Surface and Grain Boundary Segregation on and in Iron and Steels

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(Received on October 3, 1988; accepted in the final form on December 22, 1988)

The equilibrium segregation of the elements A = C, Si, Sn, N, P, O, and S was studied for binary systems Fe–A in the stability range of the α-solid solution using surface analytical methods. On the surfaces ordered structures were observed by LEED and surface concentrations were determined by AES in dependence on bulk concentration and temperature. The chemical binding state was characterized by XPS. In grain boundaries the segregation of P and Sn was determined by AES on intergranular fracture faces after equilibration at elevated temperatures and fracture in UHV. Effects of alloying elements, especially C, on grain boundary segregation are described. Correlations of surface and grain boundary segregation with the chemical and mechanical behavior of steels are shortly discussed.

KEY WORDS: surface segregation; grain boundary segregation; segregation thermodynamics; segregation structures; binding states of segregated elements; site competition; displacement equilibria; Auger-electron-spectroscopy (AES); photoelectron-spectroscopy (XPS); low energy electron diffraction (LEED); surface reactions; oxide nucleation; surface diffusion; intergranular fracture; embrittlement of steels; intergranular corrosion; creep of heat resistant steels; cavity formation.

1. Introduction

Many processes, such as gas–metal reactions (carburization/decarburization, nitrogenation/denitrogenation), corrosion, catalysis, surface diffusion, sintering, recrystallization, adhesion, friction, wear, etc., are determined decisively by the atomic composition of the surface of iron. Also the atomic composition of the grain boundaries is very important in affecting the mechanical properties and the corrosion behavior of steel. These interfaces will normally be covered with impurity atoms, the surfaces by adsorption from the gas phase or segregation of dissolved atoms from the bulk, and also the grain boundaries by segregation from the bulk.

The equilibrium segregation on iron surfaces and at grain boundaries

\[ A \text{ (Dissolved)} = A \text{ (Segregated)} \]  \hspace{1cm} (1)

where \( A = \text{C, Si, Sn, N, P, O, S, \ldots} \), has been investigated for binary systems Fe–A by surface analytical methods.

Concentrations of the extraneous elements on the surface were determined by Auger-electron-spectroscopy (AES) in dependence on the bulk concentration \( x_A \) and on the temperature of equilibration, and ordered structures on surfaces were determined by LEED, \( i.e. \), low energy electron diffraction. The binding modes were characterized by X-ray photoelectron spectroscopy (XPS). The same surface states should result from segregation or adsorption concerning surface structure, surface concentration and mode of binding.

Impurities in steels can have strong effects on the mechanical properties and on the corrosion behavior, especially if they tend to enrich at the grain boundaries. Elements of the group IV to VI of the periodic table: Sn, P, As, Sb, S, Se, and Te segregate at grain boundaries and embrittle steels. The study of this segregation, which is restricted to a few monolayers in and near the interface, was possible since the development of AES as a surface analytical tool. By fracture of specimens inside a UHV-chamber and by AES-analysis of the intergranular fracture faces grain boundary concentrations of the embrittling elements could be determined. In our studies, grain boundary segregation of C, N, and B was also detected. These elements are not embrittling and, therefore, their detection is possible only if an embrittling element such as S or P is present which initiates intergranular fracture. In our AES-investigations on different steels, deep drawing steels, tempered steels, heat resistant steels, etc., from German production only the impurity elements P and Sn were detected at grain boundaries. Obviously, other impurities such as As and Sb are present only in too small bulk concentrations, and sulfur is being scavenged by Mn so that the studies in MPI have been focussed on the grain boundary segregation of P and Sn in iron, on the effects of alloying elements on the segregation and on the effects of P and Sn on materials properties.

The equilibria were studied of grain boundary segregation of P and Sn in binary Fe–P and Fe–Sn, ternary, and quaternary alloys, by equilibrating specimens at different temperatures for sufficient time, afterwards analyzing intergranular fracture faces by AES.

The thermodynamics of segregation as well for surface segregation and for grain boundary segregation are described by the Langmuir–McLean equation:

\[ \theta_A (1 - \theta_A) = x_A \exp (- \Delta G_A / RT) \]  \hspace{1cm} (2)
where, $\theta_i$: the occupancy of the grain boundary sites with the segregating element $i$
$x_i$: the mole fraction in the bulk.

