

INFLUENCE OF STRUCTURE AND CHEMICAL COMPOSITION OF SURFACE OXIDE LAYER ON MAGNETIC PROPERTIES OF Fe—3.25% Si SINGLE CRYSTALS

BY S. SZYMURA AND B. WYSŁOCKI

Institute of Physics, Technical University, Częstochowa*

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During the decarburization of Fe—3.25% Si single crystals with (110) surface orientation in a moist (313 K dew point) hydrogen atmosphere at 1123 K an oxide layer is formed. In the early stages of the process the layer consists of fine round particles of SiO₂ which during more prolonged annealing grow in the [100] direction. Already after short annealing (1 min.) the silicon content in the layer increased and that of iron decreased. The layer reduced the anisotropy of the coercive force H_c and magnetostriction λ in the [100] direction and increased them in the other crystallographic directions.

1. Introduction

Magnetic properties of FeSi alloys are adversely affected by a number of impurities including carbon [1]. Irrespective of the method of melting, the carbon content in molten steel of this type (0.03–0.07%) is much higher than the permissible carbon concentration ($\leq 0.005\%$) in the finished material [1, 2]. This is why the problem of solid state decarburization of FeSi alloys is so important. Decarburization treatment is carried out generally at 1073–1173 K in a moist nitrogen-hydrogen atmosphere. Existing data [3–6], concerned mainly with effects of time and temperature of annealing and composition of the atmosphere on decarburization of Fe—3%Si alloys, indicate that irrespective of the atmosphere the rate of decarburization is initially high and then drops to a constant value. This effect is probably connected with formation of a compact oxide layer on the surface of the plates. Examinations of such layers on polycrystalline specimens of FeSi alloy [4, 7–9] show that depending on the dew point of the atmosphere and temperature of annealing the products of oxidation consist of amorphous silica, fayalite (2FeO·SiO₂) or ferrous oxide. In order to obtain satisfactory final magnetic properties the treatment should reduce the carbon content without oxidation of iron. This can be done if decarburization is carried

* Address: Instytut Fizyki, Politechnika Częstochowska, Deglera 35, 42-200 Częstochowa, Poland.

out in an atmosphere with a dew point not exceeding 333 K [4, 7, 8]. Under such conditions, selective oxidation of grain surface takes place (Fig. 1) with the formation of an amorphous silica layer. It should be noted that the morphology of oxidation products is different in each grain; this is presumably related to the crystallographic orientation of grain surfaces. Hitherto structure and composition of the oxide layer has been investigated on the surface of specimens only. It seems that the investigation of the distribution of elements in the oxide layer and alloy matrix could advance our knowledge of the kinetics of decarburization.

Surface layer of oxides influences magnetic properties of grain oriented polycrystalline Fe-3%Si specimens [8, 10] by reducing magnetostriction and losses in the direction of rolling and by increasing these values in other directions. Another work [11] using single crystal FeSi alloy with (110) orientation of the surface confirmed that the surface oxide layer did increase the magnetic anisotropy of coercive force, magnetostriction and losses in comparison with specimens without such layer. It should be noted, however, that neither of the [10, 11] works was concerned with structure and chemical composition of the oxide layer and its influence on the magnetic properties of FeSi alloy.

This paper is concerned with: (i) checking whether the structure of surface silica layer was affected by the crystallographic orientation of the matrix; (ii) checking whether during decarburization there was any redistribution of iron and silicon in the oxide layer or in the adjacent alloy matrix; (iii) evaluation of the effect of surface silica layer on the anisotropy of coercive force and magnetostriction.

2. Experimental procedure

The material was in the form of Fe-3.25%Si single crystals with (110) surface orientation, 0.35 mm thickness and initial composition (%): C = 0.05; Si = 3.25; Mn = 0.14; P = 0.015; Cr = 0.012; Ni = 0.02; Cu = 0.017; total Al = 0.008; S = 0.008; Ti = 0.01. The specimens were decarburized in moist hydrogen (dew point 313 K) at 1123 K 1 and 5 min. Carbon content of the alloy was determined by the conductometric method using Wösthoff apparatus. In order to obtain as complete as possible data on the structure of the oxide layer the examinations included optical and electron microscopy of both surface and cross-sections of the specimens. Composition of the oxidation products was determined by means of the X-ray method. X-ray microanalysis was used to determine the distributions of iron and silicon along a line running at a right angle from the matrix to the zone of surface oxidation. Distribution of carbon along this line was not determined owing to the high detection limit of light elements in the available instrument. Magnetic measurements were carried out on 18 mm diameter single crystal disks covered with oxide film (average thickness 4 μm) formed during 5 min. decarburization treatment (final carbon concentration 0.003%) or with the film removed by etching in 30% aq. HCl. Coercive force H_c was determined at various angles to the [001] direction by means of a Förster apparatus. Magnetostriction was determined by the strain gauge method [12]. Strain gauges were cemented within 0.5° to the three principal crystallographic directions [001], [110], $[\bar{1}11]$; the magnetizing field was always parallel to the [001] direction.

