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SURFACE SEGREGATION STUDIES OF SELENIUM ON FeSiAl ALLOY

RAZISKAVE POVRŠINSKE SEGREGACIJE SELENA NA FeSiAl ZLITINI

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Surface segregation of selenium in a polycrystalline FeSiAl alloy with 0.05% Se was investigated by high resolution Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy. Surface segregation measurements of selenium and impurities e.g. carbon, phosphorus and sulfur, were performed in situ under UHV conditions in the temperature range from 200 to 900°C. In the low temperature range, 200<T<550°C, carbon segregated due to its high diffusion and segregation enthalpy. Carbon segregated in the form of graphite clusters. At higher temperature T>850°C sulfur and selenium segregated. The selenium segregation rate was low, probably due to its low solubility in αFe and its high vapor pressure. The grain boundary segregation of selenium was negligible. The fracture facets were practically transgranular, only on some areas intergranular decohesion was noticed.

Key words: equilibrium segregation, cosegregation, diffusion, surface precipitates, selenium, HR AES, XPS

Površinsko segregacijo selena na polikristalinični zlitini FeSiAl legirani z 0,05% Se, smo raziskali z visokoločljivo spektroskopijo Augerjevih elektronov na poljsko emisijo (HR AES) in z rentgensko fotoelektronsko spektroskopijo (XPS). Meritve površinske segregacije selena in elementov nečistoč kot so ogljik, fosfor in žveplo so potekale v temperaturnem področju od 200 do 900°C in situ v ultravisokem vakuumu. V nizko temperaturnem področju 200<T<550°C, ogljik segregira na površini zaradi visokega difuzijskega koeficienta in entalpije segregacije. Ogljik je na površini segregiral kot grafit v otočkih. Pri višjih temperaturah T>850°C sta na površini segregirala žveplo in selen. Stopnja sergegacije selena je bila nizka, predvidevamo da je vzrok temu nizka topnost selena v αFe in visok parni tlak. Segregacija selena po mejah zrn je zanemarljivo majhna. Skoraj vse prelomljene facete so bile transkristalne, le nekaj je bilo interkristalnih prelomov.

Ključne besede: površinska segregacija, segregacija po mejah zrn, površinski precipitati, kosegregacija selen, HR AES, XPS

1 INTRODUCTION

The segregation of surface active elements e.g. antimony and tin on the surface and interfaces of iron base alloys is interesting from different point of view and has been discussed in several papers[1-14].

Equilibrium surface segregation is the enrichment of atoms from bulk of a condense phase to its surface and is of great importance at elevated temperatures at which the solute atoms can diffuse sufficiently rapid to the free surfaces of the solid. The driving force for equilibrium segregation is the decrease of energy attained upon formation of bonds between the segregating atoms on the surface. Surface concentrations, structural arrangements and binding states of segregating layers are determined by thermodynamic activity of solute atoms, temperature, matrix composition and crystal orientation. Segregation of atoms on surfaces and interfaces can affect the material properties (surface energy, surface diffusion, adhesion, corrosion, catallytic reactions, recrystallization). The effects of the so-called tramp elements in steels, Ni, Cu, P, S, Pb, As, Sb, Sn, Se etc., are generally deleterious[11,12]. They cause "hot shortness" and "temper embrittlement" of steels[12]. The tramp elements do not have only deleterious effects; positive efects of Sb and Sn as well as Se on texture development of non oriented electrical sheets were detected and investigated at the IMT Ljubljana[3-9,13-14].

The elements Sb, Sn and Se have a strong tendency to surface segregation on iron and FeSiAl alloy -non oriented electrical steel sheets and can improve the texture and electrical properties[3-9].

In our previous investigations it was found that the addition of surface active elements, like antimony and tin into silicon steel has an improving effect on the texture and electrical properties of the sheets[3,4,7,9,13,14]. Selenium is also a surface active element and there are virtually no data on its segregation behavior[14].

2 EXPERIMENTAL

A laboratory cast steel of composition Fe, 2.0% Si, 0.95% Al, 0.002% C and 0.05% Se with minimal content of impurities was prepared. The ingots were hot rolled to a 2.5 mm thick strip, descaled and then cold rolled with intermediate recrystallization annealing to a final thickness of 0.15 mm.