The free energy of segregation is

$$\Delta G_i^* = \Delta H_i^* - T \Delta S_i^*$$ .............(3)

where, $\Delta H_i^*$: the enthalpy of segregation
$\Delta S_i^*$: the excess entropy of segregation.

According to thermodynamics the segregation increases with decreasing temperature and with increasing bulk concentration.

All investigations of the surface segregation have been performed in the temperature and concentration range of the a- or \(\gamma\)-solid solution, in order to avoid the formation of three-dimensional, stable, or metastable compounds on the surface. Also the equilibria of grain boundary segregation have been established at elevated temperature within this range of the phase diagram and were measured on rapidly quenched specimens.

2. Surface Segregation

2.1. Carbon

The surface segregation of carbon has been investigated in the temperature range 400–800°C on single crystals with carbon concentrations between 10 to 100 ppm C. On Fe(100) a c\((2 \times 2)\) structure (Fig. 1) with 50 at% C is approached for high concentrations and low temperatures, this is the saturation coverage ($\theta = 1$). The degree of coverage $\theta$, decreases with increasing temperature and decreasing bulk concentration, as expected from thermodynamics, see Fig. 2.

These dependencies are described by the Langmuir–McLean equation (2). This equation can be rewritten according to

$$\ln \frac{\theta_i}{1-\theta_i} = -\frac{\Delta H_i^*}{RT} + \frac{\Delta S_i^*}{R} + \ln x_i$$ .............(4)

where, $\Delta H_i^*$: the enthalpy of segregation
$\Delta S_i^*$: the excess entropy of segregation.

For the case of carbon on Fe(100) the segregation enthalpy is $-85 \text{kJ/mol}$, as derived from the plot according to Eq. (3) shown in Fig. 3.

For carbon segregation on other orientations of iron, the results are not so simple and clear. The binding mode of carbon on Fe(100) has been characterized by photoelectron spectroscopy (XPS). Spectra from single crystal surfaces with segregated C have been taken and have been compared with spectra of graphite and cementite (Fe,Cr)$_3$C. In order to obtain a thermodynamically stable cementite a Fe-
2\%Cr alloy had been carburized in CH\textsubscript{4} - H\textsubscript{2}. The photolines of the C 1s photoelectrons of carbon are shown in Fig. 4.

The sample with 20 ppm C only shows the peak for segregated carbon, on the sample with 40 ppm C besides segregated carbon there is graphite deposited by oversaturation (at 600°C). The energies of the C 1s electron levels are distinctly different from the energy level of C 1s in graphite and in the carbide. The segregated carbon is a special binding state of carbon. By considering the shift of energy, about 
\(-2.0\) eV in comparison to graphite, one may deduce that a certain electron transfer has taken place from iron to carbon. The bond Fe-C is similar as in cementite, prevailing homopolar, but it is somewhat stronger polarized than in the carbide.

2.2. Silicon

The surface segregation of Si has been studied on Fe-3\%Si single crystals in the temperature range 450-900°C.\textsuperscript{9} The kinetics of segregation has been measured on surfaces which had been cleaned before by sputtering. These measurements yielded after evaluation according to a solution of the diffusion equation given by McLean, diffusion coefficients of silicon in \(\alpha\)-iron which are in good agreement with literature data. This is true for the orientation (100) but for the orientation (111) there seem to be kinetic obstacles, maybe in the transition of the silicon atoms through the surface. The dependence of surface concentration on temperature has been measured for the equilibrium of silicon segregation on Fe(100). This dependence can be described by the Langmuir-McLean equation (2). The result for the Gibbs free energy of segregation is

\[
\Delta G^\circ = -48 000 + 15T \text{ (J/mol)} \quad \text{......(5)}
\]

The value of the segregation enthalpy of silicon on iron \(\Delta H^\circ = -48 \text{ kJ/mol}\) is much lower than for carbon. Thus carbon can displace silicon from the surface on Fe-3\%Si samples which contain small concentrations of carbon:

\[
\text{C (Dissolved)} + \text{Si (Segregated)} = \text{C (Segregated)} + \text{Si (Dissolved)} \quad \text{......(6)}
\]