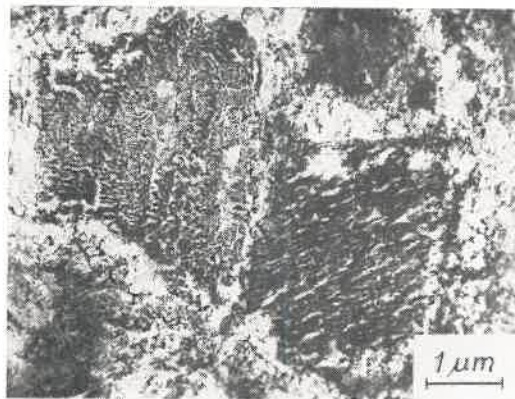


Fig. 1. Oxide layer on the surface of a polycrystalline specimen of Fe-3.25%Si with (110)[001] texture after 3 min. annealing at 1123 K in a moist hydrogen atmosphere (dew point 293 K)

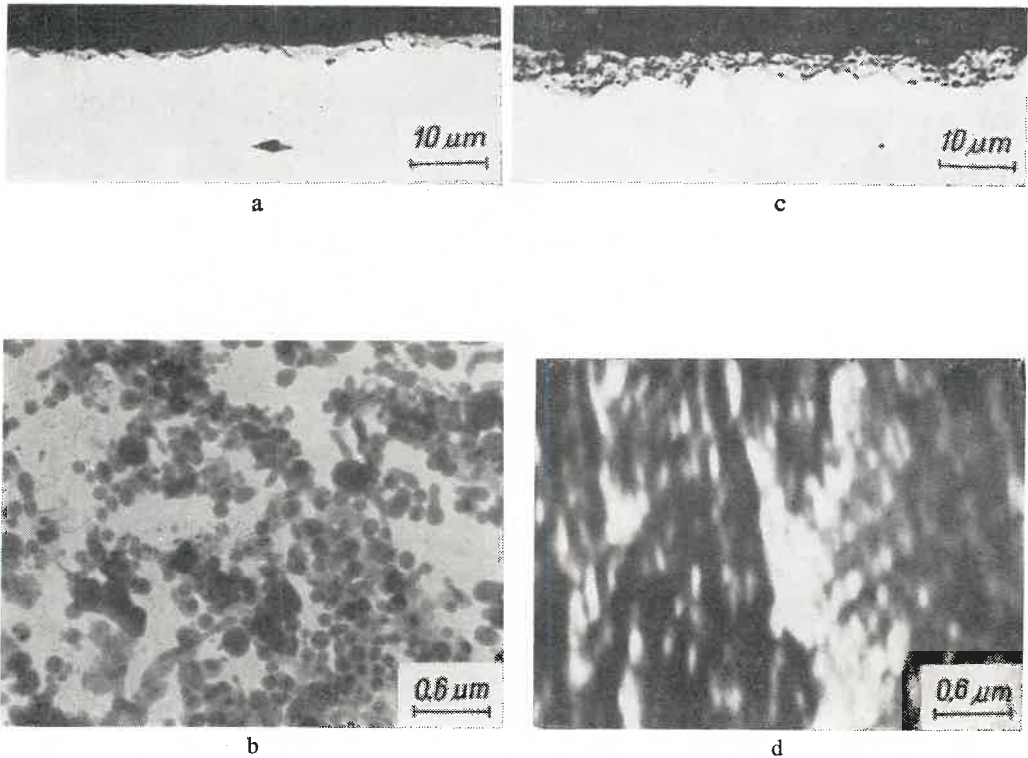


Fig. 2. Structure of the oxide layer on the (110) surface of Fe-3.25%Si single crystal annealed at 1123 K in a moist hydrogen atmosphere (dew point 313 K) for 1 min.—(a, b) and 5 min.—(c, d); a, c—subsurface regions, b, d—oxidized surfaces

3. Results, discussion and conclusions

Metallographic examinations of the annealed specimens showed that the thickness of the oxide film was strongly dependent on the duration of annealing (Fig. 2a, c). By X-ray methods it was found that oxidation products formed in annealing atmospheres with dew points as used in this study, consisted principally of amorphous silica; this was in agreement with earlier investigations [4, 7-9]. In the initial stages of oxidation SiO_2 had the form of fine round particles distributed randomly on the surface of the specimens as can be seen in electron micrographs of extraction replicas (Fig. 2b). During more prolonged annealing the particles increased in number and grew in the [001] direction (Fig. 2d). As a result, after 3-5 min. annealing, the specimens were covered with a compact layer of elongated SiO_2 particles oriented in the [001] direction.