The investigation of selenium surface segregation was performed in high resolution, field emission AES spectrometer Microlab 310-F of VG Scientific. The sample was mounted on special sample holder which enabled the annealing up to 1000°C. The temperature was controlled by a precision thermal pyrometer. At the beginning of each experiment, a constant temperature was established and impurities were removed by ion sputtering just before the AES measurements. By alternative argon ion sputtering and annealing almost all impurities were removed.

For grain boundaries segregation studies cylindrical fracture samples were prepared from the hot rolled and cold rolled strip of final thickness 4 mm. The samples were evacuated to about 10^{-6} mbar and encapsulated in quartz tubes, normalized at 1000°C, cooled in air and aged at 550°C for 200 and 500 hours, than introduced into the UHV system of Microlab at a basic vacuum $5x10^{-10}$ mbar and after cooling to approximately -120°C *in situ* impact fractured. The AES analysis were taken from as many intergranular fracture as possible.

3 RESULTS AND DISCUSSION

Selenium bulk concentration in the investigated alloy was approximately 0.02 at.% and was lower than the sensitivity of the AES method. Only after heating at the constant temperature some enrichment was detected by AES measurements, which was much lower than the enrichment of Sb and Sn reported in our previous papers[7,8,13,14].

In the low temperature range T<550°C carbon segregated on the sputtered clean surface due to its high diffusion and segregation enthalpy. **Figure 1** shows SEM image of segregated carbon on different grains of αFe and in **Figure 2** SEM image of two grains, where clusters of graphite were found. AES spectra confirmed our hypothesis that carbon nucleated on the surface of investigated alloy as a graphite, which is thermodinamically stable phase, though the graphite nucleation on the surface of iron base alloys is very difficult[12,15]. The process of faceting occurred during heating and on terraces Al_2O_3 was also found. Grabke[11,12] and Guttman[20], described that the process of surface precipitation is parallel to chemisorption induced segregation and oxidation. Oxygen came from residual atmosphere and not from the bulk and interacted with segregated aluminum on the steel in the monolayer range[12,20].

Figure 1: a) SEM image of segregated C on different grains of αFe. The sample was annealed at T<550°C

Slika 1: SEM posnetek segregiranega C na različnih zrnih αFe; vzorec je bil žarjen na T<550°C

At T>550°C phosphorus segregated on the surface of investigated alloy **(Figure 3)**. Carbon was replaced by