This equilibrium of mutual displacement has been measured in dependence on temperature, see Fig. 5. According to the higher value for \(\Delta H^\circ\) the C-segregation prevails at lower temperatures, for higher temperatures the carbon segregation decreases and silicon is able to segregate to the surface. This equilibrium was described by relatively simple equations which only consider the site competition of both segregating elements:

\[
\theta_a/(1-\theta_i-\theta_a) = x_a \exp (-\Delta G_a^\circ/RT) \quad \text{......(7)}
\]

\[
\theta_c/(1-\theta_c-\theta_a) = x_c \exp (-\Delta G_c^\circ/RT) \quad \text{......(8)}
\]

Here the thermodynamic values for the Si-segregation stay unchanged, while the value for \(\Delta H^\circ\) is increased by the presence of Si.

\[\text{Fig. 4. Investigations of the binding of carbon by photoelectron spectroscopy.}\]

\[\text{Fig. 5. Surface segregation of silicon on Fe-3\%Si(100), temperature dependence of the displacement equilibrium in carbon, and silicon segregation, Fe-3\% Si with 40 ppm carbon.}\]

2.3. Tin

The surface segregation of tin was investigated on (100)-faces of Fe-4\%Sn samples in the temperature range 600-800°C.\textsuperscript{7} During segregation of tin at 600°C by diffusion onto a surface which had been cleaned by sputtering before, in the increase of concentration with time there is a step, see Fig. 6(a) which can be associated with the formation of the saturated \(c(2 \times 2)\) structure. However, the surface concentration continues to increase, till a coverage of about 1.2 tin atoms per iron atom is obtained. During this process the LEED-diffraction pattern vanishes, obviously a change of the surface structure occurs from the ordered structure to disorder. In this transition the binding mode of the segregated tin changes, as can be seen from the photolines. The binding energies of the electrons in the Sn 3d and Fe 2\(p\) levels show distinct changes in the phase transition from \(c(2 \times 2)\) structure to disordered segregation. The \(d\)-levels of the segregated tin shift in the direction to the values determined for pure tin. At the lower surface concentration of tin the binding energies of the
2.5. Phosphorus 
Upon saturation of Fe(100)-surfaces with segregated phosphorus also a c(2×2) structure is obtained, this has been observed with Fe-10%P single crystals at temperatures 800°C, under these conditions one has the α-solid solution. Comparison of the photolines of the phosphide Fe₃P with the photolines of segregated phosphorus shows a clear distinction, Fig. 7, the segregated phosphorus is in a different state with lower binding energies of the 2s and 2p electrons. The chemical shift of -2.0 eV relative to elementar phosphorus indicates a strong electron transfer from iron to segregated phosphorus.

In AES and XPS investigations it was observed that phosphorus does not segregate only on the outer surface, but with increasing surface coverage there is also enrichment of phosphorus in the lattice near the surface. Upon increasing coverage new photolines are observed, indicating about 1 eV higher binding energies of the P 2s and P 2p electrons (Fig. 7), corresponding to the photolines for the phosphide Fe₃P. However, it can be excluded, that the phosphorus enrichment in the surface-near atom layers is a formation of this three-dimensional phase. The studies have been performed in the range of the α-solid solution.

Recent studies suggest that the "subsurface phosphorus" is segregated to dislocations, which had been introduced into the materials by surface polishing and finishing. The amount of subsurface phosphorus was enhanced in specimens deformed by compression and it decreased upon annealing at temperatures where dislocations start to move and annihilate.

Fig. 7. Photolines of phosphorus, (1) in the compound Fe₃P, (2) segregated on a single crystal Fe-10%P and (3) on polycrystalline Fe-0.08%P upon saturation with segregated phosphorus.
2.6. Oxygen