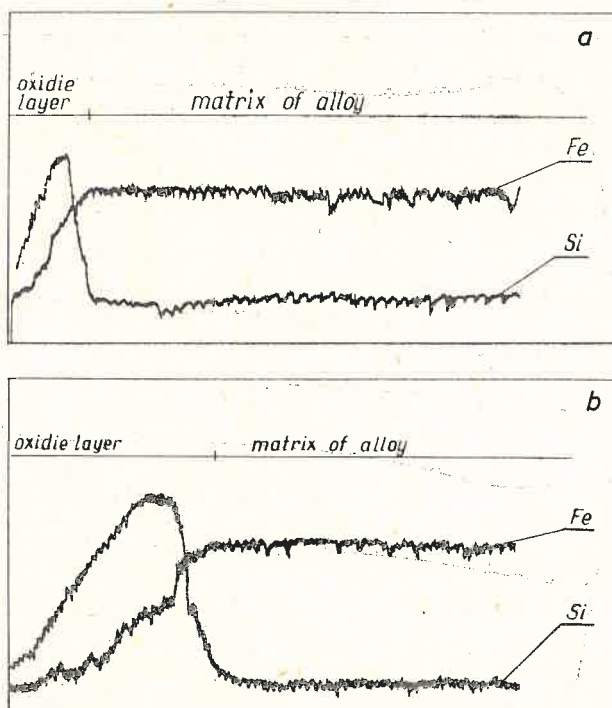


Fig. 3. Distribution of silicon and iron along a line perpendicular to the surface oxide layer on a Fe-3.25%Si single crystal specimen annealed for 1 min. — (a) and 5 min. — (b)

By qualitative point analysis along a line perpendicular to the surface of the specimens it was found that the concentration of silicon in the oxide layer increased toward the surface whereas that of iron decreased (Fig. 3a, b). It should be noted that these differences in the distribution of silicon and iron were already apparent after short annealing (1 min) and remained more or less stable during further treatment (Fig. 3a). Such redistribution of silicon contradicts the earlier suggestions [6] that the first stages of decarburization involve the oxidation of silicon on the surface producing favourable conditions for the diffusion

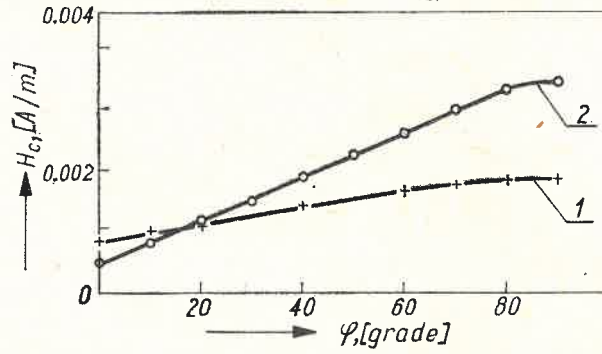


Fig. 4. Anisotropy of the coercive force H_c in Fe—3.25%Si single crystal with (110) surface orientation: 1 — without oxide layer, 2 — with oxide layer

