

## SEGREGATION AND OXIDATION

### SEGREGACIJA IN OKSIDACIJA

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An introduction will be given in the fundamentals of equilibrium segregation, i. e. the enrichment of atoms or ions from solid solution at surfaces, grain boundaries and interfaces, occurring at elevated temperatures. Some examples of segregation and cosegregation on iron and iron alloys will be described, especially of sulfur segregation.

The role of sulfur in the oxidation of iron, steels and chromia- or alumina-forming high temperature alloys is discussed in detail, since traces of sulfur can effectively deteriorate the adherence of protective scales on high temperature alloys.

Segregation in and on oxides has been studied only for a few cases as yet. Most important is the effect of segregated reactive element ions on the growth mechanism and adherence of protective chromia and alumina scales.

Key words: iron, iron alloys, equilibrium segregation, cosegregation, sulphur, segregation on oxides, adhesion of protective coatings

Podan je uvod v osnove ravnovesne segregacije, to je obogatitev z atomi ali ioni trdne raztopine, na njeni površini, mejah zrn in mejnih površinah pri povišanih temperaturah. Opisanih je nekaj primerov segregacije in kosegregacije pri železu in železnih zlitinah, posebno segregacija žvepla.

Vloga žvepla v oksidaciji železa, jekel in tvorba zlitin kroma in/ali aluminija pri visokih temperaturah je opisana podrobno, saj lahko pri visokih temperaturah žveplo v sledeh izredno poslabša adhezijo zaščitnih plasti.

Ključne besede: ravnovesna segregacija, kosegregacija, žveplo, segregacija na oksidih, adhezija zaščitnih plasti

#### 1 SEGREGATION AT SURFACES AND GRAIN BOUNDARIES

Equilibrium segregation of atoms or ions dissolved in solids, according to J. W. Gibbs leads to a decrease of surface or interface energy, according to

$$\frac{d\gamma}{d\mu_A} = -\Gamma_A \quad \frac{d\gamma}{d \ln a_A} = -RT\Gamma_A$$

where  $\gamma$  is the interfacial energy,  $\mu_A$  the chemical potential and  $\Gamma_A$  the interfacial concentration of the dissolved species A and  $a_A$  its thermodynamic activity. The segregation

$$A \text{ (dissolved)} = A \text{ (segregated)}$$

of dissolved atoms such as H, N, O etc should lead to the some states as dissociative adsorption of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> etc from the gas phase. Driving forces for segregation are

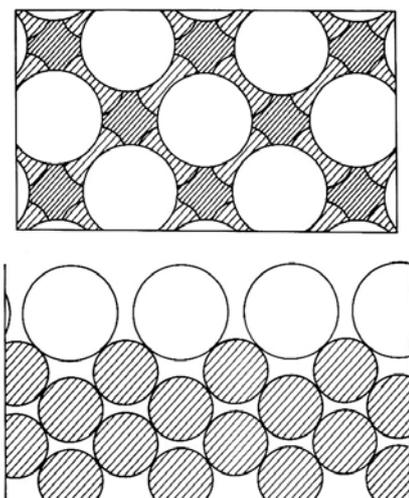
- the saturation of free bonds at the surface or interface,
- the decrease of interfacial energy,
- the release of strain energy in the case of atoms, which widen the host lattice, i.e. interstitial atoms and big substitutional atoms.

In earlier years E. D. Hondros had studied surface segregation on metals at high temperatures by using the "zero creep method" <sup>1-5</sup>, in very troublesome studies. Since the surface analytical methods are available, surface segregation has been studied by AES (Auger Electron Spectroscopy) for determination of surface

concentrations in dependence on temperature T and concentration  $c_A$ , by LEED (Low Energy Electron Diffraction) for observing surface structures and by XPS (X-ray Photoelectron Spectroscopy) for the study of binding states, especially for segregation on iron of the elements C, N, O, S, P, Sn, Si, Sb ... <sup>6-15</sup>. Thermodynamic data, segregation enthalpy  $\Delta H_A$  and segregation entropy  $\Delta S_A$  are obtained according to the Langmuir-McLean equation:

$$\ln \frac{\Theta_A}{1-\Theta_A} = -\frac{\Delta H_A^\circ}{RT} + \frac{\Delta S_A^\circ}{R} + \ln c_A$$

where  $\Theta_A$  is the degree of coverage  $\Gamma_A/\Gamma_A$  (at saturation), from a plot of  $\ln \Theta_A/(1-\Theta_A)$  at constant  $c_A$  versus  $1/T$ . For segregation on Fe (100) the segregation enthalpies were determined: –85 kJ/mol for carbon, –110 kJ/mol for nitrogen, –44 kJ/mol for silicon, –180 kJ/mol for phosphorus and about –200 kJ/mol for sulfur. Generally, the elements segregate in a negatively charged state, as indicated by XPS. This is true also for sulfur which turns from undersize S<sup>γ+</sup> to oversize S<sup>δ-</sup> upon segregation to the iron surface (see **Figure 1**). The high value of the segregation enthalpy indicates a high tendency of sulfur to segregation, and in fact iron, nickel and other metals will be covered with sulfur, when they contain only a few micrograms per gram of S and are heated to temperatures where sulfur can diffuse to the surface and displace all other segregants such as C, Si, P.... Surface diffusion on iron at high temperatures is enhanced by the presence of sulfur, as



**Figure 1:** Model of the Fe(100) surface, covered with segregated sulfur in a  $c(2 \times 2)$  structure a) topview and b) cross section in (110) direction, structure and atom sizes as derived from LEED pattern and LEED intensity measurements<sup>7</sup>

**Slika 1:** Model površine (100), prekrit s segregiranim žveplom; struktura  $c(2 \times 2)$  a) pogled z vrha in b) prerez v smeri (110); struktura in velikost atomov izhajajo iz LEED-predloge in izmerjene LEED-intenzitete<sup>7</sup>

observed by measuring grain boundary grooving and sinusoidal profile decay<sup>15</sup>. Since most segregating elements occupy the same type of sites, e. g. the "fourfold center site" in the (100) plane of iron, on top of the second layer iron atoms, they compete for these sites. Accordingly the occupancy of the surface sites is dependent on bulk concentration and free energy of segregation, for example for the system Fe-S-C the equilibria of **site competition** are described by:

$$\frac{\theta_C}{1 - \theta_S - \theta_C} = c_C \exp\left(\frac{-\Delta G_C^\circ}{RT}\right)$$

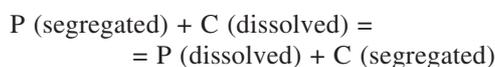
$$\frac{\theta_S}{1 - \theta_C - \theta_S} = c_S \exp\left(\frac{-\Delta G_S^\circ}{RT}\right)$$

In contrast, caused by attractive interaction there can be **cosegregation** of nonmetal elements, such as C, N, S ..... and alloying elements such as Cr, Mo, Ti etc<sup>16-23</sup>.

This leads to bidimensional surface compounds, which can strongly affect oxide nucleation, grain size and growth rate. Cosegregation of Cr and N on Fe(100), or chemisorption of nitrogen, inducing segregation of Cr lead to formation of a surface nitride "CrN", which favors nucleation and growth of  $\text{Cr}_2\text{O}_3$  upon oxidation of Fe-Cr alloys<sup>24,25</sup>. In contrast cosegregation of Cr and S hinders nucleation of the oxide and causes slow growth of large grained oxide.

