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KFKI-1977-55

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*Hungarian Academy of Sciences*

**CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS**

**BUDAPEST**

2017

KFKI-1977-55

# DECARBURIZATION RATE IN CERTAIN SOFT MAGNETIC ALLOYS

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*Paper presented at the Conference*
*SOFT MAGNETIC MATERIALS 2*
*/Cardiff, 9-11 April, 1975/*

4 K.

HU ISSN 0368 5330
*ISBN 963 371 293 9*

## ABSTRACT

Some results on the rate measurements during decarburization of pure iron, iron-manganese, iron-silicon and iron-aluminium alloys are reported. The rate of decarburization of iron-manganese and iron-aluminium was found to be similar to that of pure iron; in the iron-silicon alloy a strong decrease in the rate of decarburization was observed. The heats of activation for studied reactions have also been calculated for pure iron.

## АННОТАЦИЯ

Описываются некоторые результаты экспериментов по обезуглероживанию чистово железа и сплавов железа с марганцем, железа с алюминием и железа с кремнием. Скорость обезуглероживания железа с алюминием и железа с марганцем приблизительно равнялась со скоростью чистово железа. В случае сплава железа с кремнием мы наблюдаем значительное уменьщение скорости. Для чистого железа были определены и энергии активации исследываемых реакций.

## KIVONAT

Tiszta vason, vas-mangán, vas-aluminium és vas-szilicium ötvözeteken végzett dekarbonizálási kisérletek néhány eredményét ismertetjük. A dekarbonizálás sebessége a vas-aluminium és vas-mangán ötvözeten közel azonos volt, mint a tiszta vason; a vas-szilicium ötvözeten jelentős sebességcsökkenést mértünk. A vizsgált reakciók aktiválási energiáit is meghatároztuk tiszta vason.

## INTRODUCTION

Interstitial impurities strongly influence the magnetic properties of low-carbon steels and other soft magnetic alloys. A usual method of decreasing the carbon and nitrogen content is to anneal the solid metal in controlled gas atmosphere. Details of the surface reaction including mass transport in the gas and in the solid phase, as well as the rate and the equilibrium of the reaction should be understood to enable the processess to be optimized.

The rate of carburization and decarburization has been investigated by several authors for the reaction

$$CH_4 \rightleftharpoons [C]_{\alpha - Fe} + 2\,H_2 \qquad /1/$$

both in the austenitic [1] and ferritic [2-4] region. The purpose of our investigation was to study the influence of certain important alloying elements /mainly manganese and silicon/ on the rate of the reaction /1/. The reaction rate was measured in methane-hydrogen mixtures at 7oo-8oo °C by the resistivity relaxation method. Under the experimental conditions used the surface reaction was the rate determining step. The method is useful for the investigation of surface reactions on alloys, too. The alloying element can have various influences on the rate measurements, the most important being:

1/ The concentration of the dissolved carbon may be different in the alloy compared with that in the pure iron - at the same methane to hydrogen ratio /the alloying element influences the solubility limit of carbon in the ferrite phase/ [5];

2/ The specific resistivity increment of dissolved carbon can be changed;

3/ The alloying element considerably influences the properties of the metal surface.

The first effect can be taken into consideration by determining the equilibrium methane to hydrogen ratio /$r = p_{CH_4}/p_{H_2}^2$, where $p_{CH_4}$ and $p_{H_2}$ are the partial pressures of methane and hydrogen, respectively/ on the phase boundary of the ferrite region. If the carbon content is known at the phase boundary it can be calculated for different experiments since it is proportional to r [6].

The second effect, the change in specific resistivity increment due to the carbon in different iron-based alloys, can be determined experimentally.

The third effect is expected to influence the surface reaction most strongly. The concentration of the alloying element is generally different inside the sample to that on the surface. The difference of the bulk and surface concentrations / $\Gamma$ / is [7]:

$$\Gamma = - \frac{x}{RT} \frac{\partial \gamma}{\partial x}$$

where x is the bulk concentration of the alloying element, $\partial \gamma / \partial x$ the change in the surface free energy caused by a unit change in the bulk concentration of alloying element, R the universal gas constant and T is the absolute temperature. $\partial \gamma / \partial x$ is usually negative which means an enrichment of alloying element at the surface.

The purity of the gas mixture is obviously very important in experiments traces of oxygen or water vapour cause undesirable reactions such as:

$$\begin{aligned} C + 1/2\, O_2 &= CO \\ 2\, CO &= C + CO_2 \qquad /2/ \\ CO + H_2 &= C + H_2O \end{aligned}$$

## EXPERIMENTAL

The change in the resistivity of 6o-8o cm long 1 cm wide lo-15 $\mu$ thick foils was measured by a high sensitivity Wheatstone bridge during the heat treatments in hydrogen and then in hydrogen-methane stream. The reference resistor was an iron wire having the same length and cross-section as the sample. It was sealed into a quartz tube isolating it from the gas atmosphere of the furnace while it was in the same temperature zone as the sample. Thus, any error caused by the change in the temperature of the furnace can be eliminated, the measured resistivity change is due to the sample only. The current passing through the foil was about loo mA.

