1}{2}} (t+t_0)^{\frac{1}{2}} - C^B \left[\frac{2}{d} \left(\frac{Dt_0}{\pi} \right)^{\frac{1}{2}} - 1 \right] \tag{2}$$

plotting of C^{ϕ} against $(t+t_0^{'})^{\frac{1}{2}}$ gives a straight line with

$$\text{Gradient} = \frac{2C^B}{d} \left(\frac{D}{\pi} \right)^{\frac{1}{2}} ;$$

$$\text{y-intercept} = C^B \left[\frac{2}{d} \left(\frac{Dt_0}{\pi} \right)^{\frac{1}{2}} - 1 \right]$$

using the gradient and substituting in the parameters *d* and *D*, the bulk concentration of the sample was determined for each temperature.

3. Experimental

All measurements were performed on the PHI 590 Scanning Auger Microscope, consisting out of an electron gun, model 18-085 and a single pass cylindrical mirror analyser, model: 25-110. The ion gun used for sputter cleaning of the sample is a model 11-065 from Perkin-Elmer. The Auger spectrum was recorded in the differentiated mode, by using a lock-in amp with a time constant of 0.1 s and a sensitivity value of 100 x. In conjunction with the lock-in amp an electron multiplier control unit with modulation energy set to 2 eV was used. Data was recorded using an electron beam voltage of 5 keV and a ion current of 0.95 µA. Sputter cleaning of the surface was performed on an raster area of 2x2 mm with a ion beam voltage of 2 kV and a current of 0.073 µA . The system was kept in the UHV region with a pressure value of 10^{-9} Torr, by making use of an ion pump. Only during sputter cleaning did the pressure rise to a maximum value of $2x10^{-7}$ Torr.

Polycrystalline Fe samples of dimension 10 mm diameter and 0.5 mm in thickness were mechanically polished on diamond suspension down to 1 µm and subsequently cleaned in an ultrasonic bath of ethanol. Samples were then mounted onto the heating stage located on the sample holder of the AES system. During the heating experiments, the temperature was measured using a K-type thermocouple located on the heating stage beneath the sample.

Constant temperature heating was performed at temperatures in the range 823 K – 1073 K in increments of 50 K. Samples were heated to the desired temperature and once there, kept at that temperature for 1 hour to ensure an equilibrium state within the bulk of the crystal. Afterwards the surface was sputter cleaned for 10 min and the data acquisition started. After each segregation run the sample was heated at 1073 K for 3 hours in order to eliminate any depletion of subsurface layers that might have originated from the previous segregation run. The following peaks were monitored during the segregation run: S (153 eV), C (275 eV), N (389 eV), O (510 eV) and Fe (50 eV and 705 eV). Peaks were analysed afterwards in order to calculate the true APPH values and ensure that no peak overlapping occurred. Data was then quantified using the method for thin overlayers, described by Briggs and Seah [5] and the equations of Shimizu [6] for the calculation of the backscattering factors using elemental standards of known composition to calculate sensitivity factors. For the calculation of the inelastic mean free path (IMFP) of Auger electrons, the TPP-2 method was used [7].

4. Results and discussion

Figures 1 and 2 show the segregation profiles for temperatures 823 K and 1073 K respectively representing the segregation at lower temperature and at the higher temperatures. Three elements were observed for the temperatures 873 K, 923 K and 973 K, namely C, S and Fe. Looking at figure 1, initially the segregation of C is observed, after some time the S starts segregating and is dominating the surface. This segregation profile can be explained by looking at the diffusion mechanisms of C and S. C is known to segregate via an interstitial diffusion mechanism [8] which is a faster mechanism than the substitutional mechanism of S [9]. The dominance of S on the surface can be explained at the hand of the segregation energies, from literature the segregation energy for C is -85kJ/mol and for S it is -190kJ/mol [1, 2]. Thus the segregation of S is energetically more favourable that the segregation of C.

