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Grain boundary segregation in bright nitrided α-irons alloyed with chromium, molybdenum and silicon

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Interfacial segregation in bright nitrided binary α-iron alloys containing 3.0 at% Cr, 2.4 at% Mo and 3.6 at% Si were studied by Auger electron spectroscopy. Chromium, molybdenum and silicon were found to segregate to interfaces in these alloys. Segregation of chromium and molybdenum is, however, partly reduced by the formation of clusters or precipitate between nitrogen and solute atoms. Segregation of silicon is slight owing to the repulsive interaction between silicon and nitrogen atoms. It was not found that such surface active elements as sulphur and phosphorus had segregated to the interfaces in the bright nitrided alloys studied.

1. Introduction

Many properties of metallic materials are affected by segregation to their surfaces and interfaces. The segregation of impurities decreases the cohesion of the grain boundaries of many alloys causing various types of intergranular failures [1, 2]. Nitrogen has been found to displace sulphur from the grain boundaries of α-iron thus decreasing its tendency to grain boundary embrittlement [3]. Bright nitriding offers one way to increase the nitrogen content of the grain boundaries, this possibly reinforcing the cohesion of grain boundaries.

The grain boundary diffusion of nitrogen during nitriding and the co-segregation of alloying elements can alter the segregation pattern determined from binary α-iron alloys. Molybdenum and chromium, which are not surface active elements in α-iron, co-segregate to the surfaces and interfaces with nitrogen or other surface active elements that have a strong attractive interaction on the surface with them [4, 5]. Silicon is slightly surface active in binary α-Fe–Si alloys [1], but observations of its behaviour in the presence of nitrogen have not been presented. The aim of this study is to assess the effect of bright nitriding on the segregation behaviour of chromium, molybdenum and silicon in binary α-iron alloys.

2. Experimental details

The alloys investigated were produced by vacuum melting electrolytic iron alloyed with pure chromium or silicon powder or molybdenum rod. The chemical compositions of the alloys given in Table I were determined by spectroscopic analysis except for carbon content which was determined by combustion analysis. The alloy casts were hot forged, cold rolled and machined to 5 mm thick cylindrical specimens with notched 3 mm diameter. The specimens were first annealed for 20 min at 950° C and then nitrided in purified ammonia–hydrogen atmospheres for 8 h at 500° C to obtain about 100 ppm nitrogen at the cross section of the notched region.

Auger electron spectroscopy (AES) measurements were performed in a hemispherical electron spectrometer with a fracture stage and a scanning

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TABLE I Chemical compositions of the test materials

Material: composition of main alloying element (at %)	Element (wt %)								
	C	Si	Mn	S	P	Cr	Ni	Mo	As
3.0 Cr	0.0005	–	0.014	0.004	–	2.82	0.022	0.005	–
2.4 Mo	0.0005	0.030	0.017	0.005	0.005	0.012	0.035	4.10	0.001
3.6 Si	0.0010	1.85	0.020	0.008	0.002	0.012	0.030	0.002	0.002

Auger facility for physical and chemical imaging. The notched samples cooled with liquid nitrogen were fractured by an impact hammer and transferred to the analyser vessel in vacuum. The background pressure both in the analyser and in the specimen preparation vessel was less than 0.1 μPa. Before measurements, the surface areas to be studies were chosen from an *in situ* scanning electron microscopy picture. The time needed from fracturing to the first measurement was about one hour. The electron spectrum was obtained with an electron gun operated at 4.8 kV and 50 μA. The AES spectra were taken with a constant retardation ratio mode. Depth profiling distributions of elements at the surface were studied by using consecutive series of Auger measurements and argon sputtering cycles. The sputtering rates were estimated to be less than two monolayers per minute using ion bombardment at 2 kV and 2 μA and less than ten monolayers per minute using ion bombardment at 4 kV and 10 μA. After AES analyses the fracture surfaces of the notched specimens were studied with conventional scanning electron microscopy (SEM).