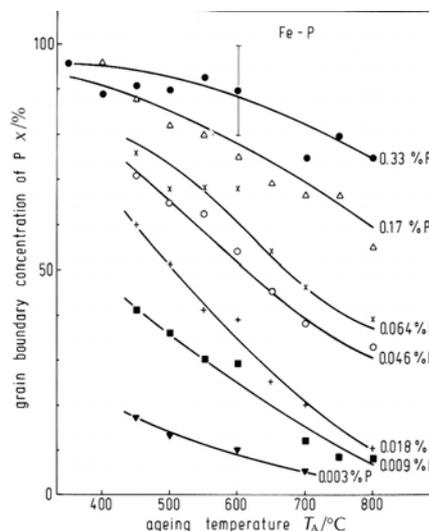
**Grain boundary segregation** of P, S, Sn, Sb etc. causes embrittlement of steels, in contrast C, N and B are increasing the strength of grain boundaries. After equilibration at elevated temperatures grain boundary segregation can be investigated by fracturing samples in the UHV (ultra high vacuum) chamber and AES

analyses of intergranular fracture faces. Intense studies have been conducted on grain boundary segregation of P in iron and steels<sup>26-31</sup>, since P is the impurity in steel causing **temper embrittlement** most frequently. It was shown that P is distributed about equally on both fracture faces of a grain boundary and that a concentration of 100 % is approached at low temperature and high bulk concentration (see **Figure 2**). Evaluation of the data for the system Fe-P according to the Langmuir-McLean equation yields  $-34.3$  kJ/mol for the segregation enthalpy  $\Delta H_p^\circ$ . With increasing grain boundary concentration of P the percentage of intergranular fracture increases. Due to the embrittling power of P, also grain boundary segregation of non embrittling elements such as C, N, B could be studied, e. g. in the system Fe-C-P. As on surfaces the atoms C and P are competing for sites and their segregation is described by a mutual displacement equilibrium:



Phosphorus also segregates to dislocations, and thus can be gettered by dislocations stabilized by precipitates of carbides in microalloyed steels, such as  $\text{Mo}_2\text{C}$ , NbC, TiC.<sup>29</sup>

The grain boundary segregation of sulfur in iron was studied by C.L. Briant<sup>32</sup> and the segregation enthalpy determined to be  $-51.5$  kJ/mol, i. e. much more negative



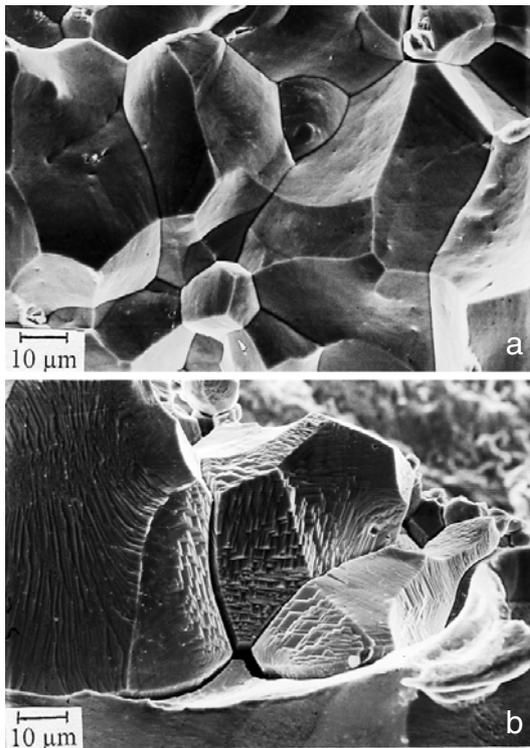
**Figure 2:** Equilibrium grain boundary concentrations of segregated phosphorus in Fe-P alloys, measured by AES on intergranular fracture faces after long-term equilibration at elevated temperatures. Assuming that on both fracture faces is about the same amount of segregated P the grain boundary coverage approaches 100 %. The AES measurement was calibrated using Fe-P single crystals with well-defined surface structure of segregated P<sup>28</sup>

**Slika 2:** Ravnovesna koncentracija segregiranega fosforja na meji zrn v zlitini Fe-P, izmerjena z metodo AES na intergranularnem prelomu po dolgotrajnem žarjenju pri povišanih temperaturah. Pri predpostavki, da je na obeh straneh preloma enaka vsebnost segregiranega P, se prekritje na meji zrn približuje 100 %. AES-meritve smo kalibrirali z uporabo Fe-P monokristala z dobro definirano površinsko strukturo segregiranega P<sup>28</sup>

than for P. However, grain boundary segregation of S is a minor problem for steels, since steels can be effectively cleaned by metallurgical removal of S and/or sulfur can be tied up by alloying additions such as Mn, Ti, Zr, Mg ... in stable sulfides.

Furthermore, carbon in steels easily displaces sulfur from the grain boundaries and strengthens the grain boundary cohesion. C, N and B are the elements which are not embrittling but strengthening grain boundaries in metals, whereas P, S, Se, Te, Sb and Sn are embrittling elements. As the reason for the embrittlement weakening of metal – metal bonds was discussed<sup>33</sup>, but it is feasible also that recrystallization and faceting of the grain boundary faces may lead to grain separation<sup>30,31</sup>, see **Figure 3**. Considering the grain boundary embrittlement by sulfur, such effect was suspected later also in the oxide/metal interface, deteriorating the oxide adherence, as will be discussed in the following chapter.

Sulfur segregated at grain boundaries, strongly retards grain boundary diffusion<sup>34</sup>. Exposure of Fe to sulfidizing environments, i. e.  $H_2S-H_2$  or FeS and  $H_2$  at 900–1300 °C causes sulfur diffusion into the polycrystals preferably at grain boundaries, and heavy segregation near the grain boundaries in dislocations,



**Figure 3:** SEM micrographs of the fracture faces of embrittled iron alloys a) Fe-10Mn-0.17P alloy after aging in the austenitic range, very smooth grain faces have developed and the grains have separated<sup>29</sup>, b) Fe-5µg/gTe after annealing at 850 °C, reconstruction of the grain faces by faceting, leads to separation of the grains<sup>30</sup>

**Slika 3:** SEM-posnetki prelomne površine krhke Fe-zlitine a) Fe-10Mn-0.17P-zlitina po staranju v avstenitem področju; razvila se je zelo gladka površina zrn in zrna so se razdelila<sup>29</sup>, b) Fe-5µg/gTe po žarjenju na 850 °C, rekonstrukcija površine zrn vodi do ločitve zrn<sup>30</sup>

created by the high sulfur activity<sup>35-37</sup>. Sulfur causes **high temperature brittle intergranular fracture** of steels, especially in heat affected zones of weldments with coarse grained martensitic or bainitic microstructures, austenitized at > 1100 °C and loaded between 300–650 °C. Sulfur is segregating to the crack tip during cracking, and promotes fracture by causing decohesion or reducing the crack flank angle. Source of sulfur segregation is either the sulfur in solution which diffuses to the crack tip, driven by the crack-tip stress field<sup>38</sup> or sulfides (MnS) in opened crack faces, oxidized and deliver sulfur by surface diffusion to the crack tip<sup>39</sup>.