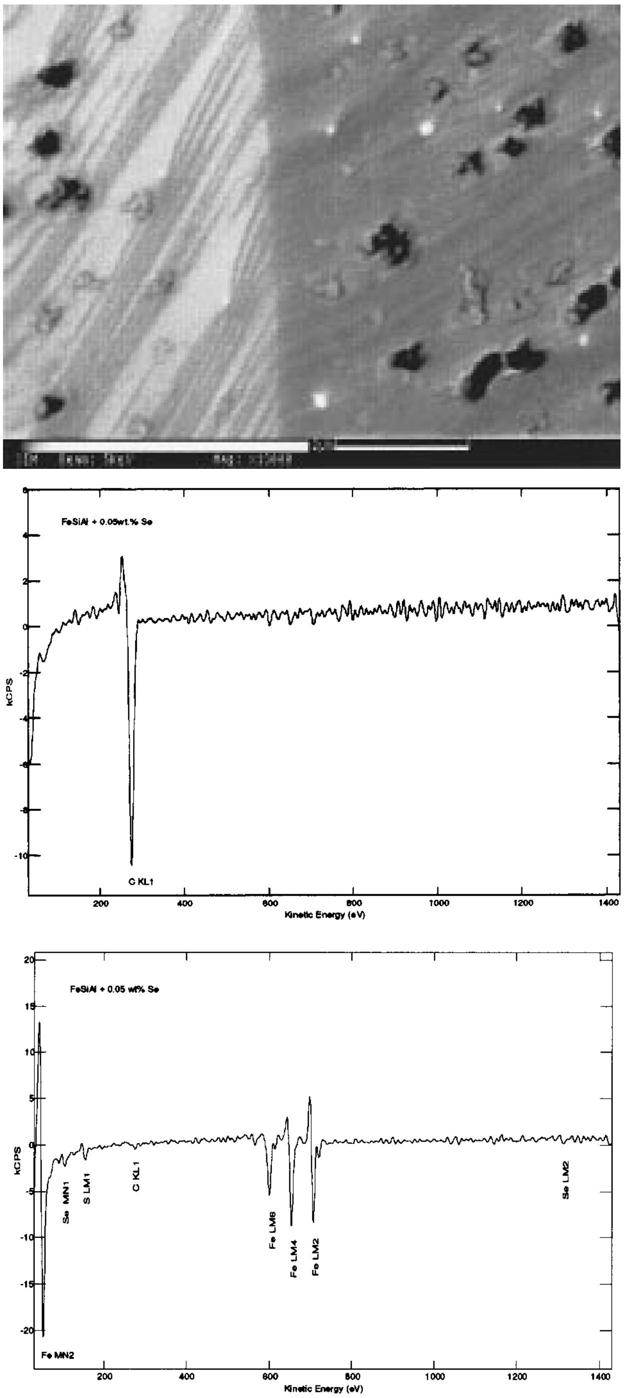

Figure 2: a) SEM image of two grains, where phenomena of faceting and clusters of graphite were found

b) AES spectra of carbon clusters

c) AES spectra of matrix

Slika 2: a) SEM posnetek dveh zrn, detajl iz **slike 1**, na katerih opazimo pojav facetiranja, C je segregiral kot grafit v otočkih

b) AES spekter otočkov ogljika

c) AES spekter matriksa

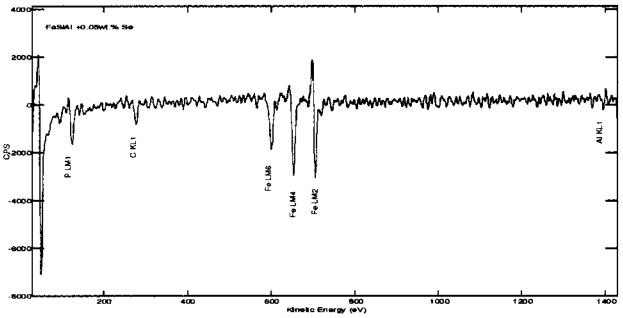

Figure 3: AES spectra of FeSiAlSe alloy, the sample annealed up to 700°C. C was replaced by P, due to its higher segregation enthalpy[12,20]

Slika 3: AES spekter zlitine FeSiAlSe, žarjene na 700°C, P je izpodrinil C zaradi višje entalpije segregacije[12,20]

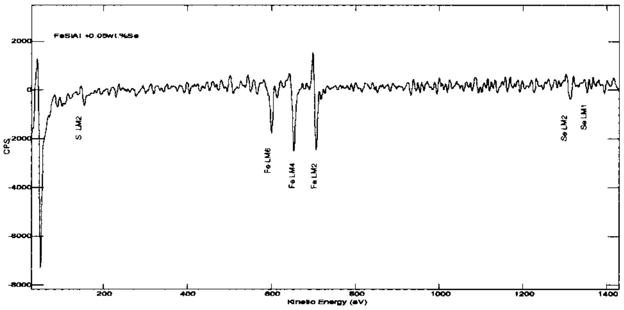

Figure 4: AES spectra of FeSiAlSe sample; annealed at T>850°C, S an Se segregated on the surface

Slika 4: AES spekter zlitine FeSiAlSe, žarjene na T>850°C, S in Se segregirata na površini

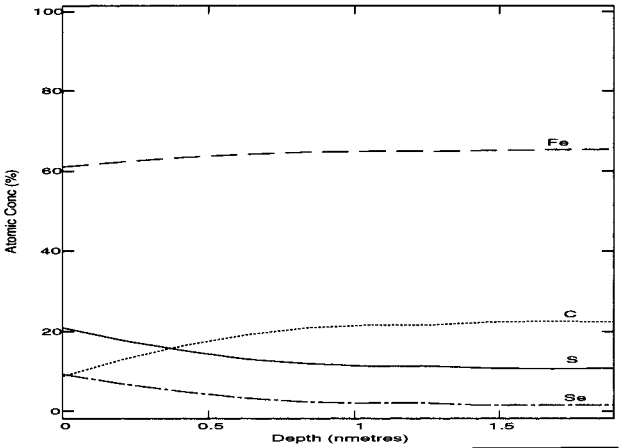

Figure 5: AES depth profile of ultra thin segregated Se on the surface. The Se enrichment was estimated to about 10 at %

Slika 5: AES profilni diagram ultra tanke segregirane plasti Se in S na površini. Ocenjena obogatitev površine z Se je okrog 10 at.%

phosphorus, because of its higher segregation enthalpy[12,20].