The surface segregation of oxygen on iron can not be investigated with the segregation method described before, since the oxygen solubility in iron is very small. In spite of that, segregation equilibria can be established, even at well-defined thermodynamic potential of the oxygen if a solid electrolyte cell is used: iron sample/oxygen-ion conducting solid electrolyte/reference electrode. Such cell, for example Fe/ThO$_2$ $\times$Y$_2$O$_3$/Cr-Cr$_2$O$_3$, can be inserted into an UHV-system, and by controlling the cell voltage the chemical potential of oxygen can be fixed in and on the sample. Thus the oxygen segregation at a certain oxygen potential is established. With this set-up measurements are possible at oxygen potentials, which correspond to oxygen pressures in the range $10^{-10} \ldots 10^{-15}$ atm. Fig. 8 shows an example of a measurement of the oxygen segregation on an iron film, vapor deposited on the solid electrolyte. A two-step isotherm is observed, obviously there are two adsorption structures, at $>10^{-25}$ bar O$_2$ with the ratio O/Fe = 0.25 and at $>10^{-25}$ bar with the ratio O/Fe=1. The oxygen adsorption at very low oxygen pressures <10$^{-30}$ bar O$_2$ can be related to oxygen adsorbed on steps, kinks, and other active sites of the surface. LEED and AES studies with iron single crystals, which had been sintered together with a mixture of Fe and of the lowest oxide FeO, showed a $p(1 \times 1)$ structure at 800°C on Fe(100), see Fig. 9. This is in agreement with the degree of coverage O/Fe=1 for oxygen pressures near the equilibrium Fe–FeO. Oxygen on Fe(100) is also embedded in central sites between four iron atoms, however, in contrast to the other nonmetal atoms it reaches not only 50 % coverage in a $c(2 \times 2)$ structure but 100 % coverage in $p(1 \times 1)$. The oxygen adsorption and oxide nucleation can be depicted as shown in Fig. 10.

Studies using the couple Fe single crystal/Fe–FeO mixture have also been performed for the orientations (110) and (111) at 800°C, see Fig. 9. On Fe(110) the degree of coverage is relatively low at 800°C and no ordered segregation structure could be detected—most probably the oxygen atoms are mobile at 800°C on Fe(110). Upon quenching, the oxygen atoms cluster together under formation of oxygen layers ordered similarly as in FeO(111) planes.

The Fe(111) surface is not stable at 800°C in equilibrium with the Fe–FeO mixture—FeO crystallites begin to grow in the epitaxial relation Fe(111)//FeO(111), see Fig. 11. In this process the high energy surface Fe(111) is reduced and the low energy surface FeO(111) increases.

2.7. Sulfur

Sulfur is extremely 'surface active' on iron sur-
faces, even for very small bulk concentrations 1 ppm in the stability range of the α-phase up to 900°C always saturation of the surface with sulfur was observed after equilibration. The presence of sulfur on the iron surface strongly affects surface reaction kinetics in the case of carburization and nitrogenation of iron and also the surface diffusion is influenced by adsorbed sulfur, the surface self-diffusivity of iron is enhanced in the presence of adsorbed sulfur. On Fe(100) the c(2 × 2) structure is obtained, up to high temperatures a very distinct LEED pattern of this structure can be observed. Fig. 12 shows this adsorption structure of segregated sulfur which was proved by measurements and theoretical calculations of the LEED-intensity-energy curves. In this schematic the diameter of sulfur is assumed to be equal to the diameter of S²⁻-ions.

Determinations of the electron levels of segregated sulfur by photoelectron spectroscopy confirmed, that these are very near to the electron levels of the doubly-ionized sulfur ion S²⁺. The binding energy of the S 2p and S 2s electrons is by some 10th eV higher than in the sulfides FeS and FeS₂, see Fig. 13.

3. Grain Boundary Segregation

3.1. Grain Boundary Segregation of Phosphorus in Ferrite and Austenite

3.1.1. Ferrite

The equilibrium grain boundary segregation of P in ferrite was studied on 7 Fe–P melts with P contents in the range 0.003 to 0.33 wt% P. As expected, according to thermodynamics, the grain boundary concentration decreases with increasing temperature and with decreasing bulk concentration, Fig. 14, and the data could be evaluated according to the Langmuir–McLean equation (4). The free enthalpy of grain boundary segregation of phosphorus in α-iron can be written:

$$
AG_r = \Delta H_r - T \Delta S_r
$$

Ishida et al. have re-evaluated the data in Fig. 14 considering the magnetic effect on grain boundary segregation, they suggest that Eq. (10) is applicable only to segregation in the fully ferromagnetic state and that the paramagnetic segregation free energy is given by

$$
AG_r = -15,000 - 33T \text{ (J/mol)}
$$
The presence of phosphorus in the grain boundaries induces grain boundary embrittlement, with increasing grain boundary phosphorus concentration the fracture mode (at low temperatures) changes from transgranular to intergranular.

