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Oxidation upon segregation: Evaluation of chemical state of segregated species in polycrystalline Fe–Si–Al alloys by AES

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ABSTRACT

Oxidation state of individual alloying elements (Si, Al) and impurity element (Cu) upon segregation onto the surface of the sample Fe–Si–Al alloys was investigated in an in situ study of segregation behavior in ultra-high vacuum. Chemical state of surface Si, Al and O as well as Cu was evaluated, by measuring the kinetic energy shifts that affect Si KLL, Al KLL, O KLL but also Cu LMM transitions, depending on chemical state of the element. It was found that Al oxidizes with temperature in all samples while Si behaves differently with maximum oxidation occurring around 300 °C, and oxidation not occurring at all in some samples. Segregated Cu stays predominantly in its elemental state which is consistent with relevant literature reports.

1. Introduction

The chemical properties of an alloy surface depend on the detailed surface composition. This compositional and concomitant geometric and electronic structure is not only different from the corresponding surfaces of the parent metals, but differs often also substantially from the bulk alloy due to segregation of one species to the surface. The resulting segregation profile can depend on the surface orientation, the bulk composition, and temperature. A reactive environment can further modify the chemical composition of the surface, if one alloy component interacts more strongly with a gas phase species than the others, resulting in adsorbate-induced segregation [1].

Oxidation behavior of Fe–Si alloys of various chemical compositions is of great interest due to its technological importance in production of electrical steel sheets [2–6]. In one of our previous study [7] on non-oriented electrical silicon steel sheets the surface segregation of oxygen was detected from the very onset of the annealing and was present in the whole temperature range of the annealing in the ultra-high vacuum environment. Moreover, the fact that Si and Al exhibited roughly similar segregation patterns prompted the question of the chemical state of Si and Al as well as O, especially in a view of the well known kinetic energy shifts that affect Si KLL, Al KLL, O KLL but also Cu LMM, depending on chemical state of the element [8–11]. Usually, XPS is employed to evaluate the chemical state of the element, especially for oxide layers on different Fe alloys (e.g., [12]). However, in AES the exact position, as well as the shape of the peak in a spectrum, also depends on the chemical state of the element. While in XPS this is a well-developed technique with databases of the shifts in the peak positions for different compounds being readily available (e.g., [8,9]), it is much less frequently used in AES, where the influence of the chemical state on the energy shifts has been given less attention than in XPS. There are, nevertheless, a number of well-described cases in the literature of shifts of up to several eV between the elemental (metallic) state and various compounds [8,11], Al, Si and Cu among them.

2. Experimental

Industrial, fully processed, non-oriented Fe–Si–Al alloy steel sheets from two different batches were used. For comparison, model materials of the Fe–Si–Al alloys were prepared under laboratory conditions using a melting, casting, hot and cold rolling in order to simulate the industrial manufacturing route of 0.5 mm thick non-oriented electrical steel. Afterwards, all samples of the model and industrial alloys were cold-rolled to 0.1 mm thick foil suitable for resistive heating. Their overview and chemical compositions are given in Table 1. Typical dimensions of a sample were 15.0 mm × 5.0 mm × 0.1 mm. Prior to introducing samples into the UHV system of the AES spectrometer they were metallographically polished.

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Table 1
Chemical composition of Fe–Si–Al alloys after cold rolling (in wt.%) obtained by chemical analysis of bulk material.

Fe–Si–Al alloys					
	No Cu	Alloys with Cu			
	Model alloys			Industrial alloys	
	S1	S2	S3	S4	S5
C	0.040	0.011	0.009	0.023	0.022
Si	1.73	1.90	1.86	1.68	1.74
Al	0.70	0.55	0.46	0.24	0.47
Mn	0.21	0.24	0.24	0.24	0.26
P	0.002	0.005	0.005	0.010	0.021
S	0.002	0.005	0.005	0.002	0.002
O	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	0.01	0.24	0.43	0.33	0.60
As	<0.001	<0.001	<0.001	0.010	0.006
Sb	0.0004	0.0004	0.0006	0.0050	0.0092
Sn	0.005	0.005	0.003	0.019	0.027
Cr	0.01	0.01	0.01	0.13	0.22
Ni	0.05	0.05	0.05	0.15	0.19
Fe	Balance	Balance	Balance	Balance	Balance

2.1. *Auger electron spectroscopy (AES)*

AES was performed by a VG-Microlab 310F instrument equipped with a Schottky field-emission gun and a hemispherical electron-energy analyzer. The spectra were typically measured at 10-kV electron-beam energy and were recorded with a constant retard ratio 4 of the analyzer at 1 eV channel width. Typical pressure at the start of the AES analysis was 10^{-9} mbar, increasing up to 10^{-7} mbar with resistive heating of the samples up to 850 °C. Detailed description of the heating arrangement can be found elsewhere [7].