## 2 OXIDATION AND SEGREGATION

The main question in this chapter is, if segregation at the interface oxide/metal plays a role in the growth and adherence of the oxide. For the high temperature alloys, the formation of a slowly growing, well-adherent oxide scale is most important for protection against the environment, which often is not only oxidizing, but also sulfidizing, carburizing, nitriding, chlorinating ... Only a dense, healing and adhering oxide scale, such as chromia  $Cr_2O_3$  or alumina  $Al_2O_3$  can protect high temperature alloys, based on Fe-Cr, Fe-Ni-Cr, Fe-Cr-Al, Ni-Cr, Ni-Cr-Al etc.

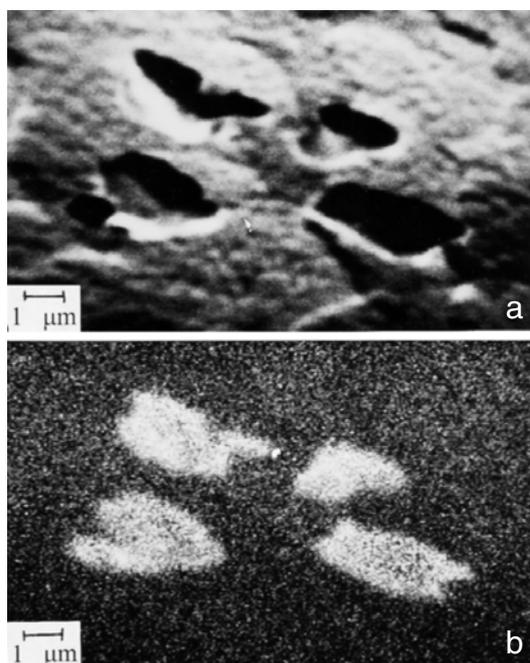
At first the difference must be emphasized of **segregation** and **accumulation** of more noble alloying elements or impurities which occurs due to fast growth of oxide scales, i.e. on iron and steels. Well-known is the accumulation of Cu and Ni beneath scales on steel during annealing or hot rolling which causes "hot shortness". Also sulfur accumulates unoxidized beneath the FeO scale on iron upon oxidation at 650–1050 °C<sup>40</sup>, until eventually an FeS layer is formed, which enhances the adhesion of the scale due to its relatively high plasticity. Upon oxidation of high temperature alloys such as Fe-Cr-Al and Ni-Cr-Al soon the solubility limit of CrS will be exceeded, and most probably some researchers have observed (by electron microprobe) such sulfide precipitates assuming segregation. In contrast to sulfur, Al or Si are oxidized beneath the scale and form  $FeAl_2O_4$  or  $Fe_2SiO_4$  layers which deteriorate the adherence.

Some fundamental studies were conducted on the question where sulfur remains upon oxidation, which had been adsorbed on the metal surface. J. M. Blakely and coworkers<sup>41</sup> oxidized a Ni-Fe alloy, covered with S in ordered  $p(2 \times 2)$  or  $c(2 \times 2)$  adsorption structures. Upon oxidation at 500 °C oxide islands grew, compressing the adsorbed sulfur into the more condensed  $c(2 \times 2)$  structure, there was no sulfur at the oxide/metal interface. Upon oxidation at 100 °C the oxide islands overgrow the adsorbed sulfur, but this state with S at the oxide/metal interface is unstable, when heated to higher temperatures. G. M. Michal<sup>42</sup> and coworkers oxidized iron at 800 °C for 20 min, and

expected to find sulfur at the oxide/metal interface upon sputtering, since a free metal surface was covered with segregated S after 5 min – but no S was detected at the interface. In contrast, after oxidation of a sample which was covered with segregated S before oxidation, the sputter profile after oxidation showed sulfur at the interface, which had remained there. These studies already show that obviously there is no equilibrium segregation of sulfur to the intact interface of grown oxide on metals such as Fe and Ni.

Considering the statements in the previous chapter about surface segregation, especially of sulfur, such segregation to an oxide/metal interface should be highly improbable. There are **no free bonds** at this interface but strong metal – oxygen bonds. According to thermodynamics it is nearly impossible to replace oxygen – metal bonds by sulfur – metal bonds. Also there is **no free space** at an intact interface for segregation of the big negatively charged sulfur ions (see **Figure 1**). Only when there are defects arising at the interface, maybe misfit dislocations, voids or microcracks, sulfur has a chance to segregate.

On the other hand the "sulfur effect" on the adherence of chromia and alumina scales was detected about 1986, i. e. that trace levels of sulfur in Fe-Cr-Al or

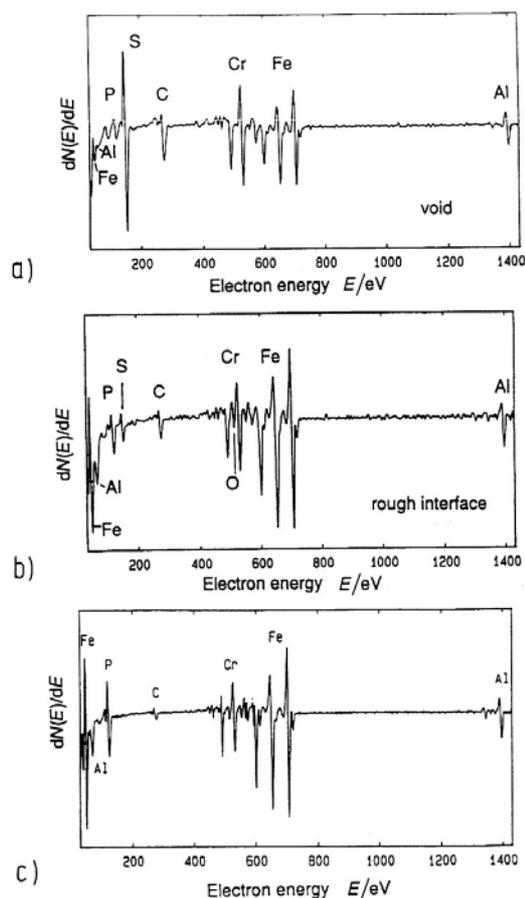


**Figure 4:** Investigation of the metal surface of an Fe-Cr-Al alloy after oxidation for 30 min at 1000 °C and removal of the alumina scale a) SEM-micrograph showing the metal surface of the interface with four cavities, b) scanning Auger mapping of the sulfur distribution in the area, demonstrating the high concentration of segregated sulfur in the cavities<sup>55</sup>

**Slika 4:** Raziskava kovinskih površin zlitine Fe-Cr-Al po oksidaciji 30 min na 1000 °C in odstranitvi aluminijve tanke plasti, a) SEM-posnetek prikazuje kovinsko površino na mejni ploskvi s štirimi luknjami, b) SAM-posnetek porazdelitve žvepla na področju prikazuje visoko koncentracijo segregiranega žvepla v luknjah<sup>55</sup>

Ni-Cr-Al alloys cause spallation of Al<sub>2</sub>O<sub>3</sub> scales. This effect was explained by sulfur segregation and bond deterioration at the oxide/metal interface<sup>43-51</sup>. The role of sulfur was proven by its removal using metallurgical measures, or annealing in H<sub>2</sub> or vacuum – an efficient removal led to well-adherent scales. In addition, the "sulfur effect" was taken as an explanation of the beneficial **effects of reactive elements** on scale adhesion – it was concluded that the major effect of the reactive elements is to prevent sulfur segregation.