In a similar way the grain boundary segregation in Fe-C-P alloys was investigated. Different concentrations in the range 10 to 100 ppm C were introduced to specimens with constant bulk concentrations of P by carburization in CH₄-H₂ mixtures. The specimens were annealed at different temperatures to establish the equilibrium grain boundary segregation of C and P, quenched and analyzed by AES. The results indicate displacement of phosphorus by carbon at the grain boundaries, according to

\[ C(\text{Dissolved}) + P(\text{Segregated}) = C(\text{Segregated}) + P(\text{Dissolved}) \]  \hspace{1cm} (11)

With increasing carbon content the grain boundary concentration of phosphorus decreases and the grain boundary concentration of carbon increases, see Fig. 15. At 600°C the solubility limit of carbon is about 55 ppm, at higher concentrations cementite precipitates and no further changes of grain boundary concentrations are to be expected.

The increasing carbon concentration in the bulk and in the grain boundaries causes a decrease in the percentage of intergranular fracture, thus carbon acts as a de-embrittling element. The displacement of phosphorus and carbon according to Eq. (3) can be described by equations considering only the site competition of both elements.

\[ \theta_p(1 - \theta_p - \theta_c) = x_p \exp \left( -\frac{AG_p}{RT} \right) \]  \hspace{1cm} (12)

\[ \theta_c(1 - \theta_p - \theta_c) = x_c \exp \left( -\frac{AG_c}{RT} \right) \]  \hspace{1cm} (13)

From more extensive investigations in this system also the Gibbs' free energy could be determined for grain boundary segregation of carbon in ferrite which is \(-72 \text{ kJ/mol at 500°C}\) compared to \(-49 \text{ kJ/mol for phosphorus}\). This description of the displacement equilibrium (11) at grain boundaries corresponds to the result for the displacement equilibrium of carbon and silicon on the iron surface, see Eqs. (6) to (8). Site competition without additional energetic interaction between carbon and phosphorus at grain boundaries also was confirmed by H. Kimura and coworkers.

In carbon steels with carbon contents higher than the maximum solubility in ferrite (0.02% at 750°C) the carbon concentration is given by equilibrium with cementite and is relatively high in the critical temperature range concerning phosphorus segregation, thus grain boundary segregation in carbon steels generally will be low. However, the addition of carbide-forming elements, e.g., some percents of Cr or Mn, decreases the solubility of carbon, therefore the equilibrium (11) is shifted to higher grain boundary segregation of phosphorus. This effect is not caused by direct interaction of Cr or Mn with P, by some ‘synergistic cosegregation’ as assumed by other authors, but by the reduction of carbon concentration in bulk and grain boundaries in the presence of Fe₃C and respectively (Fe,Mn)₃C, whereby phosphorus can segregate to the grain boundaries. Fig. 16 demonstrates these results, grain boundary segregation in carbon-free alloys Fe-P and Fe-Cr-P is the same and unaffected by the presence of Cr, grain boundary segregation in Fe-Cr-C-P, however, is considerably increased compared to Fe-C-P.
3.1.2. Austenite

Grain boundary segregation of P in austenite was investigated after annealing of samples in the austenitic range and quenching in water.\(^{20}\) The evaluation of data obtained with binary alloys containing 0.09, 0.145, and 0.20 %\(^{\text{P}}\) yielded a value of \(-49 \pm 4\) kJ/mol at 1000°C, similar as for ferrite at 500°C. Thus, the grain boundary concentrations are considerable, between 15-30 at% of a monolayer for these alloys. As to be expected, the grain boundary concentration decreases with increasing temperature. Also in austenite the presence of carbon decreases grain boundary segregation of P and Eqs. (12) and (13) can be applied, the free energy of grain boundary segregation can be derived for carbon in austenite to be

\[
AG_c = -30 \text{ kJ/mol.}
\]

The effect of boron on phosphorus segregation in austenite is similar to the effect of carbon but much more pronounced. Even very small concentrations of boron in the range 5 to 30 ppm B strongly decrease the phosphorus segregation. Boron also was detected at the grain boundaries,\(^{30}\) its free energy of grain boundary segregation is relatively high, \(AG^*_c \approx -100\) kJ/mol.