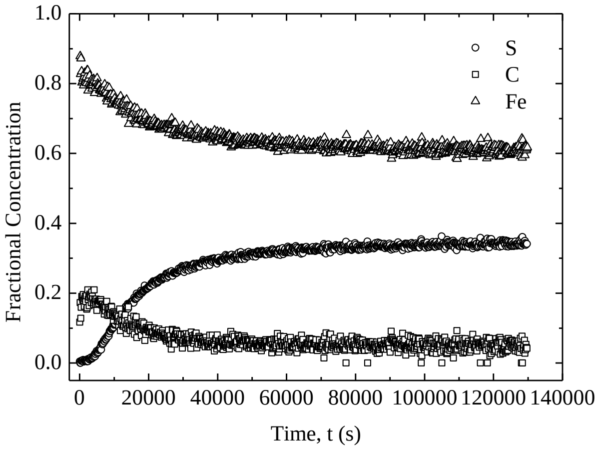

Figure 1: Segregation profile of the Fe sample for constant temperature heating at 823 K.

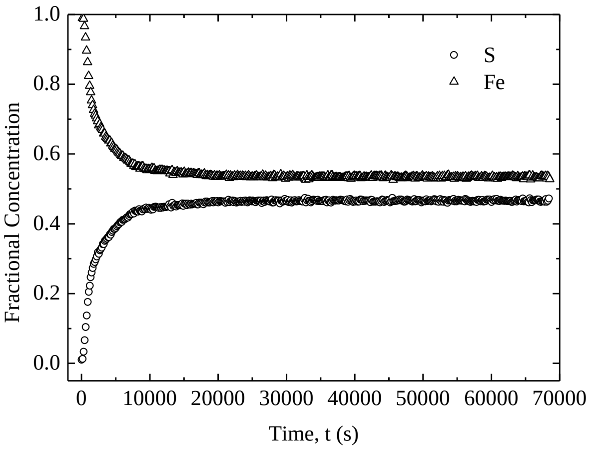

Figure 2: Segregation profile of the Fe sample for constant temperature heating at 1073 K.

Figures 3-5 shows the best fits of equation 2 to the kinetic part of the segregation profiles. The diffusion parameters used for the fit was obtained from literature [1].

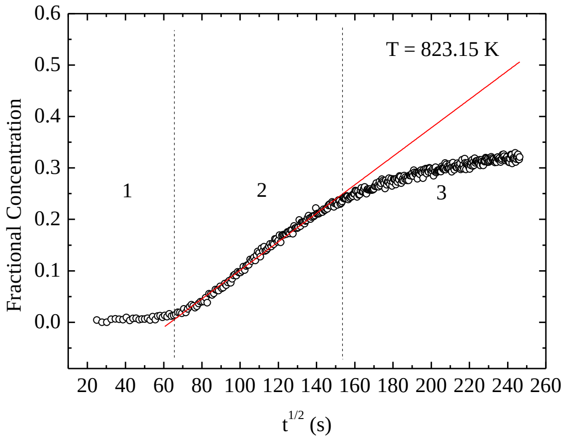

Figure 3: Linear fit to the segregation profile of S obtained at a temperature of 823 K. Three regions in the segregation profile can be distinguished: the first region as a result of sputtering, the second is the kinetic part of the segregation run and the third is the region in which segregation slows down.

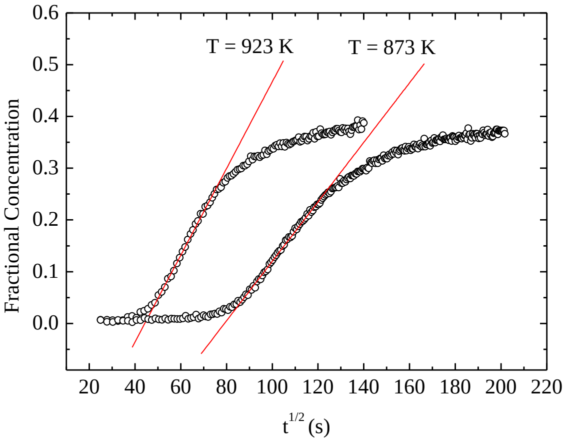

Figure 4: Linear fits to the segregation profiles of S obtained at temperatures 873 K and 923 K.