So the community of high temperature corrosion researchers was very happy with the sulfur effect, but did not like the statement given above, that sulfur should not segregate to intact oxide/metal interfaces. But this statement was further confirmed, by studies on Fe-15Cr-160 µg/g S, Ni-10Cr-9Al-90 µg/g S, β-Ni-Al-110 µg/g S and various Fe-Cr-Al alloys<sup>52-57</sup>. On the Fe-Cr alloy and the NiAl after short-term oxidation (10 min at 800 °C) in the AES sputter profile no sulfur



**Figure 5:** Auger spectra of Fe-Cr-Al oxidized 260 h at 1000 °C after oxide removal<sup>55</sup> a) metal surface in a cavity, high sulfur concentration, some P and C, b) metal surface which had been covered by oxide – low concentration of P, C and S, c) metal surface of a sample, doped with yttrium – no segregation of sulfur

**Slika 5:** Augerjev spekter Fe-Cr-Al, oksidirane 260 h na 1000 °C, po odstranitvi oksida<sup>55</sup> a) kovinska površina v luknji, visoka koncentracija S, nekaj P in C, b) kovinska površina, ki je bila prekrita z oksidom – nizka koncentracija P, C in S, c) kovinska površina vzorca, dopiranega z itrijem, – ni segregacije žvepla

was detected, only after prolonged oxidation when voids or cavities had formed beneath the scale, there was plenty of S in the metal surface of these cavities. Also scanning Auger mapping on Fe-Cr-Al alloys showed high sulfur concentrations in cavities, which were visible since the scale had spalled (see **Figure 4**). On the rough "indented" interface, where the scale had been adherent before stripping, was much less sulfur and some P and C. On an alloy Fe-18Cr-12Al-0.02Y no sulfur was found (**Figure 5**). About 1995 these results led to the conclusions<sup>57</sup>:

- sulphur does not segregate to an intact oxide/metal interface,
- as soon as a void is formed or a microcrack at the interface, sulfur segregates to the fresh metal surface formed,
- the sulfur surface segregation decreases the metal surface energy, thereby voids and cracks are stabilized and their growth is accelerated,
- in this way loss of adherence occurs by cavity growth and scale buckling,
- S, C and P segregate also to defects at or near the interface, misfit dislocations, grain boundaries .... but this does not affect the scale adherence.

So these points do not deny the "sulfur effect" but give a reasonable theoretical explanation for its occurrence, it is questioned only that sulfur acts by segregating to an intact interface and weakening or replacing metal – oxygen bonds. However, for incomprehensible reasons numerous researchers have tried to prove sulfur segregation to oxide/metal interfaces. Some authors have used rather improper methods for preparation of the investigated interface, e. g. hot pressing at 1450 °C for diffusion bonding of a Ni-foil on sapphire<sup>58</sup>, or evaporation and oxidation of Al onto Fe-foils with segregated sulfur<sup>59</sup>, – no conclusions can be drawn from such studies on interfaces of oxides grown on high temperature alloys.

P. Y. Hou conducted very careful AES analyses of Al<sub>2</sub>O<sub>3</sub>/metal interfaces on FeCrAl-alloys and the intermetallic phases Fe<sub>3</sub>Al and NiAl, after laying bare the interface by in-situ scratching<sup>60-63</sup>. Ample sulfur was found on the free metal surface of voids and cavities, but some sulfur also on areas where scale and metal phase had been in contact during oxidation. However, additional observations leave doubt if in these areas equilibrium segregation occurred, since the segregation kinetics for these areas is generally slower than expected in the case of diffusion control, and in FeCrAl-alloys cosegregation with Cr was observed. Even CrS-precipitation may be possible, since sulfur solubility in Fe-Cr-Al is very low. Segregation on free surfaces is very fast – saturation occurs after 10 min at 700 °C on iron surfaces<sup>64</sup> – and the slowness of "interfacial segregation" indicates occurrence of more complex processes, e. g. generation of dislocations or cosegregation resp. precipitation. For the intermetallic NiAl the slow process

accompanying S-segregation is void formation and cavity growth as well proven now<sup>63</sup>, the major role of sulfur is to accelerate these processes and it was shown that the interface strength is dictated by the density of interfacial cavities. Also by a study using PIXE (Particle Induced X-ray Emission), a method which can detect atomic layers buried under an oxide layer, it was proven that sulfur segregation is connected to void and cavity formation and takes place only after some delay<sup>64</sup>.

But favouring void nucleation and crack growth by decreasing the surface energy of the newly formed metal surface is probably not the only action of sulfur at the oxide/metal interface. In the voids and cracks sulfur will not sit quietly and weaken bonds, but the sulfur atoms will move about, enhancing **surface diffusion** on the metal surface<sup>15</sup> and inducing reorientation and **facetting** under formation of low-energy adsorption structures. Facetting caused by the presence of sulfur has been observed in the oxidation of Fe-Cr-Al<sup>65</sup> and it is well-known that annealing of steel sheet in the presence of sulfur causes recrystallization and development of certain textures<sup>66</sup>. This effect of sulfur is similar to that of small alloying additions of tin or antimony. These elements can be useful to improve the texture and magnetic properties of nonoriented silicon steel sheet, caused by surface segregation favoring certain grain orientations and textures<sup>67-69</sup>. Sulfur also will take part in the separation of scale and metal by entering the crack tip when oxides scales buckle and spall due to growth stresses. **Decohesion caused by sulfur** at a crack tip is well-known from the **high temperature brittle intergranular fracture** of steels<sup>38,39</sup>. To summarize: The main point of the sulfur action at an oxide/metal interface will be to generate free metal surface, where it can find or create nice comfortable sites, well-coordinated to the metal atoms (see **Figure 1**), to be segregated under high energy decrease. But sulfur should not segregate to an intact oxide/metal interface, only after defects have formed such as dislocations, voids and microcracks.

### 3 REACTIVE ELEMENT EFFECTS IN THE FORMATION OF PROTECTIVE SCALES (Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>)

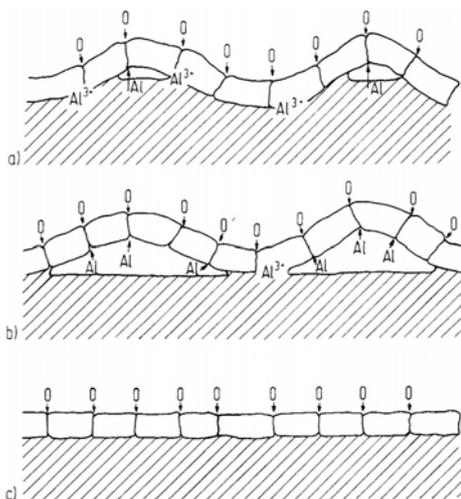
Very early it was observed that small additions of rare earth elements improve the oxidation resistance of steels considerably, later also beneficial effects of many "reactive elements" i. e. elements with a high oxygen affinity were detected and the "reactive element effect" of elements such as Ce, Y, La ... Ti, Zr, Hf ... has been applied for improving many high temperature alloys. There are four effects, which are all very positive:

- the adherence oxide/metal is improved,
- the selective oxidation of Al resp. Cr is favored,
- often a fine grained oxide layer with improved plasticity is obtained,

- the oxide growth rate may be retarded, but not in all cases.