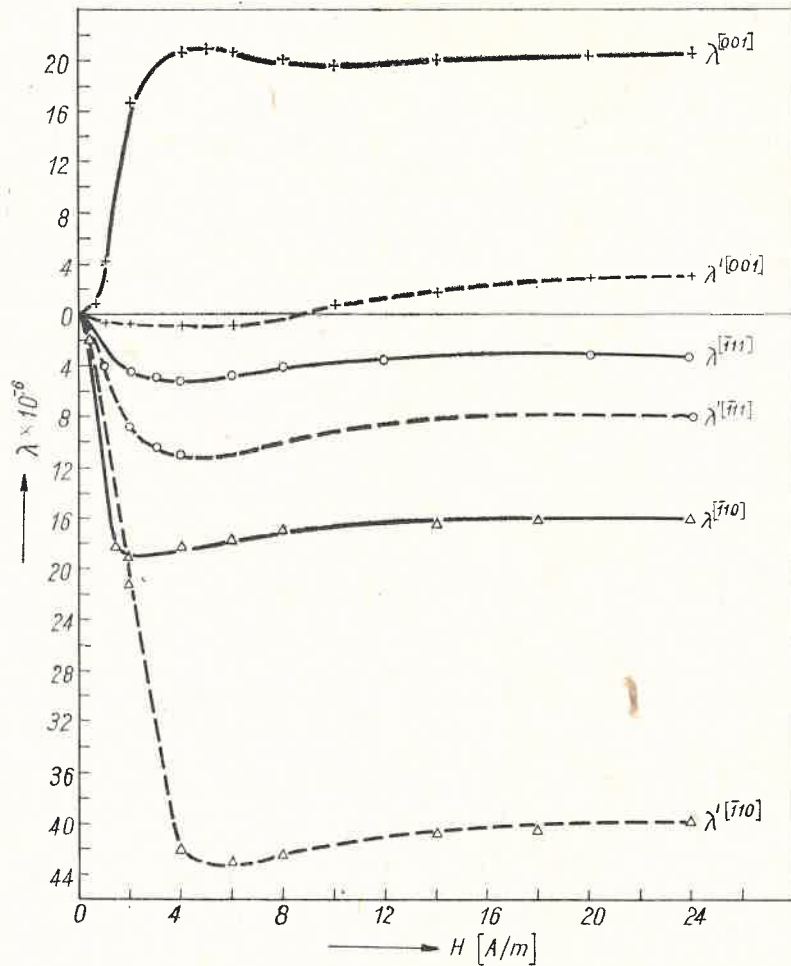


Fig. 5. Magnetostriction $\lambda^{[hkl]}$ ($[hkl] = [100], [\bar{1}10], [\bar{1}\bar{1}1]$) in a Fe-3.25% Si single crystal vs. strength of magnetic field parallel to [100] direction for specimens with ($\lambda'^{[hkl]}$) and without ($\lambda^{[hkl]}$) oxide layer

of carbon from high-silicon to low-silicon zones. It seems that in order to improve our understanding of the kinetics of decarburization it is necessary to include in future investigations examination of distribution of other elements which could influence diffusion of carbon and also to determine the distribution of carbon in the alloy.

The results show once more that the rate of decarburization of FeSi alloy is highest in the initial stages ($C = 0.009\%$ after 1 min. and $C = 0.003\%$ after 5 min.) when the surface of the specimens is still not covered with compact layer of SiO_2 . It seems that decarburization is controlled by two processes: 1 diffusion of carbon from deeper layers to the surface, and 2 removal of carbon from the surface by interaction with the oxidizing atmosphere. In the latter process chemical reactions seem to play an important role.

Surface silica layers exert a significant influence on the anisotropy of the coercive force H_c (Fig. 4). For angles φ between the direction of the applied magnetic field and the [001] crystallographic direction not exceeding 17° , the coercive force was reduced by the presence of such an oxide layer. On the other hand, the coercive force grew with increasing φ .

In Fig. 5, magnetostriction for the principal crystallographic directions [001], $[\bar{1}10]$ and $[\bar{1}\bar{1}1]$ was plotted vs. external magnetic field parallel to the [001] direction. It can be seen that the oxide layers decreased to a large extent magnetostriction in the [001] direction (at 20 A/m the decrease was approximately tenfold; up to 8 A/m magnetostriction was small and negative) and increased it the other two directions.

This increase of the anisotropy of coercive force and magnetostriction by the action of surface oxide films is evidence of stronger magnetic anisotropy and facilitation of magnetization in the [001] direction.

REFERENCES

- [1] M. N. Nekrasova, *Fiz. Met. Metalloved.* **28**, 190 (1963).
- [2] R. Laska, *Bänder Bleche Rohre* **12**, 11 (1972).
- [3] A. Mayer, *Stahl u. Eisen* **83**, 1169 (1963).
- [4] T. Ymazaki, *Trans. ISIJ* **9**, 66 (1969).
- [5] I. A. Tomilin, V. G. Borisenko, A. G. Petrenko, L. A. Shvartsman, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **34**, 329 (1970).
- [6] A. I. Rogov, I. A. Tomilin, L. A. Shvartsman, *Izv. Akad. SSSR, Metally* **3**, 182 (1975).
- [7] A. Židek, Z. Huliciova, *Hutnicke Listy* **27**, 424 (1972).
- [8] S. Szymura, B. Wysłocki, A. Maciosowski, *Prace Inst. Hutniczych* **25**, 253 (1973) (in Polish).
- [9] Z. Huliciova, A. Židek, *Hutnicke Listy* **31**, 583 (1976).
- [10] E. A. Prokopchenko, F. D. Miroshnichenko, I. K. Krutsilo, V. F. Myshlaev, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **34**, 276 (1970).
- [11] E. A. Prokopchenko, D. H. Zmetko, S. K. Ivanchenko, A. B. Moroshkin, *Izv. VUZ Chern. Met.* **7**, 114 (1971).
- [12] H. Lampa, S. Szymura, B. Wysłocki, *Prace Inst. Hutniczych* **23**, 263 (1971) (in Polish).