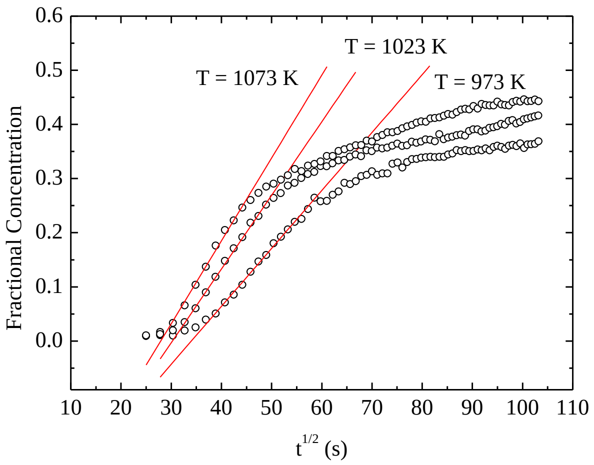

Figure 5: Linear fits to the segregation profiles of S obtained at temperatures 973 K, 1023 K and 1073 K respectively. An increased gradient of the linear fit is observed as the temperature is increased from one segregation run to the next, indicative of a larger diffusion coefficient for the higher temperatures.

Looking at the data, there are three distinctive regions, illustrated in figure 3: The first region is a result of sputtering, during the sputtering process a depletion layer is created beneath the surface. As the S starts to segregate out from the bulk, this depletion region is filled, once filled the surface is populated with the segregating S. The second region is marked by an increasing S concentration, immediately after sputtering the Fe surface is poor in S, but as more and more S segregates to the surface an increasing rate is observed. This region is the rate determining region in the segregation run, this is also the region in which the fits of equation 2 was performed. The third region is seen as a plato area, this is where the surface has reached a maximum S coverage and the segregation process is slowing down. From figures 4 and 5, an increased gradient of the fits can be seen as the temperature is increased, indicating an increase in the diffusion coefficient as expected. Bulk concentration values as extracted numerically for each of the temperatures are given in table 1 below.

Table 1: Values for bulk concentration of S in the Fe-S sample, as numerically extracted from experimental data using the adapted $t^{\frac{1}{2}}$ equation describing segregation.

Temperature, T (K)	**Bulk concentration, C_B (ppm)**
823	17.10 ± 0.1500
873	19.40 ± 0.1528
923	16.40 ± 0.2278
973	12.90 ± 0.2200
1023	10.60 ± 0.1990
1073	7.99 ± 0.2181
Average bulk concentration	**14.065 ± 0.1946**

5. Conclusion

The use of the $t^{\frac{1}{2}}$ equation to describe the kinetic part of a segregation profile has been fitted in the linear form for temperatures in the range 823 K -1073 K increased in 50 K increments. Values for the diffusion parameters were obtained from literature where a similar sample was studied. As expected, an increase in the gradient of the fit was observed going from one temperature to the next higher temperature, indicating an increased diffusion coefficient. At 873 K, the segregation of both C and S was observed. At first the C segregates due to its faster diffusion mechanism which follows an interstitial path. After sufficient time the substitutional diffusing S segregates to the surface and dominates the surface due to its large segregation energy of -190 kJ/mol over the segregation energy of -85 kJ/mol for C. At 1073K only the segregation of S was observed on the surface, this illustrates the dominance of S on the surface at high temperatures and the ability of S to segregate even at low concentrations of 14.065 ± 0.1946 ppm.

6. References

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Acknowledgments

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