The "reactive element effects" (R. E. effects) have been discussed by the high temperature corrosion community since many years, numerous studies have been conducted and some review papers were published<sup>70-74</sup>. Different explanations have been put forward, and most of them are true, more or less, applying in certain cases. Since generally small amounts of reactive elements are effective, their enrichment by segregation and/or accumulation can play a role and this question will be tackled here. And it should be noted from the beginning, that mostly **dispersions of their oxides** have the same effects. This however is to be expected, since in the oxidation process these elements will be the first to be oxidized, due to their high oxygen affinity ( $-\Delta G^\circ$  of oxide formation), either by internal or external oxidation, and will rarely be effective as dissolved elements.

The most important R. E. effect appears to be a change of the growth mechanisms of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . On undoped alloys these oxides grow by inward diffusion of O and outward cation diffusion at grain boundaries, this mechanism causes lateral growth and growth stresses see **Figure 6**. By doping, e. g. Fe-Cr-Al alloys with yttrium the cation diffusion is largely suppressed and columnar well-adherent oxide is growing<sup>75-79</sup>. This change of growth mechanism is caused by



**Figure 6:** Mechanisms and morphologies of alumina scale growth a) and b) on an undoped alloy, by counter diffusion of oxygen and cations mainly at grain boundaries leads to a convoluted scale, and (a) separations of scale and metal in regions of high stress only and (b) nearly complete separation in case of low energy metal surface orientation or surface energy lowered by sulfur segregation, c) outward diffusion of cations suppressed on an Y-doped alloy and growth of a plane scale with good adherence<sup>76</sup>

**Slika 6:** Mehanizem in morfologija rasti aluminijeve tanke plasti a) in b) nedopirane zlitine z difuzijo kisika in v glavnem s kationi na mejah zrn vodi do zgibane plasti: (a) ločitev tanke oksidne plasti od kovine samo v predelih visokih obremenitev, (b) skoraj popolna ločitev v primeru kristalografske orientacije kovinske površine z nizkim indeksom, c) zavrtja zunanja difuzija kationov v zlitinah, dopiranih z Y, in površinska rast oksidne plasti z dobro oprijemljivostjo<sup>76</sup>

segregation at oxide grain boundaries, a phenomenon which is treated in the following chapter.

A case of R. E. effect clearly connected to surface segregation, was described for the oxidation of Fe-Al-Ti alloys, studied by LEED and AES<sup>80,81</sup>. Exposure of such alloy to an oxidizing atmosphere leads to segregation of Ti and C from the alloy, which form a thin layer of epitaxial Ti-oxycarbide. On this layer  $\text{Al}_2\text{O}_3$  easily nucleates and forms a well adherent scale. The Ti (C,O) layer acts as a "graded seal", allowing a gradual transition of lattice dimensions and thermal expansion coefficient from the metal phase to the oxide.

Additions of yttrium to Fe-Cr-Al alloys not only change the oxide growth mechanism, but even very low amounts, e. g. 3  $\mu\text{g/g}$  Y in Fe-21.7 % Cr-5.42 % Al clearly favor and enhance the nucleation of  $\text{Al}_2\text{O}_3$  instead of  $\text{Cr}_2\text{O}_3$ <sup>82,83</sup>. Obviously small particles of  $\text{Y}_2\text{O}_3$  formed in the initial oxidation act as nuclei, some oxidation-induced segregation may play role in assembling such particles on the surface of the alloy. By AES the yttrium oxide was not detected, but by TEM-studies<sup>84,85</sup> Y was found enriched at the  $\text{Al}_2\text{O}_3$ /metal interface.

For nucleation of  $\text{Cr}_2\text{O}_3$  doping of Fe-Cr or Fe-Ni-Cr alloys with cerium appears to be most effective, small additions of Ce suppress the iron oxide growth on Fe-Cr alloys and favor  $\text{Cr}_2\text{O}_3$  formation<sup>86,87</sup>. The role of Ce-oxide particles as nucleation sites for  $\text{Cr}_2\text{O}_3$  was proven by internal oxidation of the Fe-Cr-Ce alloy under formation of many fine oxide particles near the surface, becoming less and coarser in the interior. So, after polishing to different depths distributions with different particle densities are obtained, and upon oxidation  $\text{Cr}_2\text{O}_3$ -layers with different grain sizes, fine at high Ce-oxide particle density and large grained at a low Ce-oxide particle density. The favoring of nucleation and selective oxidation leads to fine-grained scales, therefore also **enhanced ductility** of such scales is attained and better protection is possible in case of materials creep.

In the oxidation of alumina-forming alloys, a problem is the initial formation of metastable aluminas,  $\gamma$ -,  $\delta$ - and  $\Theta$ - $\text{Al}_2\text{O}_3$  in a lower temperature range  $< 1000$  °C, which transform to the slow growing, stable  $\alpha$ - $\text{Al}_2\text{O}_3$  only at high temperatures relatively fast. This formation of metastable aluminas can be largely suppressed by doping with reactive elements, e. g. yttrium in  $\beta$ -NiAl suppresses  $\Theta$ - $\text{Al}_2\text{O}_3$  at 950 °C after 5 h, whereas without yttrium this process lasts for 50 h<sup>88</sup>. At 1000 °C Y suppresses  $\Theta$ - $\text{Al}_2\text{O}_3$  formation completely, while without Y the metastable oxide is present about 10 h. This effect can be explained again by favored nucleation of  $\alpha$ - $\text{Al}_2\text{O}_3$ , not by an effect of the R. E. elements on the transformation of the metastable aluminas.

There are some "old" explanations for the R. E. element effects<sup>70,71</sup>, which are applicable in certain cases: The "pegging" of scales, a mechanical anchoring by oxide intrusions into the metal phase, which is

observed for alloys doped with rare earth elements and is caused by oxidation of intermetallic inclusions. And the generation of "vacancy sinks" by an internal oxide dispersion, avoiding formation of cavities or separation at the oxide/metal interface, especially in the case of oxides growing by outward cation diffusion.

And there are some "new" explanations of the reactive element effects: That sulfur deteriorates the adherence of scales was discussed already in the previous chapter, and obviously the presence of reactive elements or of their dispersed oxides can suppress this "sulfur" effect is proven<sup>46-51</sup>, whereas the way how the sulfur is gettered is not clarified as yet. Probably the small amounts of sulfur impurity in high temperature alloys can be tied up in dislocations stabilized by fine dispersed R. E. oxides or at their interfaces.