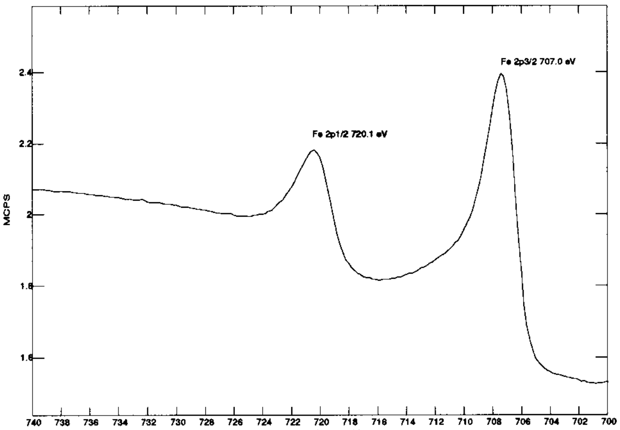

Figure 6: XPS measurements showed that Fe ($2p_{1/2}$ and $2p_{3/2}$) was in elemental form

Slika 6: XPS meritve so jasno pokazale, da je Fe ($2p_{1/2}$ and $2p_{3/2}$) elementaren

At T>850°C sulfur and selenium segregated on the surface of experimental alloy (**Figure 4**). Selenium segregation rate was surprisingly low. Two possible explanations of the selenium surface segregation rate are suggested. Selenium segregation on the surface was afterwards covered by the sulfur segregation, and the segregated selenium evaporated from the surface due to its high vapor pressure. AES depth profile analysis (**Figure 5**) showed that there is no selenium in the layers near the surface. Experiment confirmed the hypothesis that due to its high vapor pressure, segregated selenium evaporated from the surface. From AES depth profile analysis the Se enrichment on the surface was estimated to about 10 at.%.

Physical properties of selenium, tin and antimony as well as solute elements e.g. S, P, C, Si and Fe are given in **Table 1**.

Table 1: Physical properties of Fe, Sb, Sn, Se, C, S, P, Al, and Si[12,15,17,18]

Element	Atom. radius nm	Melt. point °C	Boiling point °C	D_o cm^2s^{-1}	Q $kJmol^{-1}$	ΔH_{seg} $kJmol^{-1}$
antimony Sb	0.159	630	1635	1100	270.0	-
tin Sn	0.162	232	2507	6.1x104	316.0	-
selenium Se	0.140	217	685	0.127	192.5	-
iron Fe	0.126	1538	3000	-	209.0	-
silicon Si	0.132	1410	2355	8.0	249.9	-44.0
aluminum Al	0.143	660	2327	5.90	239.4	-
carbon C	0.091	3727	4827	2.2	123.1	-85.0
sulfur S	0.104	115	446	34.6	231.5	-
phosphorus P	0.128	44	280	7.16	168.0	-180.0

Data for the diffusion coefficient and the activation energy of selenium, given in **Table 1**, confirmed the hypothesis, that at the temperatures T<850°C on the surface an equilibrium was reached and all segregated Se atoms evaporated from the surface. At T>850°C the process of selenium diffusion or segregation is faster than evaporation process and for that reason a limited enrichment of Se on the surface was detected.

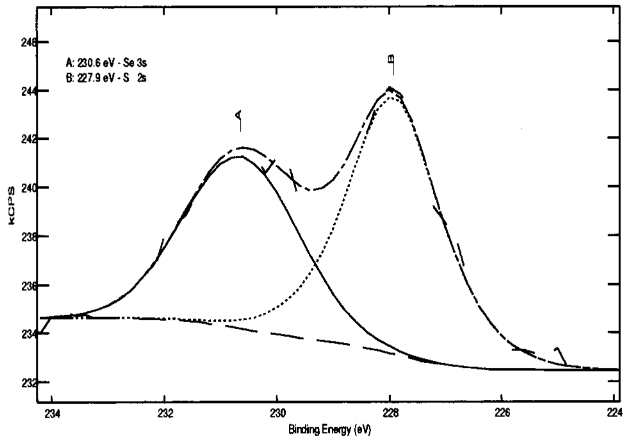

Figure 7: XPS peaks of S and Se; there is no clear evidence that on the surface compounds of S and Se was formed