The Auger peak amplitude ratios were converted into approximate atomic fractions X_X^s using relationship presented by Guttmann *et al.* [5];

$$X_X^s = k_X^s \frac{I_X^s/I_X^o}{\Sigma_M(I_M^s/I_M^o)} - (k_X^s - 1)\frac{I_X^b/I_X^o}{\Sigma_M(I_M^b/I_M^o)} \qquad (1)$$

where I_X and I_M are the Auger peak-to-peak amplitudes of element X and the main constituents M, respectively, in the differentiated spectra. The superscript s refers to measurements performed on the segregated surface, the superscript b corresponds to the bulk values as obtained from the transgranular region of a specimen after sputtering and the superscript o refers to the Auger peak height ratios of the pure elements given by (or calculated according to) Davis *et al.* [6]. The values of k_X^s calculated for the spherical deflector analyser (SDA) using the data compiled by Seah and Dench [7] are listed in Table II. The calculation of k_X^s was made assuming that all the surface excess of segregated elements is confined within one atomic layer below the intergranular fracture surface. The Auger peak-to-peak amplitudes at 598 eV were used for iron.

3. Results

Surfaces fractured in the vacuum chamber are shown in Fig. 1. They exhibit both intercrystalline and transcrystalline fracture. The areas analysed mainly showed intercrystalline fracture. The relative peak-to-peak amplitudes of analysed specimens are drawn in Fig. 2. The Auger spectra corresponding to the peak concentrations of the alloying elements are given in Fig. 3. The determinations of the relative peak-to-peak amplitudes of chromium, molybdenum and silicon were disturbed by the interference between the lines of chromium and oxygen, molybdenum and chlorine, and silicon and iron. Hence the amplitudes presented are inaccurate to some extent. Carbon monoxide adsorbed onto the faces fractured from the residual gas atmosphere in the analyser vessel and therefore the carbon and oxygen peak heights increased with analysing time. Hence the measurements of carbon and oxygen segregation were impossible in the vacuum used. The peak-to-peak ratios of nitrogen and the alloying elements in Fig. 2 are lower on the fracture surface than in some distance from it, this being due to carbon and oxygen contamination during the time needed from cracking the sample to the first measurement. During sputtering the concentrations of the con-

TABLE II Calculated values of the multiplying factors k_X^s in Equation 1 for segregated elements X