About 1993 B. Pieraggi and R. A. Rapp put forward the idea that blocking of the interface oxide/metal by segregated R. E. elements should retard the transfer of atoms for the metal phase into the oxide scale<sup>89,90</sup>. The presence of large foreign atoms or ions at the interface should hem the motion of steps, ledges and dislocations at the interface which is necessary for the interfacial reactions. As yet this theory is not proven satisfactorily and the concentration of reactive elements at the interface was generally found to be rather low<sup>84,85</sup>. This fact also disproves the theoretical approach of A. B. Andersen et al.<sup>91</sup> in which segregation of yttrium at the  $\text{Al}_2\text{O}_3/\text{Ni}$  was assumed and it was concluded from molecular orbital quantum theory that this should enhance the scale adherence. This theory cannot apply since not much yttrium was observed at this interface, and it cannot be present in the metallic state (as assumed by the authors!?) but only in oxide particles, which cannot exert such bonding forces.

#### 4 SEGREGATION IN AND ON OXIDES

On equilibrium segregation in and on the oxides of interest,  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ , only very few fundamental studies have been conducted. J. M. Blakely and coworkers studied the segregation of dissolved and implanted MgO on  $\text{Al}_2\text{O}_3$  in the temperature range 1200–1550 °C<sup>92</sup>. The thermodynamics could be described as for metals using Gibbs' and Langmuir-McLean equation, but in principle it must be considered that surfaces and interfaces in ionic solids have a net charge at equilibrium, due to the existence of surface electronic states and differences in binding energies of ions in bulk and surface. In the example MgO in  $\text{Al}_2\text{O}_3$ , the Mg-ions are charged negatively in the lattice  $\text{Mg}_{\text{Al}}^-$  and therefore have the tendency to attach to oxygen vacancies, the complexes  $\text{Mg}_{\text{Al}}^- - \text{V}_{\text{O}}^{2+}$  being formed with an enthalpy of -135 kJ/mol. The segregation enthalpy of  $\text{Mg}^{2+}$  to a surface kink site was found to be -183 kJ/mol. Presence of  $\text{Mg}^{2+}$  on the surface enhances the surface diffusion rates, as observed by measuring the

decay of sinusoidal modulation on a sapphire surface at 1500 °C.  $\text{Mg}^{2+}$  segregates because of its missing charge in relation to the  $\text{Al}^{3+}$  ions, since there are less neighbouring  $\text{O}^{2-}$  ions in the surface. The formation of the  $\text{Mg}_{\text{Al}}^- - \text{V}_{\text{O}}^{2+}$  complexes leads to transport of  $\text{Mg}^{2+}$  to the surface in the oxidation of Fe-Cr-Al alloys<sup>93</sup>, because during  $\text{Al}_2\text{O}_3$  growth oxygen ions diffuse inward and oxygen vacancies outward. The enrichment of magnesium on the scale was observed on Fe-Cr-Al doped with 88 µg/g Mg using TEM, after continued oxidation  $\text{MgAl}_2\text{O}_4$  is formed on the surface.

These fundamental studies on the system  $\text{Al}_2\text{O}_3$ -MgO are not directly applicable for understanding the processes in scales on commercial Fe-Cr-Al alloys, doped with Y, Zr, Hf ... and of improved scale adherence, but give some clues for the interpretation of the "reactive element effect" in the alumina growth on alloys. In the previous chapter the effect was described already that presence of R. E. elements, especially yttrium, suppresses the outward cation diffusion, the scale grows mainly by inward diffusion of oxygen at grain boundaries and becomes columnar and well adherent (see **Figure 6**). This explanation was proven mainly by many studies, using oxygen isotopes<sup>78</sup>. STEM studies have shown that the reactive elements are enriched at the metal/oxide interface and at grain boundaries in the oxide<sup>84,85</sup>. In addition, it is reported<sup>79</sup> that the R. E. ions are transported along the grain boundaries outwards, toward the scale surface, similarly as described above for  $\text{Mg}^{2+}$ . So studies on the whereabouts of  $\text{Y}_2\text{O}_3$  in  $\text{Al}_2\text{O}_3$  are of great interest. In a study of the system by sintering at 1550 °C, J. Philibert and A. M. Huntz<sup>94</sup> have observed precipitation of  $\text{Y}_3\text{Al}_5\text{O}_7$  from  $\text{Al}_2\text{O}_3$  with molar fractions 0.1 %  $\text{Y}_2\text{O}_3$ , but in  $\text{Al}_2\text{O}_3$ -0.03 %  $\text{Y}_2\text{O}_3$  no precipitates were found, only grain boundary enrichment by a factor 50. The bulk solubility at 1550 °C is 6 µg/g  $\text{Y}_2\text{O}_3$ , the  $\text{Y}^{3+}$  ions are situated on the  $\text{Al}^{3+}$  sites, but due to the ratio of ion radii 0.092 nm/0.054 nm a strong interaction of  $\text{Y}^{3+}$  with oxygen vacancies can be assumed. And as in the case of the  $\text{Mg}_{\text{Al}}^- - \text{V}_{\text{O}}^{2+}$  complexes the  $\text{Y}_{\text{Al}}^x - \text{V}_{\text{O}}^{2+}$  complexes are transported in growing alumina scales to the oxide surface. B. Pint concludes in his "dynamic segregation theory"<sup>95</sup> that the slow diffusion of yttrium ions blocks the way for the  $\text{Al}^{3+}$ - or  $\text{Cr}^{3+}$ -ions along grain boundaries. In addition, sulfur is gettered by Y, Al-oxide particles in the alloy and at the oxide/alloy interface, so that well-adherent scales are obtained on Y-doped Fe-Cr-Al and Ni-Cr-alloys.

#### 5 CONCLUSIONS

This review paper reports and discusses some correlations of the oxidation of metals and alloys, and of segregation. At first some features are described of Gibbs' equilibrium segregation on surfaces and in grain boundaries of metals. Nonmetal atoms, such as C, N, O,

sites, where they are well coordinated to the metal atoms, and generally are negatively charged. This leads to an increase of size, especially for sulfur. At grain boundaries, for example upon segregation of phosphorus, high coverages are approached of up to 100 %, and the P is distributed about equally on both grain boundary faces, causing a smoothing of these faces. Even faceting is observed, in the case of Fe-Te alloys, and this reconstruction of the grain boundary faces may be considered as reason for embrittlement and grain separation. Sulfur at high temperature and high activities can cause formation of dislocations in iron, and likes to enter crack tips, causing decohesion and high temperature brittle intergranular fracture.

In oxidation of metals, one must distinguish between the enrichment by accumulation of more noble elements beneath the scale and possible segregation to the oxide/metal interface. However, for most nonmetal atoms such as C, N, P and S equilibrium segregation to an intact oxide/metal interface is most improbable, since there are no free sites and bonds and there is no free space, especially not for big species as sulfur ions. When, however, in the run of oxidation defects occur at the interface, misfit dislocations, voids and microcracks, there will be segregation to the face metal sites and surface of such defects. Continued segregation of sulfur to voids and cavities, growing beneath oxide layers on high temperature alloys will be the reason of the "sulfur effect", i. e. the deteriorating effect of small sulfur concentrations in alumina- or chromia-forming high-temperature alloys. The sulfur favors the nucleation and growth of the voids and cavities by decreasing the metal surface energy. Sulfur also enhances surface diffusion on the metal surface of the cavity and causes smoothing and faceting of the metal bottom of such cavities.

