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AUGER ELECTRON SPECTROSCOPY OF PHOSPHORUS SEGREGATION IN AN Fe-Ni-C-P ALLOY AT 400°C

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Résumé : L'étude par spectroscopie des électrons AUGER de la ségrégation superficielle du P dans un alliage austéno-martensitique Fe-Ni-C-P à 400°C a montré une interaction répulsive entre C et P ségrégés et un coefficient de diffusion de P de \(1,3 \times 10^{-17} \text{m}^2/\text{s}\). Cette valeur est environ d’un ordre et demi plus grand par rapport au coefficient donné dans la littérature pour la ferrite. Ceci peut s'interpréter séparément ou concomitamment par l’un des faits suivants: diffusion en surface, composition chimique et/ou microstructure. L'enthalpie libre de ségrégation du P a été trouvée être égale à \(-48,8 \text{kJ/mol}^{-1}\).

Abstract : The study of AUGER electron spectroscopy of the P surface segregation in an austenomartensitic Fe-Ni-C-P model alloy at 400°C has showed a repulsive interaction between segregated C and P and a P diffusion coefficient of \(1.3 \times 10^{-17} \text{m}^2/\text{s}\). This value is about one and a half order of magnitude higher than the P diffusion coefficient reported in the literature for ferrite. This was explained as the separate or concomitant effect of either surface diffusion, chemical composition and/or microstructure. The free energy of P segregation was determined to be equal to \(-48,8 \text{kJ/mol}\).

1 - Introduction

Phosphorus plays an important role as a segregant element on the temper embrittlement of many ferrous alloys. The intensity of its segregation to high angle boundaries in these alloys is a function of the temperature and time allowed for the segregation to take place, as well as to the actual chemical composition and microstructure. The most critical temperature range lies between 350 and 600°C, which is frequently attained during heat treatments, representing also the application conditions for creep resisting steels. The thermodynamic equilibriums between chemical elements present in the alloy and the kinetics of segregation are highly dependent on the type of metallic and metalloid elements existent and their respective concentrations. For example, sulfur is a powerful segregant in pure iron (1) and nickel (2) but not in steels because it is efficiently scavenged by manganese, whereas phosphorus and sulfur segregate competitively in Fe-P-S alloys (1) and in nickel (2). That is, an increase in the activity of either element in solution results in decreased concentration of the other element at high angle boundaries. On the other hand, in Fe-P-Sb alloys Sb does not affect but is affected by the segregation of P (1). In steels, the inherent presence of carbon at greater or lesser levels changes the dynamic equilibrium of P segregation as compared to what is found in carbon-free alloys. This is so because there is site competition between C and P (3-6). This equilibrium of mutual displacement may be represented by the relation [1] (3).

\[ P_{\text{segregated}} + C_{\text{dissolved}} = P_{\text{dissolved}} + C_{\text{segregated}} \]  

A similar behaviour to the one indicated by relation [1] is experienced for P in the presence of N (7), however N is scavenged in steels by Al and Si (4).

There may exist synergistic segregation of a metallic element with P, such is the case for Ti (8). It was also thought to be the situation for the Mn-P interaction (4-9). Nevertheless Grabke et al. (3), have shown that in fact there is no synergistic Mn-P segregation to high angle boundaries, unless C is present in the alloy. Experiments with carbon-free Fe-Mn-P (with up to 10% Mn) alloys showed a high but approximately constant P grain boundary concentration with increasing manganese content upon tempering at 500°C up...
to four weeks, whereas increasing (but lower) P grain boundary contents were observed for similar alloys containing 0.15 % C. This was rationalized not as a direct action of Mn but by its effect on the C-P interaction, as described by equation [1]. At low Mn contents the activity and the concentration of dissolved carbon are in equilibrium with cementite and are relatively high, which permits P displacement from segregation sites. Increased Mn concentrations yield a decrease on the content of dissolved and segregated C by the formation of more stable \((Fe, Mn)_2C\) carbides. As a consequence, less P is displaced by C from segregation sites, leading to an increased P segregated concentration.

The analysis of the segregation kinetics of some substitutional alloying elements themselves in ternary ferrous 0.4 wt% C alloys has shown a large enrichment factor for Mo, intermediate values for Mn and Si and no enrichment for Ni and Co (10). Guttman et al. (3), have also remarked that the intrinsic segregation of Ni is virtually zero, although it presents an attractive segregation with P. They have also shown that the Mo-P co-segregation is a very strong one, and that the Cr-P segregation is attractive, whereas the P-P one is slightly repulsive.