Slika 7: XPS vrha S in Se v ultra tanki segregirani plasti kažeta, da je prišlo do pojava, kosegregacije in ne do tvorbe površinskih spojin

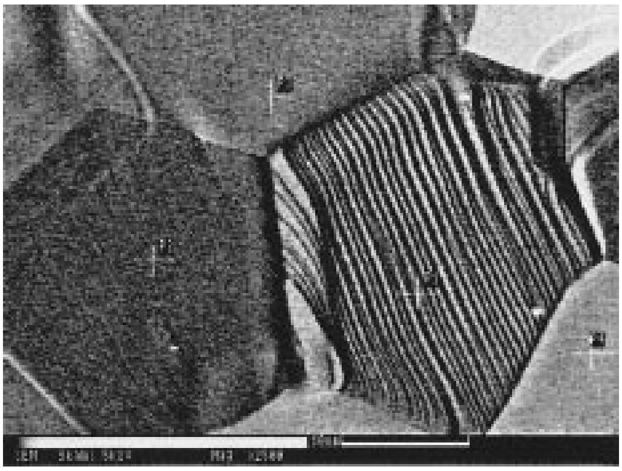

Figure 8: SEM image of faceting phenomenon on the surface of FeSiAlSe alloy

Slika 8: SEM posnetek pojava facetiranja na posameznih zrnih zlitine FeSiAlSe

On the surface the AES peaks intensity of S, Fe and Se were measured. It is known that some elements cosegregate like Sb and Ni and some form surface compounds[12,20]. The segregated ultra thin film was investigated using XPS and from XPS measurements it was concluded that Fe ($2p_{1/2}$ and $2p_{3/2}$) was in elemental form[19,22,24] **(Figure 6)**. XPS peaks of S and Se are in the same energy region **(Figure 7)** and there is no evidence that on the surface a compound of S and Se, selenium sulfide e.g Se_2S or $SeS_{(g)}$ was formed[21,22,23] and it was suggested that the process of cosegregation occurred.

The grain boundary segregation of selenium was negligible. The fracture facets were practically transgranular, only on some areas intergranular decohesion was noticed.

The grain growth kinetics and micromorphology was also observed in situ in UHV during the segregation experiments at elevated temperature where the process of faceting was observed by SEM. In **Figure 8** the grain growth at 550<T<900°C was in the first stage two dimensional and only after certain time at elevated temperature, three dimensional grain growth occurred.

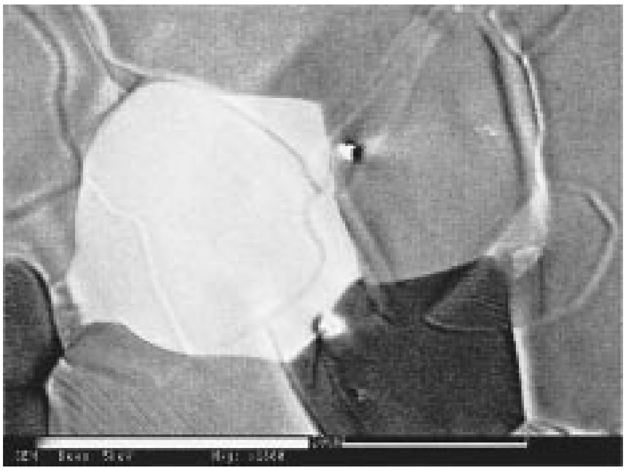

Figure 9: SEM image of grain growth of FeSiAlSe alloy. In the first stage 2D grain growth occurred

Slika 9: SEM posnetek rasti zrn na površini zlitine FeSiAlSe. V začetni stopnji se pojavi najprej dvodimenzionalna rast zrn

The phenomena of micromorphology of faceting process, **(Figure 9)**, micromorphology, recrystallization and grain growth kinetics as well as interactions with neighboring grains with different faceting morphology, and precipitates were observed with HR AES and SEM methods and will be discussed in a separate paper.

4 CONCLUSIONS

The selenium surface segregation on FeSiAlSe alloy was investigated *in situ* in the UHV chamber of HR AES spectrometer in the temperature range from 200 to 900°C.

In the low temperature range T<550°C carbon segregated on the sputtered clean surface due to its high diffusion and segregation enthalpy as graphite in clusters.

At T>550°C phosphorus segregated on the surface of the alloy and replaced carbon due to its higher segregation enthalpy.