Element X	Energy (eV)	k_X^s
N	383	4.22
Cr	489	4.88
Mo	186	3.37
Si	92	2.69

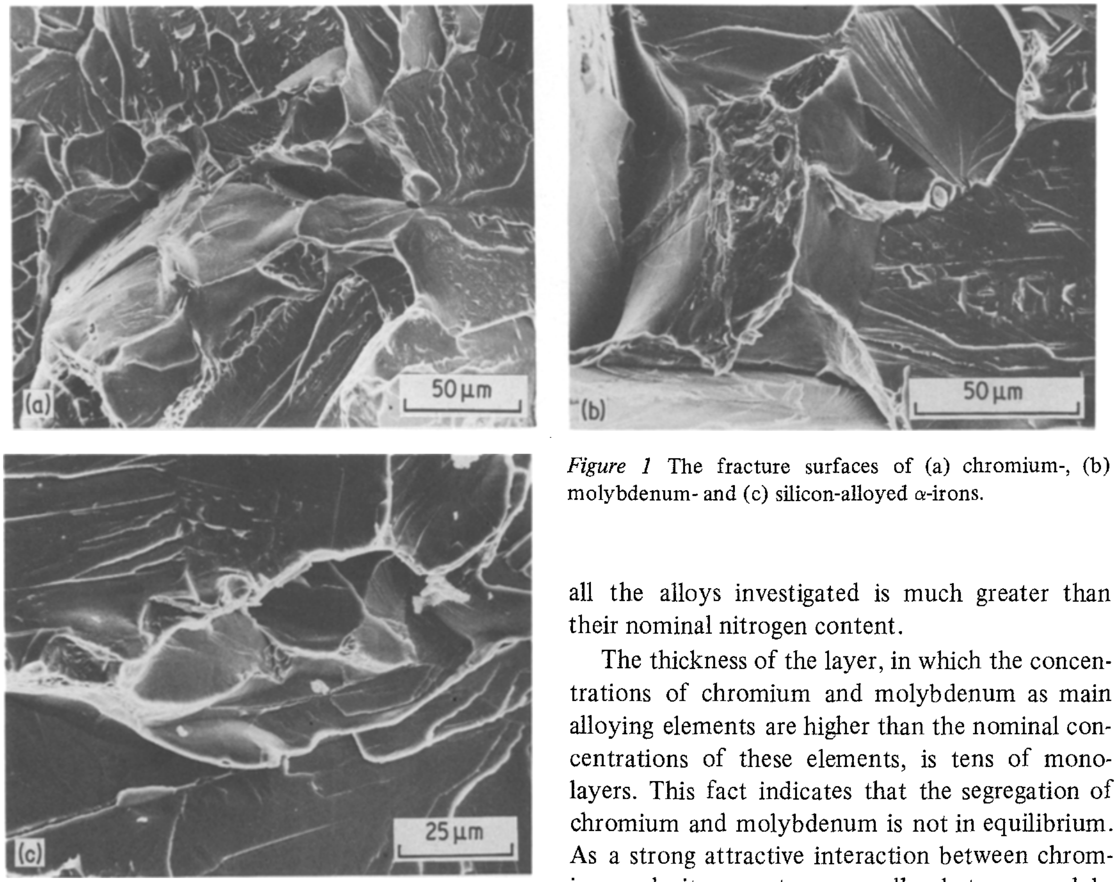

Figure 1 The fracture surfaces of (a) chromium-, (b) molybdenum- and (c) silicon-alloyed α-irons.

taminants decreased and the peak-to-peak ratios of the elements of the base metal were enhanced. No traces of such surface active elements as sulphur and phosphorus were detected in the analysed Auger spectra.

The maximum surface concentrations and enrichment ratios evaluated from the measured spectra according to Equation 1 are presented in Table III assuming segregation to be one atom layer thick. Both these values are assumed to be underestimated because the analysed areas had partly fractured transcrystallinely and because knowledge about the effect of adsorbed carbon and oxygen on the measured peak-to-peak ratios is lacking.

4. Discussion

The nitrogen content of the nitrided samples at the grain boundaries is greater than in the grain interior because nitrogen segregates to the interfaces and also because grain boundary diffusion is more rapid than ordinary volume diffusion [8]. The nitrogen content below the segregated layer in all the alloys investigated is much greater than their nominal nitrogen content.

The thickness of the layer, in which the concentrations of chromium and molybdenum as main alloying elements are higher than the nominal concentrations of these elements, is tens of monolayers. This fact indicates that the segregation of chromium and molybdenum is not in equilibrium. As a strong attractive interaction between chromium and nitrogen atoms as well as between molybdenum and nitrogen atoms exists, these atom pairs cluster or form pre-precipitates where the solute concentrations are sufficient [9]. The minima in the chromium and molybdenum contents at distances from the surface where the nitrogen content decreases to a constant level presumably separate the real segregated layers from the clustered or precipitated zones. Since in the bulk the affinity of chromium for nitrogen is greater than that of molybdenum for nitrogen, the segregation of chromium and nitrogen in the chromium alloyed samples is less than the segregation of

TABLE III The approximate maximum surface concentrations $C^{s}_{X(\max)}$ and evaluated enrichment ratios β^{s}_{X} ($= C^{s}_{X(\max)}/C^{s}_{X(\text{nominal})}$) of segregated nitrogen, chromium, molybdenum and silicon in alloys investigated

Alloy	Element	$C^{s}_{X(\max)}$ (approx. at %)	β^{s}_{X}
3.0 Cr	N	2.8	
	Cr	7.1	2.4
2.4 Mo	N	5.7	
	Mo	19.0	7.9
3.6Si	N	1.9	
	Si	8.1	2.2

