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THE EFFECT OF CATHODE HYDROGEN ON RELAXATION PROCESSES IN SILICON STEEL

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Metals, including iron, form interstitial solid solutions as well as substitutional solutions. The interstitial sites can be occupied only by elements which have small atomic diameters, such as hydrogen, boron, nitrogen, carbon and oxygen. Owing to the appreciable mobility of these atoms, even at relatively low temperatures, they bear a large effect on the physical properties of metals.

The elementary jumps of single atoms, clusters and atoms interacting with the impurity atoms forming the substitutional solution or with lattice imperfections, lead to the appearance of mechanical or magnetic after-effects, also known as relaxation effects. After-effects attributed to hydrogen have been found in samples of iron and its alloys of body-centered cubic structure in three temperature ranges: *1)* near 50°K (relaxation I), *2)* intermediate range above 100°K (relaxation II), and *3)* high-temperature range over 1000°K (relaxation III, for a frequency of one cycle per second).

Hitherto the largest number of studies has been devoted to relaxation II [1, 2, 3, 6, 7, 8, 9, 10]. The internal friction method and bridge measurements of magnetic losses were the techniques used. The results of these studies are arranged in Table I.

It is commonly presumed that the relaxation in the second range is due to dislocations interacting with interstitial hydrogen atoms [1, 2, 3] and is the counterpart of the Köster relaxation appearing near 200°C at a measuring frequency $f = 1$ cps which arises in plastically deformed α-iron samples containing carbon or nitrogen [4].

Studies on the effect of cathode hydrogen on magnetic properties, primarily dealing with the coercive force, have shown that this element bears more weight on the change of this quantity in α-Fe-Si alloys than in pure iron [5].

For this reason we have undertaken studies on the effect of cathode hydrogen on the magnetic after-effects in this alloy.

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TABLE I

Compilation of results concerning relaxation H II

Method	Samples	Measuring frequency[1] f	Peak temperature[2] °K	Activation energy cal/mol	Peak temperature °K at 1 kcps	Hydrogenation method	Ref.
friction	Fe		130	—	—	molecular hydrogen under high pressure	[1]
friction	Fe	80 kcps	180	—	—	electrolytic 0.02—0.2 A/cm^2	[2]
friction	Fe very pure	80 kcps	145 220	2000	—	electrolytic, H_2SO_4 with $NaASO_2$, 0.02—0.2 A/cm^2	[3]
friction	Fe electrolytic and Fe+ 0,2% Mo	2-3 cps	100	—	—	electrolytic or at 600°C and 60 atm. for 4 hrs	[6]
friction	techn. steel 1020	20 cps	100	6000	120	electrolytic or 500°C and 50 atm.+2 hrs at 50 atm. and 600°C	[7]
friction	pure Fe	0.6 — 0.9 cps	105 — 120	—	—	electrolytic 4% H_2SO_4 with CS_2	[8]
Wilde bridge	Fe-Si 2.5% and pure Fe	8 cps— 5 kcps	195	7500	209	samples relieved in moist H_2 for 3.5 hrs at 670 and 1050°C	[9]
Wilde bridge	Fe-Si-C	60 cps— 10 kcps	203	—	203	samples relieved in H_2 observed as side effect	[10]

[1] The frequency of pendulum virbrations or the frequency of the magnetizing current.

[2] The temperature at which the peak of losses appears (at the measuring) frequency.

Measuring equipment

The studies on the effect of hydrogen and other factors on the magnetic after-effect were performed on a measuring arrangement whose basic element was a Wilde a. c. bridge [11]. It enables making measurements of the inductance of the examined samples with an accuracy of up to ± 0.2 per cent and the tangent of the angle of losses with an accuracy of up to ± 0.3 per cent. A low-temperature thermostat made it possible to stabilize the temperature with an accuracy of ± 0.05°C. Sample demagnetization was done with the use of an original electronic device described in Ref. [12].

The samples

The studies involved a number of samples made from silicon steel strip containing 3.2 per cent Si, prepared in the Magnetic Materials Department of the Institute of Iron Metallurgy, Gliwice.

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The strip supplied by the manufacturer, 30 mm wide and 0.35 mm thick, was cut into two 15 mm strips and then looped into toroids of the dimensions: auter diameter 40 mm and inner diameter 25 mm. The individual layers of metal were insulated by powdered magnesium oxide. In order to relieve the samples of stresses they were annealed at 950°C for twelve hours and then cooled slowly with the furnace. Cutting the strip into the two parts, each 15 mm wide, ensured an identical chemical composition of the samples hydrogenated and submitted to cold working.

Hydrogenation was executed by electrolytic polarization in 1 n sulpheric acid with 0.2 g/liter of thiocarbanilide added. For this purpose the samples were placed in a vessel with the acid; the samples were formed into spirals by stretching the inner windings of the toroid. The mean polarization current was 2 mA/cm^2. Platinum wire was used as the anode.