3.2. Grain Boundary Segregation of Tin in Ferrite

For a study of the equilibrium grain boundary segregation of tin, 7 Fe-Sn melts were prepared with tin contents in the range 0.02 to 0.2 wt% Sn.\(^{20}\) The scatter of the measured values is very large, possibly according to a strong orientation dependence of tin grain boundary segregation, see Fig. 17. However, the average values could be fitted with the Langmuir–McLean equation (2), the values were obtained for the free energy of segregation

\[
AG_{Sn}^o = -(22.500 \pm 2.800) - (26.1 \pm 0.9) T \text{ (J/mol)}
\]

These data indicate a rather low tendency to grain boundary segregation of tin.

Furthermore, tin can be displaced by carbon from grain boundaries. With increasing carbon content in Fe-Sn-C alloys the tin concentration at the grain boundaries decreases and the carbon concentration at the grain boundaries increases, see Fig. 18, simultaneously the tendency to intergranular fracture is reduced.

According to these results there is no great danger of tin segregation to grain boundaries for most steels. According to thermodynamics in equilibrium with usual bulk concentrations \(\leq 0.02\) wt% Sn, the grain boundary concentration will be low, additionally small concentrations of dissolved and segregated carbon will keep the tin from the grain boundaries in carbon steels. Furthermore, the diffusion of Sn in iron is slow, during usual processing and heat treatment of steels there will be no time for tin segregation to grain boundaries.

However, upon application of heat resistant steels
at elevated temperatures >500°C effects of tin are expected which result less from grain boundary segregation but more from surface segregation in cavities, since the tendency to surface segregation is very high.31

In creep experiments with a 1% CrMoV steel doped with different concentrations of tin it was shown that tin does not affect the primary and secondary periods of creep but tin causes earlier start of tertiary creep and premature failure of the tin doped steels,24,42 the earlier the failure the higher the tin content. The surface segregation of tin favors the nucleation and growth of cavities at grain boundaries. When these cavities coalesce they form an intergranular fracture path. AES analysis of fractured specimens shows high tin (and sulfur) segregation in the cavity compared to the relatively low segregation at the grain boundary.

4. Conclusion

The surface segregation of the elements \( A = C, Si, Sn, N, P, O, \) and \( S \) have been studied in the concentration and temperature range of stability of the \( \alpha \)-solid solution. Under these conditions, only adsorption phases can be formed, no three-dimensional phases and compounds.

In most cases ordered adsorption structures are formed in the range of a mono-atomic layer on the surface with degrees of coverage corresponding to \( \Delta /Fe < 1 \). One exception is the system \( Fe-P \), where also enrichment of phosphorus takes place in the lattice immediately beneath the surface. The other exception is the system \( Fe-Sn \), where enrichment of tin with degrees of coverage \( Sn/Fe > 1 \) were observed on the outer surface and a transition from the ordered adsorption structure to a disordered surface phase.

The dependencies of the segregation equilibria \( A(\text{Dissolved})=A(\text{Segregated}) \) on temperature and on bulk concentration can be described by the Langmuir-McLean equation. In this equation the following values for the segregation enthalpies \( \Delta H^*_A \) are obtained: \( C = -85 \text{kJ/mol}, Si = -48 \text{kJ/mol}, N = -110 \text{kJ/mol} \), \( P = -180 \text{kJ/mol} \), \( S = -190 \text{kJ/mol} \) (C, Si, and N on Fe(100), P and S on polycrystalline materials).

In the simultaneous segregation of different elements the adsorbed atoms compete for the surface sites, also in the case of substitutional and interstitial elements, such as carbon and silicon. The surface concentrations are determined by the respective bulk concentration \( x_A \) and the free energies of segregation \( \Delta G^*_A \).

Studies of the binding modes of segregated atoms \( (C, Si, Sn, N, P, S) \) by photoelectron spectroscopy (XPS) always showed a more or less distinct shift of the photolines to diminished binding energies of the core electrons (in comparison to the binding energies in the element). This may be interpreted by an electron transfer from iron to the segregated elements. The chemical shift and the electron transfer are similar but not equal as in the compounds with these elements: carbides, silicides, nitrides, phosphides, sul-

fides, etc. of iron.