After introducing samples into the UHV system they were surface-cleaned by Ar^+ sputtering to remove contamination adsorbed from the atmosphere. Cleaned samples were then heated and AES spectra measured. The temperature was increased from 50 °C up to 850 °C in steps of 50 °C and the samples were kept for 5 minutes at each temperature before AES was measured. After each heating step the surface concentration of the elements was determined from the measured AES spectra. There was no Ar^+ sputtering between the heating steps.

Surface concentrations of the segregands were calculated from the differentiated AES spectra, from the measured peak-to-peak ratios and corresponding sensitivity factors [13,14]. Sensitivity factors measured and supplied by the manufacturer of the AES equipment were used. Matrix effects and sample inhomogeneities which may be considerable in case of surface segregation were disregarded.

Spectra were acquired by Avantage V 3.41 data-acquisition and analysis software and processed by CasaXPS data-analysis software [15].

3. Results and discussion

Characteristic results on segregation behavior of the selected Fe–Si–Al alloys obtained by AES during annealing in ultra-high vacuum are shown in Fig. 1. Surface concentrations of segregating species are represented as a function of temperature. The values given represent the cumulative values of the surface enrichment of the segregands during annealing after the performed heating step.

The surface segregation of the alloying and impurity elements in Fe–Si–Al alloys for non-oriented steel depends on the annealing temperature and their bulk concentration [7]. The surface segregation of silicon in analyzed Fe–Si–Al alloys [7] increased up to approximately 500 °C, and that of aluminum was more intensive at temperatures above 400 °C. The surface segregation of copper, when present, reached its maximum values at temperatures $T = 550$ and 600 °C. After reaching the maximum values the surface concentration of the segregated copper decreased with the increasing temperature of the annealing. It can be seen from the chemical composition of the alloys that the model and industrial steels differ very much in their tin and sulphur contents (Table 1). In the case of industrial alloys, tin was predominantly present at the steel's surface at temperatures above 600 °C. In the model alloys the surface is enriched by sulphur at temperatures above 700 °C. The surface segregation of antimony in the industrial alloys started at 600 °C and was detectable on the surface up to 850 °C.

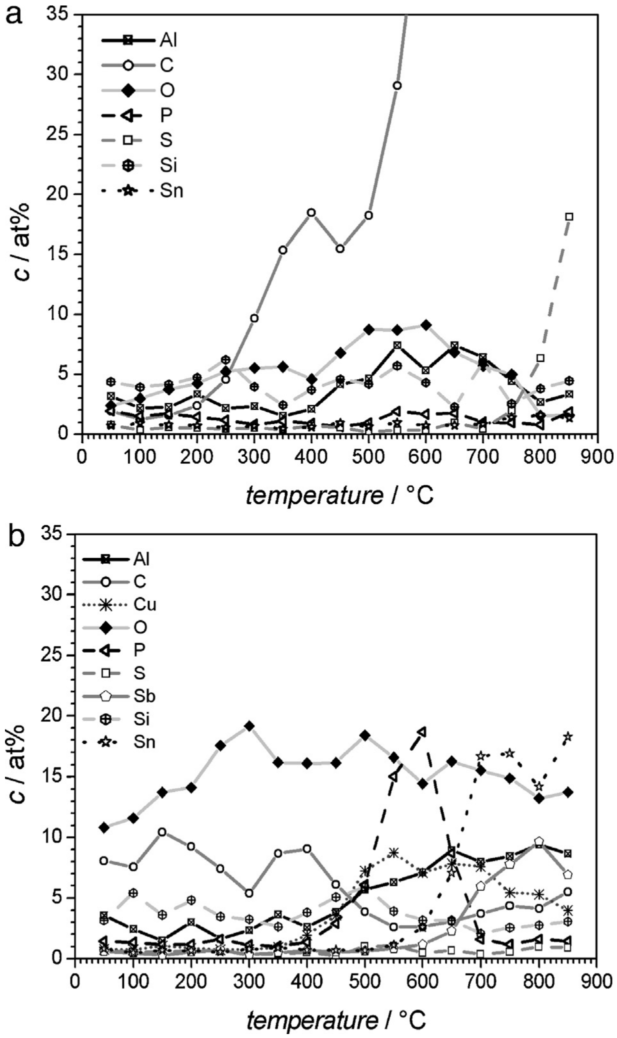

Fig. 1. Concentrations of surface segregated elements vs. temperature in a Fe–Si–Al alloy: (a) model alloy S1 with 0.01 wt. % Cu and (b) industrial alloy S5 with 0.6 wt.% Cu.

As can be seen the surface segregation of oxygen was detected from the very onset of the annealing and was present in the whole temperature range of the annealing (Fig. 1). Maximal surface segregation of oxygen in model alloy S1 was measured in temperature range from 500 °C to 600 °C, whereas in the industrial one (S5) broader maximum was observed, between 300 °C and 500 °C. The fact that Si and Al exhibited roughly similar segregation patterns prompted the question of the chemical state of Si and Al as well as O, especially in a view of the well known kinetic energy shifts that affect Si KLL, Al KLL, O KLL but also Cu LMM, depending on chemical state of the element [8–11]. Detailed view of O KLL for one of the samples (S3) at all temperatures is shown in Fig. 2 where