A test showed that the stretching of the toroid does not bear any effect on the shape of the curves $\tan \delta = f(T)$.

The plastic working consisted in rewinding the previously de-stressed samples in the opposite direction. This ensured plastic deformation of the order of 2 per cent for the samples of the dimensions stated.

Samples prepared in this way were wound, set in a thermostat, ready for measurements.

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Results of measurements

Measurements were initiated at room temperature, and then the sample was cooled by several degrees, after which the temperature was stabilized and the readings of the bridge were taken. For it was found that after a sudden cooling of the stress-relieved sample to the lowest measuring temperature (−180°C), there appear on the curve of the tangent of the angle of losses *versus* temperature some relaxation peaks which arise because of stresses introduced during hardening [11].

Figure 1 shows the curves of the temperature-dependence of the angle of losses for an annealed sample, taken at three frequencies of the magnetizing field. As it is seen, they are monotonic.

Figure 2 presents the same dependence for a sample hydrogenated for 12 hours at a current density of 2 mA/cm^2. We see that the hydrogenation caused the appearance of relaxation peaks at the temperatures of 152°K for 220 cps, 156°K for 320 cps and 160°K for 520 cps. Utilizing these data the parameters of the Arrhenius law have been determined, getting $Q = 5300 \pm 200$ cal/mole and the pre-exponential factor $\theta_0 = 2 \times 10^{-11}$ sec.

It is known that during polarization the hydrogen causes the material to be deformed plastically. Therefore, a test was made to see whether or not the relaxation peaks obtained for the hydrogenated samples are due to dislocations which formed during this process.

Figure 3 shows the curves of the tangent of the angle of losses taken for the sample submitted to cold working. We see that there are maxima lying near the same temperatures for the given frequencies (160°K for 220 cps, 167°K for 320 cps and 170°K for 520 cps). From the position of the peaks we obtained $Q = 5400 \pm 200$ cal/mole and $\theta_0 = 1.3 \times 10^{-11}$ sec.

During the performance of this work there arose the supposition that the relaxation found in the silicon iron samples hydrogenated electrolytically or sumbitted to cold working