Ehrart et al. (6), have measured the grain boundary concentration (GBC) of P in several ferrous alloys containing a bulk P concentration of 0.05 % after tempering at 550°C. They found very large P GBC for the Fe-P alloy, about 65 at %, and much smaller amounts for the Fe-Ni-C-P and Fe-C-P alloys, about 15 at % and 13 at %, respectively. The objective of the present paper was to analyse the kinetics and thermodynamics of P surface segregation in an Fe-Ni-C-P austeno-martensitic model alloy, by the determination of the P bulk diffusion coefficient and the free energy of segregation at 400°C.

2 - Experimental Procedures

The iron-nickel base alloy used in this research had the following chemical composition in weight percent : C = 0.40 ; Ni = 23.18 ; P = 0.0363 ; Mn = 0.548 ; Si = 0.423 ; S = 0.019 ; Cu = 0.14 ; Mo = 0.025 ; Cr = 0.0438 ; O = 0.0011 ; N = 0.0038 ; Al = 0.0070 ; As = 0.0405 ; Sb = 0.0050 ; Sn = 0.0026 ; Fe = balance. Fabrication heat treatments included 2 h at 1050°C, water quenching followed by liquid nitrogen quenching; re-heating to room temperature and then to 1050°C, and repeating the same sequence of events once more ; heating up to 1200°C for 2h, followed by water quenching. This resulted in a microstructure containing about 78% martensite and 22% retained austenite, as determined by X-ray diffractometry. Samples measuring 10x10x1 mm² were ground up to 1200 grid paper, and polished up to 1µm diamont paste. Electrolytic polishing was avoided not to change the surface chemical composition. Auger electron spectroscopy was performed in a Riber equipment with a cylindrical mirror analyser, using primary beam energy and current of 3 keV 20µA, respectively, modulation amplitude of 7 eV (pic to pic), electron multiplier voltage of 2.2 kV, time constant of 0.3 s and a vacuum of 0.067 µPa. The temperature of 400°C was chosen for the study of the kinetics of P surface segregation because it is within the tempering temperature of interest and also because this is the highest temperature below which no martensite-austenite phase transformation takes place for this alloy (11). Before starting the kinetic studies the samples underwent cycles of pre-heating to 390°C, cooling to room temperature and argon ion beam sputtering for cleaning the surface. This had the objectives of decreasing the amount of diffusible C, trapped as carbides, and to eliminate the presence of other impurity elements, such as S, N, Sb, etc... from the surface to be analysed. 24 hour kinetic measurements were performed at 400°C for four different samples and the results were averaged up. All the measurements were made taken the peak to peak heights for P (120 eV), C (272 eV), Fe (651 eV) and Ni (848 eV). Although the Fe (703 eV), peak is more intense and more frequently used, the Fe (651 eV) peak was chosen because it is less affected by neighbouring peaks.

Since the P bulk concentration is negligible compared to its surface segregated concentration, \(C_p^{surf}(t)\), it follows that:

\[
C_p^{surf}(t) = K_p^{surf} \frac{H_{p}^{surf}(t)}{H_{M}^{surf}(t)} [2]
\]
where $H^{\text{surf}}_P(t)$ and $H^{\text{surf}}_M(t)$ are the peak to peak heights of P and of the "material" for each time, t, during the period allowed for the diffusion to take place at 400°C, and $K^{\text{surf}}_P$ is a calibration constant. Since the main elements in the chemical composition of the alloy are Fe and Ni, and since the ratio of the peak to peak heights of these pure elements (at 3 keV) is $H^{\text{surf}}_{Fe}/H^{\text{surf}}_{Ni} = 0.77$, it was defined that:

$$H^{\text{surf}}_M(t) = H^{\text{surf}}_{Fe(651)}(t) + 0.77H^{\text{surf}}_{Ni(848)}(t) \quad [3]$$