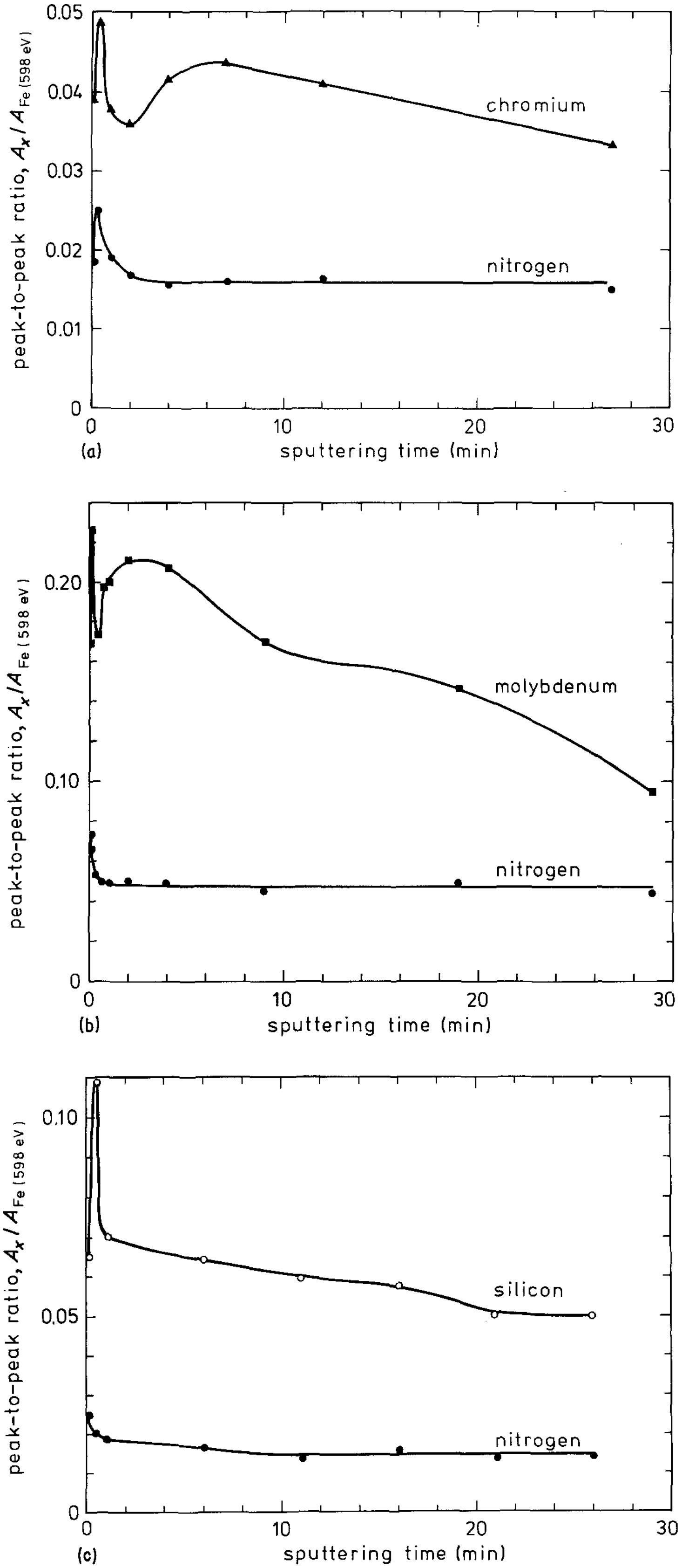

Figure 2 Depth profiles for (a) chromium-, (b) molybdenum- and (c) silicon-alloyed α-irons. (Argon sputtering: (a)–(b) 2 kV, 2 μA and (c) 4 kV, 10 μA).