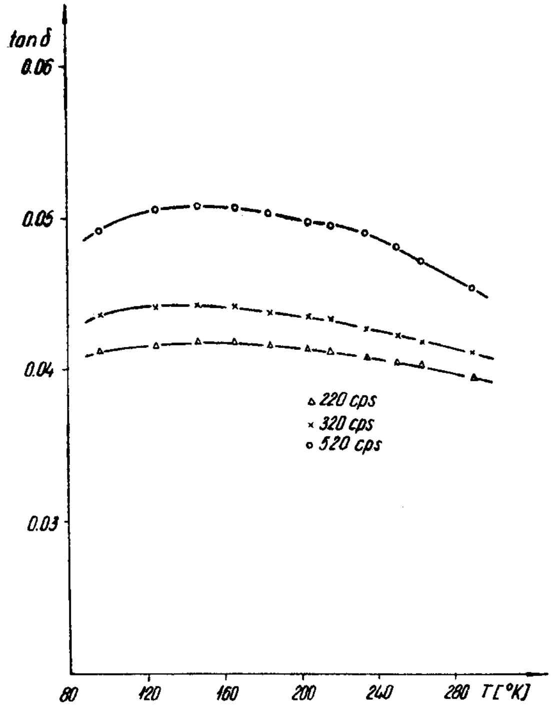

Fig. 1. tan $\delta = f(T)$ for stress-relieved sample

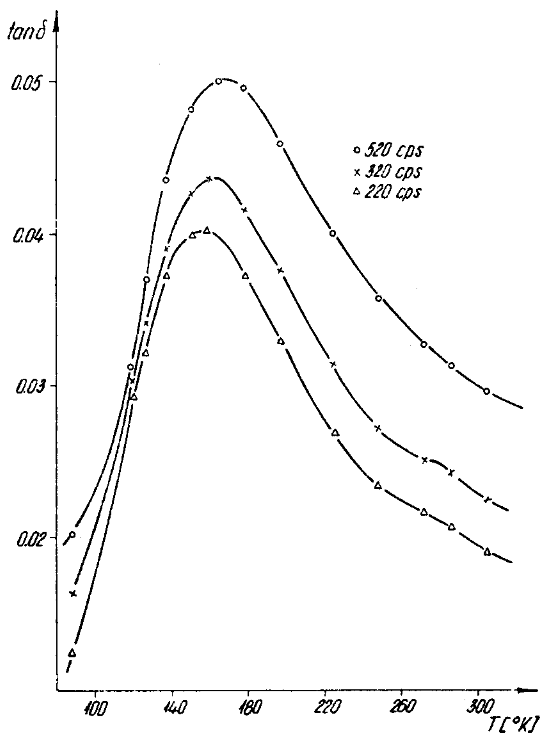

Fig. 2. tan $\delta = f(T)$ for hydrogenated sample

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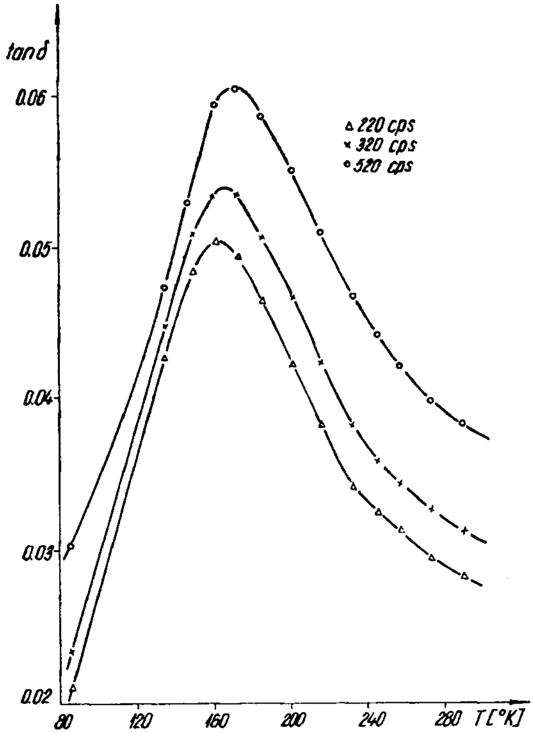

Fig. 3. tan $\delta = f(T)$ for deformed sample

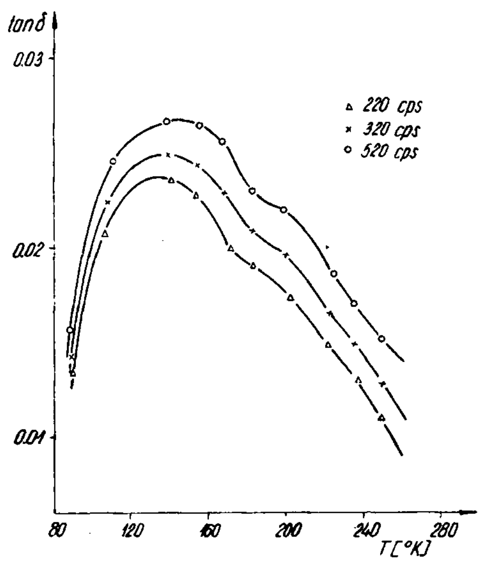

Fig. 4. tan $\delta = f(T)$ for samples treated according to Hasiguti

is identical to the relaxation of Hasiguti and co-workers. In the work [13] the iron sample was submitted to approx. 10 per cent cold working and within 15 minutes measurements were begun from the lowest temperature, *i. e.* the temperature of liquid nitrogen.

In connection with this, we repeated this procedure for the sample of α Fe–Si used in this work, which after being relieved of stress, was submitted to 1 per cent plastic working. The lowest temperature was reached after 25 minutes. In Fig. 4 we see that the curves $\tan\,\delta = f(T)$ obtained in this way also have distinct maxima which, however, are much broader than those in Figs 1 and 2. Apart from the main relaxation peak, each curve has an additional inflection lying 30°K higher. Estimates of the parameters of the Arrhenius law are $Q = 6300$ cal/mole and $\theta_0 = 10^{-13}$ sec.

All of the observed relaxation curves are very stable. Ageing at room temperature (up to two weeks) has little effect on the height of their maxima.

Discussion

It has been shown by this work that in stress-relieved α Fe–Si samples the curves of the tangent of the angle of losses are monotonic in the range from 110 to at least 210°K. At these temperatures the shape of the $\tan\,\delta = f(T)$ curves is quite independent of the frequency of the magnetizing current.

Samples previously saturated with hydrogen or deformed plastically to the order of 2 per cent, which during the performance of the measurements were cooled slowly from room temperature to that of liquid air, demonstrated very distinct maxima of the tangent of the angle of losses (for 320 cps: hydrogen treatment 156°K and deformation 167°K). Their position shifts towards the higher temperatures with increasing frequencies, which implies that the processes responsible for the observed losses have a relaxation character. These peaks are very stable. Although the maxima of the curves for a given frequency appear at somewhat different temperatures, nonetheless the parameters of the Arrhenius law are very close.

On the other hand, the curves obtained for samples submitted to Hasiguti's treatment exhibit a broad pek at 136°K and an inflection in the vicinity of 170°K (320 cps). It seems that in this case we are dealing with a whole series of relaxation processes of similar values of Q and θ_0.

The results presented here suggest that in the examined range of temperatures two relaxations can arise in α Fe–Si: relaxation due to a deformation caused directly or indirectly by hydrogenation, and relaxation of the type of Hasiguti occurring at much lower temperatures. On the other hand, this work did not reveal the relaxation corresponding to the process II observed in samples of pure iron saturated with hydrogen.

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