The calibration constant was taken as (12):

$$K_P = \left( \frac{H^*_P}{H^*_M} \right)^{-1} \left[ 1 - \exp \left( -\frac{e}{\lambda \cos \theta} \right) \right]^{-1} \quad [4]$$

where $H^*_P$ is the peak to peak height for the pure element P (at 3 keV) and $H^*_M$ is given by:

$$H^*_M = (at\%Fe)H^{\text{surf}}_{Fe} + (at\%Ni)0.77H^{\text{surf}}_{Ni} \quad [5]$$

$e$ is the thickness of the segregated layer, expressed as a function of the interatomic distance in martensite and austenite.

$$e = \text{vol}\%\text{martensite}.d_{\text{mart}} + \text{vol}\%\text{austenite}.d_{\text{aust}} \quad [6]$$

$\lambda$ is the mean free path of the Auger electron emitted by P and C atoms, about 0.5 nm and 0.77 nm, respectively (13), and $\theta$ is the emergence angle of the Auger electron out of the cylindrical mirror analyser used, equal to 42° 18' ($\cos \theta = 0.741$). For the present experiments at 400°C $K^{\text{surf}}_P = 1.7$ and $K^{\text{surf}}_C = 2.9$. The volume percentages of martensite and austenite for the present alloy at 400°C, respectively 77% and 23%, used for determining $e$, were precisely obtained by X-ray diffractometry (11), subjecting the samples to the same thermal history as those used for the AUGER kinetics measurements.

3 - Results and Discussion

Figure 1 shows the P and C surface concentrations as a function of the tempering time at 400°C. It can be seen that the maximum in P concentration coincides with the beginning of the C concentration build up at the surface. This confirms the already known repulsive interaction between C and P (3-6). However, it should be mentioned that measuring the C surface concentration by Auger electron spectroscopy is not a simple task. It is very difficult to sputter C entirely away under rare gas ion bombardment. There may occur C contamination due to the adsorption of residual gases and C may also diffuse from contaminated outer surfaces of the samples or the grips, spreading over the irradiated surface. In the present experiments, as it was mentioned before, a pre-treatment was performed in the Auger ultra-high vacuum chamber to decrease the amount of diffusible C, trapping it as carbides. As a result, the possibility of having electron beam induced C segregation to the free surface by dissociating carbides may not be neglected. However, this pre-treatment was efficient for allowing the build up of P surface concentration with time at the beginning of the kinetics measurements under essentially constant C surface concentration. This avoided interference with the analysis of the P segregation, and permitted the P bulk diffusion coefficient (D) to be determined for the present alloy at 400°C. This determination was done on the basis of the approach developed by Mc Lean (14, 23) for binary alloys, which is valid for the initial linear part of the segregated concentration versus $\sqrt{t}$ plot is:

$$C^{\text{surf}}_P(t) = \left( \frac{2C^{\text{sol}}_P}{\sqrt{D/\pi}} \right) \sqrt{t} \quad [7]$$

where $C^{\text{sol}}_P$ is the P concentration in solid solution, and $e = 0.25$ nm.

An average D value of $1.3 \times 10^{-17}$ m²/s was obtained. This is a fairly high value as compared to other ones available from the literature, which were put all together in figure 2. The high P diffusion coefficient obtained
at 400°C for the present alloy may be explained by the separate or concomitant effect of either surface diffusion, chemical composition or microstructure, as follows:

1) There may be a combined action of bulk and surface diffusion, yielding an overall faster diffusion coefficient. It has been proposed by White and Losch (20) that values of diffusion coefficients measured using the Auger technique and McLean's approach may be seriously influenced by surface diffusion, spreading out the diffusing species throughout the surface analyzed. This would be emphasized under the presence of a faster path for bulk diffusion as a way to reach the surface, where there could be created points acting as sources for surface diffusion.

2) The chemical composition of the alloy may play a role for the obtaining of a faster kinetics of segregation. The results of Luckman et al. (5) compiled in figure 2 show that this may effectively be the case. It is remarkable to notice that their higher values occur for the C containing alloy. (denominated 3340 + 0.06P). They have interpreted this as being possibly due to differences in the activity coefficient of P in C containing alloys or due to the existence of faster diffusion paths.