At T>850°C sulfur and selenium segregated on the surface. Selenium segregation rate was low. Two explanations of the Se surface segregation rate were suggested. Se segregated to the surface first and sulfur covered it and the cosegregation of selenium and sulfur. AES depth profile showed no selenium near the surface while the experiment confirmed hypothesis that due to its high vapor pressure segregated selenium evaporated from the surface. Selenium surface enrichment was estimated to about 10 at.%.

XPS mesurement showed that on the surface of experimental alloy Fe was in elemental form, while XPS peaks of S and Se were in the same energy region and there was no clear evidence that a surface compound was formed. A cosegreagation process seems more probable.

The grain boundary segregation of selenium was negligible. The fracture facets were practically transgranular, only on some areas intergranular decohesion was noticed.

The grain growth kinetics and micromorphology was observed also in situ in UHV chamber of HR AES spectrometer, during the segregation experiments at elevated temperature and the process of faceting was observed by SEM also. The grain growth at 550<T<900°C was in the first stage two dimensional and only after certain time at elevated temperature, three dimensional grain growth occurred.

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5 REFERENCES

[1] F. Vodopivec, F. Marinšek, D. Gnidovec, B. Praček, M. Jenko, *J. Magn. Magn. Mat.*, 97 (1991) 281

[2] P. Ševc, J. Janovec, M. Lucas, H. J. Grabke, *Steel resarch*, 12, 66 (1995) 537-542

[3] M. Jenko, F. Vodopivec, B. Praček, *App. Surf. Sci.*, 70/71 (1993) 118

[4] M. Jenko, F. Vodopivec, B. Praček, M. Godec and D. Steiner, *J. Mag. Mag. Mat.*, 133 (1994) 229

[5] G. Lyudkovski, *IEEE Trans. Magnetics Mag.*, 22 (1986) 5, 508

[6] G. Lyudkovski, A. G. Preban, J. M. Shapiro, *J. Appl. Phys.*, 5 (1982) 3, 2419

[7] M. Jenko, F. Vodopivec, H. J. Grabke, H. Viefhaus, B. Praček, M. Lucas, M. Godec, *Steel research*, 65 (1994) 11, 500

[8] M. Jenko, H. Viefhaus, M. Lucas, F. Vodopivec, M. Godec, D. Steiner, *J de phys.*, IV (Les Ulis), 11 (1995) 5, C7-225-C7-231

[9] V. Rusenberg, H. Viefhaus, *Surf. Sci.*, 172 (1986) 615

[10] H. J. Grabke, *Kovine, zlitine, tehnologije*, (1993) 1/2, 9

[11] H. J. Grabke, *Iron and Steels, ISIJ*, 35 (1995) 95-113

[12] M. Godec, L. Kosec, M. Jenko, H. J. Grabke, Metal, *Berl. West*, 51 (1997) 12, 702-705

[13] M. Jenko, M. Godec, H. Viefhaus, H. J. Grabke, *Antimony, tin and selenium segregation in FeSiC alloys*, iib98 Praga, 1998 in print

[14] O. Kubaschewski, C. B. Alcock, P. J. Spencer, *Materials Thermochemistry* 6th Ed., Pergamon Oxford, 1993

[15] J. W. Martin, R. D. Doherty, B. Cantor, *Stability of Microstructure in Metallic system*, University Press, Cambridge, 1997

[16] J. L. Margrave, *The Characterization of High-Temperature Vapors*, J. Wiley&Sons, NY 1967

[17] CRC Handbook of Chemistry and Physics, ED.D.R.Lide 76th ed., CRC Press NY 1996

[18] D. Briggs, M. P. Seah, *Practical Surface analysis*, 2nd Ed., J. Wiley&Sons, Chichester 1994

[19] M. Guttman, *Surf. Sci.*, 53 (1975) 213

[20] C. L Hedberg Ed, *Handbook of Auger Electron Spectroscopy 3 ed.*, Physical Electronics, 1995, Eden Prairie, Minessota

[21] J. Chastain, R. C. King Jr, Eds., *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics, 1995, Eden Prairie, Minessota

[22] T. B. Massalski et.al., *Binary Alloy Phase Diagrams 2ed.*, ASM Int.: Materials Park, OH

[23] E. Adem, *XPS and AUGER Handbook*, 1991, VG Scientific, East Grinstead, UK