In the literature also segregation is assumed of the "reactive elements" such as Y, Ce, Ti, Zr, Hf .... which exert some beneficial effects in the oxidation of high temperature alloys: improval of scale adherence, favored nucleation of protective oxide, fine-grained oxide-scale, retarded oxide growth, for which numerous explanations have been put forward, which are discussed in this review. Segregation of the "reactive elements" may play a role, since they were found to be enriched at the oxide/metal interface and in oxide grain boundaries. The enrichment at the oxide/metal interface must be due to an oxidation-induced segregation, i.e. in the initial oxidation the very stable oxides of the reactive elements are formed at first by interaction of oxygen and the R. E. elements diffusing to the alloy surface, then the fine oxide particles formed act as nucleation sites for the protective oxides,  $Al_2O_3$  or  $Cr_2O_3$ . Segregation in the oxide scale may be caused by size or charge effects, e. g. the large  $Y^{3+}$ -ions will segregate from  $Al^{3+}$ -sites in  $Al_2O_3$  to the grain boundaries. Since complexes  $Y_{Al}^x - V_O^{2+}$  are formed, these are transported through the grain boundaries slowly to the oxide surface, and this process

suppresses the outward diffusion of  $Al^{3+}$  at grain boundaries. This effect has important consequences on the mode of oxide growth and the oxide adherence is greatly improved.

So segregation can play an important role in oxidation of metals and alloys, but it must be clearly established what kind of segregation processes really takes place.

## 6 REFERENCES

- <sup>1</sup> E. D. Hondros, D. McLean: Surface Phenomena in Metals, Soc. Chem. Ind. Monograph 28, UK, 1968
- <sup>2</sup> E. D. Hondros: *Proc. R. Soc. A* 286 (1965), 479
- <sup>3</sup> E. D. Hondros: *Met. Sci. J.* 1 (1967), 36
- <sup>4</sup> E. D. Hondros: *Acta Metall.* 16 (1968), 1377
- <sup>5</sup> E. D. Hondros, L. E. H. Stuart: *Philos. Mag.* 17 (1968), 711
- <sup>6</sup> H. J. Grabke, G. Tauber, H. Viehhaus: *Scr. Met.* 9 (1975), 1181
- <sup>7</sup> H. J. Grabke, W. Paulitschke, G. Tauber, H. Viehhaus: *Surf. Sci.* 63 (1977), 377
- <sup>8</sup> H. J. Grabke, H. Viehhaus, G. Tauber: *Arch. Eisenhüttenwes.* 49 (1978), 391
- <sup>9</sup> H. J. Grabke: *Mater. Sci. Eng.* 42 (1980), 91
- <sup>10</sup> H. de Rugy, H. Viehhaus: *Surf. Sci.* 173 (1986), 418
- <sup>11</sup> H. Viehhaus, M. Rösenberg: *Surf. Sci.* 159 (1985), 1
- <sup>12</sup> M. Rösenberg, H. Viehhaus: *Surf. Sci.* 172 (1986), 615
- <sup>13</sup> G. Panzner, B. Egert: *Surf. Sci.* 144 (1984), 651
- <sup>14</sup> G. Panzner, W. Diekmann: *Surf. Sci.* 160 (1985), 253
- <sup>15</sup> H. J. Grabke, E. M. Petersen, S. R. Srinivasan: *Surf. Sci.* 67 (1977), 501
- <sup>16</sup> H. Viehhaus, J. Peters, H. J. Grabke: *Surf. Interface Anal.* 10 (1987), 280
- <sup>17</sup> C. Uebing, H. Viehhaus, H. J. Grabke: *Appl. Surf. Sci.* 32 (1988), 363
- <sup>18</sup> C. Uebing, H. Viehhaus, H. J. Grabke: *Surf. Interface Anal.* 16 (1990), 483
- <sup>19</sup> C. Uebing, H. Viehhaus, H. J. Grabke: *Ber. Bunsenges. Phys. Chem.* 93 (1990), 1363
- <sup>20</sup> C. Uebing, H. Viehhaus: *Surf. Sci.* 236 (1990), 29
- <sup>21</sup> C. Uebing: *Surf. Sci.* 22 (1990), 975
- <sup>22</sup> C. Uebing, H. Viehhaus, H. J. Grabke: *Surf. Sci.* 264 (1992), 114
- <sup>23</sup> C. Uebing, H. Viehhaus, H. J. Grabke: *Fresenius J. Anal. Chem.* 346 (1993), 275
- <sup>24</sup> H. J. Grabke: *Kovine, zlit., tehnol.* 27 (1993), 9–20
- <sup>25</sup> H. J. Grabke, R. Dennert, B. Wagemann: *Oxidation of Metals* 47 (1997), 495
- <sup>26</sup> H. Erhart, H. J. Grabke: *Met. Sci.* 15 (1981), 401
- <sup>27</sup> H. Erhart, H. J. Grabke: *Scripta Met.* 15 (1981), 531
- <sup>28</sup> R. Möller, H. Viehhaus, H. Erhart, H. J. Grabke: *Beitr. elektronenmikroskop. Direktabb. Oberfl.* 15 (1982), 79
- <sup>29</sup> H. J. Grabke, R. Möller, H. Erhard, S. Brenner: *Surface and Interface Anal* 10 (1987), 202
- <sup>30</sup> M. Paju, H. J. Grabke: *Materials Sci. Technol.* 5 (1989), 148
- <sup>31</sup> K. Hoffmann, K. H. Sauer, H. J. Grabke: *Steel research* 59 (1988), 251-258
- <sup>32</sup> C. L. Briant: *Acta Metall.* 33 (1985), 1241
- <sup>33</sup> R. P. Messmer, C. L. Briant: *Acta Metall.* 30 (1980), 457
- <sup>34</sup> L. Stratmann, H. Keller, H. J. Grabke, H. Hänsel: Proc. Int. Conf. Soc. Chimie Physique, Paris 1983, Elsevier Amsterdam 1984, 309–317
- <sup>35</sup> N. G. Ainslie, A. U. Seybolt: *J. Iron Steel Inst.* (1960), 341
- <sup>36</sup> N. G. Ainslie, R. E. Hoffmann, A. U. Seybolt: *Acta Met.* 8 (1960), 523