3) The microstructure of the alloy may also play an important role on the observed increased P diffusibility at 400°C, especially if one takes into account the possibility for the existence of faster diffusion paths. This will be analyzed as a function of the morphology of the phases present in the alloy and the kinetics of carbide nucleation at 400°C. It has been observed (21) by optical and transmission electron microscopy that the martensitic structure of the present alloy is plate-like by nature. Each martensite platelet consists in two parts: a twinned region around its mid-rib and an untwinned region stretching along the platelet periphery. This microstructure offers a great amount of interfaces for carbide precipitation. Very fortunately, an extensive study has been performed (21) using differential scanning calorimetry for a large group of Fe-Ni-C alloys, which includes the one presently used, having determined the kinetics of ageing and tempering for C bulk segregation and precipitation in a wide temperature interval. Four stages of heat release were identified: stage I : bulk segregation of C atoms from 70 to 150°C; stage II : formation of C atom clusters from 70 to 170°C; stage III : precipitation of C(n) carbides from 50 to 340°C. The C(n) carbides in steels are iron carbides with an hexagonal close packed structure, whose chemical composition is not well defined, and may vary up to the Fe2.3C stoichiometry; stage IV : precipitation of cementite from 200 to 450°C. These authors (21) have concluded that the total measured enthalpy involved with stage IV corresponds to the enthalpy of formation of cementite, meaning that almost the whole carbon available in the sample is used in Fe2C formation. Since the volume percentage of carbides present in the 400°C tempered Fe-Ni-C-P alloy used in this work is high, about 6% (11), and since the tempered martensite microstructure presents a great quantity of interfaces, it is likely that the heterogeneous nucleation of carbides at 400°C have created a network of precipitates. These could offer faster paths for P diffusion in the present conditions.

The unexpected finding of such a high P diffusion coefficient at 400°C has further support on the fact that the same set of data which yielded the present D value was used to obtain thermodynamic parameters with values similar to those reported in the literature. This was the case for the determination of the free energy of segregation of P, \( \Delta G_{P}^{seg} \), expressed as:

\[
\Delta G_{P}^{(surf)}^{seg} = -RT \ln \left\{ \frac{Y_{P}^{surf}}{C_{P}^{sol, sat} \left( 1 - Y_{P}^{surf} \right)} \right\} \tag{[8]}
\]

where \( Y_{P}^{surf} \) is the coverage of the segregating surface, given by:

\[
Y_{P}^{surf} = \frac{C_{P}^{surf, (eq.)}}{C_{P}^{surf, (sat)}} \tag{[9]}
\]

\( C_{P}^{surf, (eq.)} \) is the equilibrium segregated P concentration at 400°C and \( C_{P}^{surf, (sat)} \) is the saturation value for the segregated P concentration, determined on the basis of the saturation number of surface segregated P atoms (22) equal to \( 1.4x10^{15} \text{P atoms/cm}^2 \). The average value obtained for the P surface coverage at 400°C was \( Y_{P}^{surf} = 0.8 \). This yielded a free energy of P segregation for the present conditions equal to - 48.9 kJ/mol. This is in very good agreement with the value of \( \Delta G_{P}^{seg} = 48.8 \text{kJ/mol} \) (for \( Y_{P}^{surf} = 0.8 \)) presented by Guttmann et al. (4), as a result of a least square correlation based on several data compiled from the literature and shown in their figure 22.
4 - Conclusions

The analysis of the kinetics and thermodynamics of P surface segregation by Auger electron spectroscopy of an austenomartensitic Fe-Ni-C-P alloy has led to the following conclusions:
1) a marked repulsive interaction between carbon and phosphorus was observed at the segregated surface.
2) the diffusion coefficient of phosphorus at 400°C is equal to $1.7 \times 10^{-17} m^2/s$. This value is about one and a half orders of magnitude higher than the one reported in the literature for the diffusion of phosphorus in ferrite which was rationalized by the separate or concomitant effect of either surface diffusion, chemical composition and/or microstructure. The existence of faster diffusion paths is highly probable due to the intensive carbide precipitation taking place at 400°C for the present alloy;
3) the thermodynamic analysis of P surface segregation yielded a P surface coverage of 0.8 and a free energy for P surface segregation of - 48.8 kJ.mol$^{-1}$, which are in very good agreement to the values reported in the literature.

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5 - References

/11/ DE MIRANDA, P.E.V., GARNIER, P. and HABASHI, M., To be submitted for publication in Metallurgical Transactions.
Fig 1: P and C surface segregated concentrations (at %) versus tempering time at 400°C, as measured by A.E.S.

Fig 2: Dependence of phosphorus diffusion coefficient with temperature.