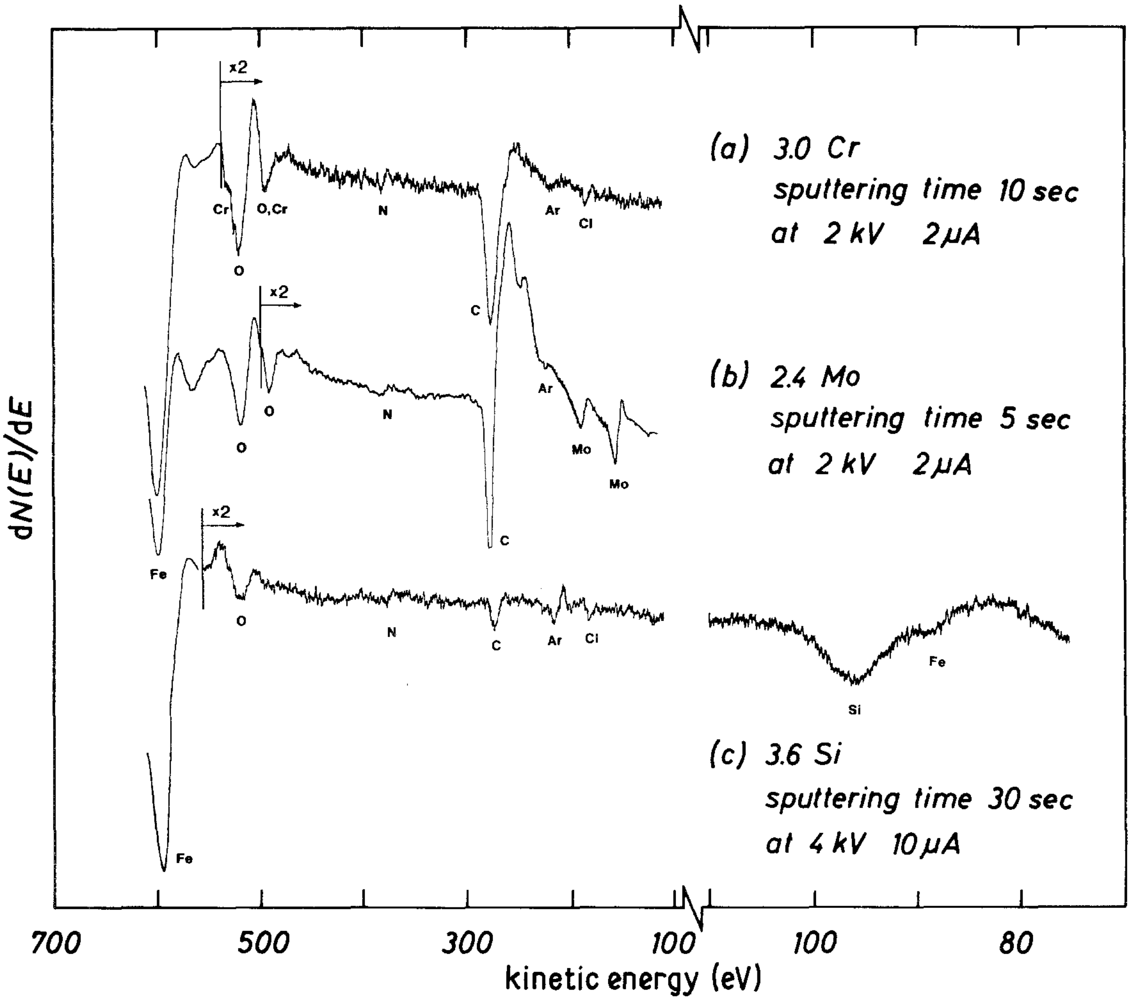

Figure 3 Auger spectra of (a) chromium-, (b) molybdenum- and (c) silicon-alloyed α-irons.

molybdenum and nitrogen in the molybdenum alloyed sample.

The silicon content below the segregated layer in the silicon alloyed sample is nominal within the limits of the accuracy of measurements. This fact is indicated by silicon not reacting with nitrogen to form precipitates in that layer. Because interaction between silicon and nitrogen is repulsive [10], the segregation of both these surface active elements is slight.

The reason for the absence of sulphur and phosphorus amplitudes in the Auger spectra might result from the high nitrogen content at the grain boundaries and in the molybdenum alloyed sample also from the high molybdenum content in the segregated layer and below it. According to Tauber and Grabke [3] nitrogen partly displaces sulphur from grain boundaries. Presumably the high nitrogen content at grain boundaries also reduces the segregation of other surface active impurities, e.g. phosphorus, which have a repulsive interaction with nitrogen. Phosphorus can also be scavenged by the dissolved molybdenum from grain boundaries to the grain interior, where it may be tied up in Mo–Fe–P clusters [5, 11]. Though chromium generally enhances the segregation of phosphorus at the boundaries [12], the segregation is prevented in the chromium alloyed sample investigated by nitrogen atoms similarly as mentioned above.

5. Conclusions

Chromium, molybdenum and silicon segregate to the interfaces in binary bright nitrided α-iron alloys. The segregation of chromium and molybdenum is probably reduced by the formation of clusters or precipitates between nitrogen and solute atoms. As the attractive interaction between chromium and nitrogen in the bulk is greater than that between molybdenum and nitrogen, there are a smaller number of the atoms first mentioned in the solution to segregate in chromium alloyed α-iron than the atoms last mentioned in molybdenum alloyed α-iron. Segregation of silicon is slight owing to the repulsive interaction between silicon and nitrogen atoms.

The surface active elements like sulphur and phosphorus are at least partly displaced by nitrogen at the grain boundaries, thus reducing the tendency of α-iron alloys to brittle intercrystalline rupture.

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