- <sup>37</sup> N. G. Ainslie, V. A. Phillips, D. Turnbull: *Acta Met.* 8 (1960), 528
- <sup>38</sup> C. A. Hipsley: *Acta Met.* 35 (1987), 2399
- <sup>39</sup> J. Shin, C. J. McMahon: *Acta Met.* 32 (1984), 1535
- <sup>40</sup> F. K. Petersen, H. J. Engell: *Arch. Eisenhüttenwes.* 30 (1959), 275
- <sup>41</sup> R. J. Lad, A. G. Schrott, J. M. Blakely: *J. Vac. Sci. Technol.* A3 (1985), 1282
- <sup>42</sup> W. D. Jennings, G. S. Chottiner, G. M. Michal: *Surface + Interface Anal.* 11 (1988), 377
- <sup>43</sup> A. W. Funkenbusch, J. M. Smeggil, N. S. Bornstein: *Met. Trans.* 16A (1985), 1164
- <sup>44</sup> J. G. Smeggil, A. W. Funkenbusch, N. S. Bornstein: *Met. Trans.* 17A (1986), 923
- <sup>45</sup> J. G. Smeggil, C. G. Peterson: *Oxid. Met.*, 29 (1988), 103
- <sup>46</sup> J. L. Smialek: *Met. Trans.* 18A (1987), 163
- <sup>47</sup> D. G. Lees: *Oxid. Met.* 27 (1987), 75
- <sup>48</sup> P. Fox, D. G. Lees, G. W. Lorimer: *Oxid. Met.* 36 (1991), 491
- <sup>49</sup> J. L. Smialek: *Met. Trans.* 22 (1991), 739
- <sup>50</sup> J. L. Smialek, D. T. Jayne, J. C. Schaeffer, W. H. Murphy: *Thin Solid Films* 253 (1994), 285
- <sup>51</sup> J. L. Smialek: *Oxid. Met.* 55 (2001), 75
- <sup>52</sup> H. J. Grabke, D. Wiemer, H. Viehhaus: *Appl. Surf. Sci.* 47 (1991), 113
- <sup>53</sup> D. Wiemer, H. J. Grabke, H. Viehhaus: *Fresenius Z. Anal. Chem.* 341 (1991), 402
- <sup>54</sup> H. J. Grabke, H. Viehhaus: in "Microscopy of Oxidation" Eds. M.J. Bennett, G. W. Lorimer, The Institute of Metals London 1991, 19–33
- <sup>55</sup> H. J. Schmutzler, H. Viehhaus, H. J. Grabke: *Surf. Interface Anal.* 18 (1992), 581
- <sup>56</sup> G. Kurbatow, H. Viehhaus, H. J. Grabke: *Surf. Interface Anal.* 20 (1993), 967
- <sup>57</sup> H. J. Grabke, G.- Kurbatow, H. J. Schmutzler: *Oxidation of Metals* 43 (1995), 97
- <sup>58</sup> J. D. Kiely, T. Yeh, D. A. Bonnell: *Surface Sci.* 393 (1997), 126
- <sup>59</sup> L. Chen, N. P. Magtoto, S. Addepalli, B. Ekstrom, H. A. Kelber: *Oxid. Metals* 54 (2000), 285
- <sup>60</sup> P. Y. Hou, J. Stringer: *Oxid. Met.* 58 (1992), 323
- <sup>61</sup> P. Y. Hou, Z. Wand, K. Prüßner, K. B. Alexander, I. G. Brown: *3<sup>rd</sup> Int. Conf. "Microscopy of Oxidation"* (1996), 141
- <sup>62</sup> P. Y. Hou: *Mat. & Corr.* 51 (2000), 329
- <sup>63</sup> P. Y. Hou: *Oxid. Met.* 63 (2005), 113
- <sup>64</sup> H. D. Carstanjen, Max-Planck-Institut for Metals Research, Stuttgart, private communication
- <sup>65</sup> D. R. Sigler: *Oxid. Met.* 29 (1988), 23
- <sup>66</sup> W. L. Elban, M. A. Hebbbar, J. J. Kramer: *Met. Trans.* 6A (1975), 1929
- <sup>67</sup> M. Jenko, F. Vodopivec, H. J. Grabke, H. Viehhaus, B. Pacek, M. Lukas: *steel research* 65 (1994) 500–504
- <sup>68</sup> R. Mast, H. J. Grabke, M. Jenko, M. Lucas: *Materials Sci. Forum* 207–209 (1996), 401
- <sup>69</sup> H. J. Grabke: *Kovine, zlit., tehnol.* 30 (1996), 483–495
- <sup>70</sup> D. P. Whittle, J. Stringer: *Phil. Trans. R. Soc. London A* 295 (1980), 309
- <sup>71</sup> J. Stringer: *Mat. Sci. Engg. A* 120 (1989), 129
- <sup>72</sup> D. P. Moon: *Mat. Sci. Techn.* 5 (1989), 754
- <sup>73</sup> D. P. Moon, M. J. Bennett: *Mat. Sci. Forum* 43 (1989), 269
- <sup>74</sup> J. Jedlinski: *Solid State Phenomena* 21/22 (1992), 335
- <sup>75</sup> V. K. Tolpygo, H. J. Grabke: *Oxid. Metals* 41 (1994), 343
- <sup>76</sup> H. J. Grabke, M. Siegers, V. K. Tolpygo: *Z. Naturforschg.* 50a (1995), 217
- <sup>77</sup> F. A. Golightly, F. H. Stott, G. C. Wood: *Oxid. Met.* 10 (1976), 163, 14 (1980), 218
- <sup>78</sup> W. J. Quadackers, H. Holzbrecher, K.G. Briefs, H. Beske: *Oxid. Met.* 32 (1989), 67
- <sup>79</sup> B. A. Pint, L.W. Hobbs: *Oxid. Metals* 41 (1994), 203
- <sup>80</sup> J. Peters, H. J. Grabke: *Werkstoffe u. Korros.* 35 (1984), 245
- <sup>81</sup> J. Peters, H. J. Grabke, H. Viehhaus: Proc. 10<sup>th</sup> Symp. Reactivity of Solids, Dijon, Eds. P. Barret, L.C. Dufour, Elsevier 1985, 151
- <sup>82</sup> M. Siegers, H. J. Grabke, H. Viehhaus: in "Microscopy of Oxidation 2", Eds. S.B. Newcomb, M.J. Bennett. The Inst. Of Materials, London 1993, 269
- <sup>83</sup> M. Siegers, H. J. Grabke, H. Viehhaus: *Fresenius J. Anal. Chem.* 346 (1993), 269
- <sup>84</sup> E. Schumann, J.C. Yang, M. J. Graham, M. Rühle: *Materials and Corrosion* 46 (1995), 218
- <sup>85</sup> E. Schumann, J. C. Yang, M. Rühle, M. J. Graham: *Oxid. Metals*, in press
- <sup>86</sup> T. N. Rhys-Jones, H. J. Grabke, H. Kudielka: *Corros. Sci.* 27 (1987), 65
- <sup>87</sup> T. N. Rhys-Jones, H. J. Grabke: *Materials Sci. Technol* 4 (1988), 446
- <sup>88</sup> I. Rommerskirchen, V. Kolarik: *Materials and Corrosion* 47 (1996), 625
- <sup>89</sup> B. Pieraggi, R. A. Rapp: J. de Physique IV, Colloque C9, supplément au J. de Physique III, 3 (1993), 275
- <sup>90</sup> B. Pieraggi, R. A. Rapp: *J. Electrochem. Soc.* 140 (1993), 2844
- <sup>91</sup> A. B. Anderson, S. P. Mehandru, J. Smialek: *J. Electrochem. Soc.* 132 (1985), 1695
- <sup>92</sup> J. M. Blakely, Sh. M. Mukhopadhyay: Segregation at Ceramic Surfaces and Effects on Mass Transport, in L. C. Dufour et al. (eds.) *Surfaces and Interfaces of Ceramic Materials* 1989 by Kluwer Academic Publishers, 285–299
- <sup>93</sup> Dimiyati, H. J. Penkalla, P. Untoro, D. Naumenko, W.J. Quadackers: *Z. Metallkd.* 94 (2003), 3
- <sup>94</sup> J. Philibert, A. M. Huntz: *Microscopy of Oxidation* 2 (1993) 252
- <sup>95</sup> B. A. Pint: *Oxid. Met.* 45 (1996), 1