The grain boundary segregation of phosphorus in polycrystalline iron can be described well by the Langmuir-McLean equation, in spite of some scatter of the values. This is not valid for the grain boundary segregation of tin. In this case the segregation obviously is strongly dependent on the grain boundary orientation, such orientation dependence also has been observed in the studies of the surface segregation of tin.

Also in grain boundary segregation displacement equilibria are observed of elements which compete for the sites in the grain boundary. In this site competition, substitutional and interstitial elements have equal rights as shown for the elements phosphorus and carbon and for the elements sulfur and nitrogen and sulfur and carbon.

For the actual grain boundary segregation also the diffusion is decisive, the segregating elements must diffuse to the grain boundaries which is possible only at elevated temperatures during coiling of carbon steels, tempering of low alloy steels and in application of heat resistant steels. Generally, the temperature range 400 to 600°C is critical, at higher temperatures the equilibrium concentrations decrease markedly and at low temperatures the diffusion and segregation rate is too slow for considerable enrichment of deleterious elements such as \( P \) and \( Sn \).

In the production and application of many steels this range of temperatures can be avoided. In any case, it must be tested if the impurities really have negative effects on the properties which are important for the use of certain steels. Only with this knowledge it can be decided if it is really necessary to keep the level of impurities low or to remove them from the steel melts.

The deleterious role of phosphorus in temper embrittlement and long-term embrittlement of low alloy steels is well established. The temper embrittlement, caused by grain boundary segregation during tempering and upon cooling after heat treatment, can be suppressed somewhat by the alloy elements Mo and V. These effects recently could be explained by the effects of fine \( Mo_2C \) and \( VC \) particles which generate and stabilize dislocations—where phosphorus is scavenged.27,28 The long-term embrittlement by segregation during application of steels at elevated temperatures can not be suppressed by alloying, but the phosphorus content of the steels, \( e.g., \), 3.5% NiCrMoV steels used for low pressure steam turbine wells, indeed must be very low to avoid embrittlement.24,42 Tin, too, causes problems—but as shown only in heat resistant steels applied at 550°C in turbines—where tin initiates and accelerates cavity growth leading to premature tertiary creep and rupture.25,42

In carbon steels phosphorus may segregate during rolling in the austenitic range and upon coiling at relatively high temperature. Phosphorus at grain boundaries in carbon steels will not cause embrittlement, but can have some effect in enhancing intergranular stress corrosion cracking (IGSCC) and hydrogen induced stress corrosion cracking (HSCC).
Phosphorus in carbon steels aggravates IGSCC in nitrate and hydroxide solutions\textsuperscript{4,44} and it increases HSCC,\textsuperscript{45,46} The effect on IGSCC, however, is only in certain potential ranges and hardly ever at that corrosion potential which is mostly established in the investigated solutions. Furthermore, it must be emphasized that at a low anodic polarization all steels become susceptible independent of phosphorus content. An especially low phosphorus content in carbon steels, therefore, is no protection against IGSCC in nitrates and hydroxides. Decisive for the occurrence of IGSCC is not the phosphorus content of bulk and grain boundaries but the corrosion conditions, electrolyte and potential,—under certain conditions, all carbon steels are very susceptible and the maximum susceptibility is independent of the phosphorus content.

In 1 m H\textsubscript{2}SO\textsubscript{4} at cathodic polarization carbon steels show hydrogen induced stress corrosion cracking. The susceptibility towards HSCC is increased with the phosphorus content and reduced with the higher manganese content. The mode of cracking is transgranular. The susceptibility to HSCC is not related to the grain boundary concentration but to the bulk content of phosphorus. HSCC is correlated to the hydrogen uptake of the steels which increases with the phosphorus content and decreases with the manganese content.\textsuperscript{46,47} To summarize: the studies on surface segregation provide a better understanding of the state of the surface and the mechanism of surface reactions in annealing and heat treatments, carburization and decarburization, nitrogenation and denitrogenation and similar processes at elevated temperature. The studies on grain boundary segregation are very valuable to understand effects of impurities in steels on the material properties, and it may be derived for which steels and applications the level of impurities must be kept low.

REFERENCES