Tha samples were prepared from a high purity electrolyte iron by induction melting and cold rolling. Thin foils were made from a high purity iron, an iron-manganese alloy /with o.33 weight percent manganese/ an iron-aluminium alloy /with l.o weight percent aluminium/ and an iron-silicon alloy /with l.o weight percent silicon/.

The gas mixture leaving the reaction tube was analysed for oxygen content by an ANACON oxygen trace monitor. The oxygen content of the gas was usually about 4o ppm, though in some experiments it was about 15 ppm.

A typical experimental resistance versus time curve is shown in Fig. 1. The rate constants of the reaction /1/ can be determined from the derivation of this curve. For details of the application of the resistivity relaxation method we refer to the literature [3].

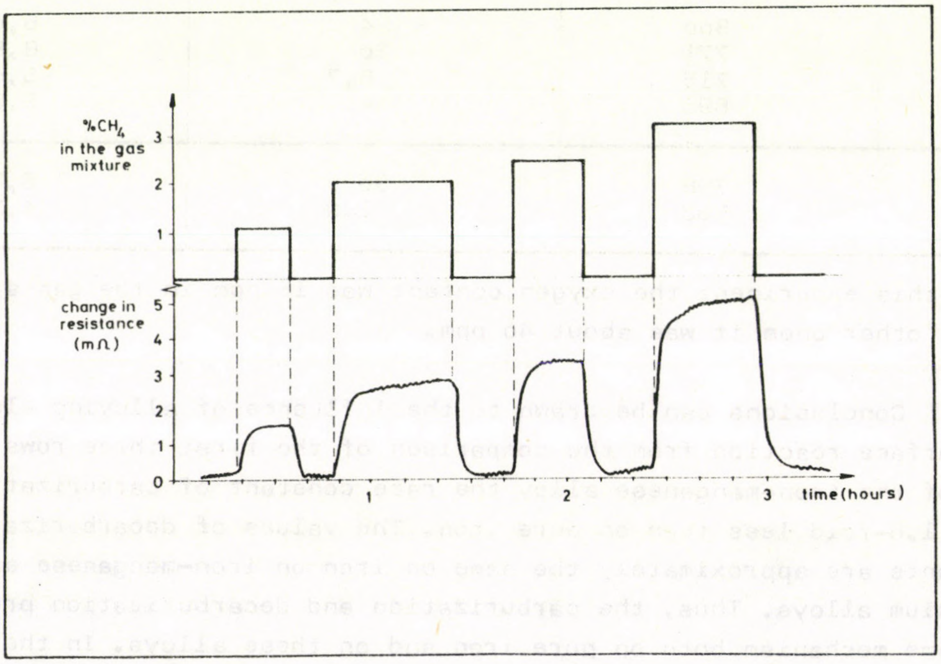

Fig. 1. Change in resistance of 12 μ iron foils at 8oo °C in different methane-hydrogen mixtures.

## RESULTS

The results of measurements are shown in Table 1.

Table 1.

| Sample | Temperature | Rate constant | |
|---|---|---|---|
| | | Carburization / $\overrightarrow{k}$ / | Decarburization / $\overleftarrow{k}$ / |
| | $^{o}C$ | mol $cm^{-2}s^{-1}atm^{-1/2}.1o^{9}$ | $cm\ s^{-1}atm^{-3/2}.1o^{6}$ |
| Fe-Mn | 774<br>7oo | 18<br>2,7 | 6,9<br>6,1 |
| Fe-Si | 773 | - | o,58 |
| Fe-Al | 81o | - | 8,9 |
| Fe | 8oo<br>771<br>715<br>695 | 34<br>3o<br>6,7<br>- | 6,o<br>8,8<br>5,o<br>5,6 |
| Fe$^{x}$ | 798<br>693 | 3o<br>1,9 | 5,5<br>4,3 |

x/ In this experiment the oxygen content was 15 ppm in the gas stream, in the other ones it was about 4o ppm.

Conclusions can be drawn to the influence of alloying elements on the surface reaction from the comparison of the first three rows. In the case of the iron-manganese alloy the rate constant of carburization is about 1.6-fold less than on pure iron. The values of decarburization rate constants are approximately the same on iron on iron-manganese and iron-aluminium alloys. Thus, the carburization and decarburization probably have the same mechanism both on pure iron and on these alloys. In the case of iron-silicon alloy we have found a sharp difference when compared with pure iron; the rate of decarburization is only one tenth of that for pure iron. The strong decrease in the rate is probably due to the enrichment of alloying element at the surface mentioned above and to a slight surface oxidation. /A similar problem has been investigated by Fast and Bruning [8] ./

An other influence of the oxygen content in the gas is also shown in the last rows of the Table 1. and in Fig.2. The rate of carburization and decarburization decreased in the purer gas in a similar degree than in the case of the iron-manganese alloy presumably due to absence of reactions /2/.

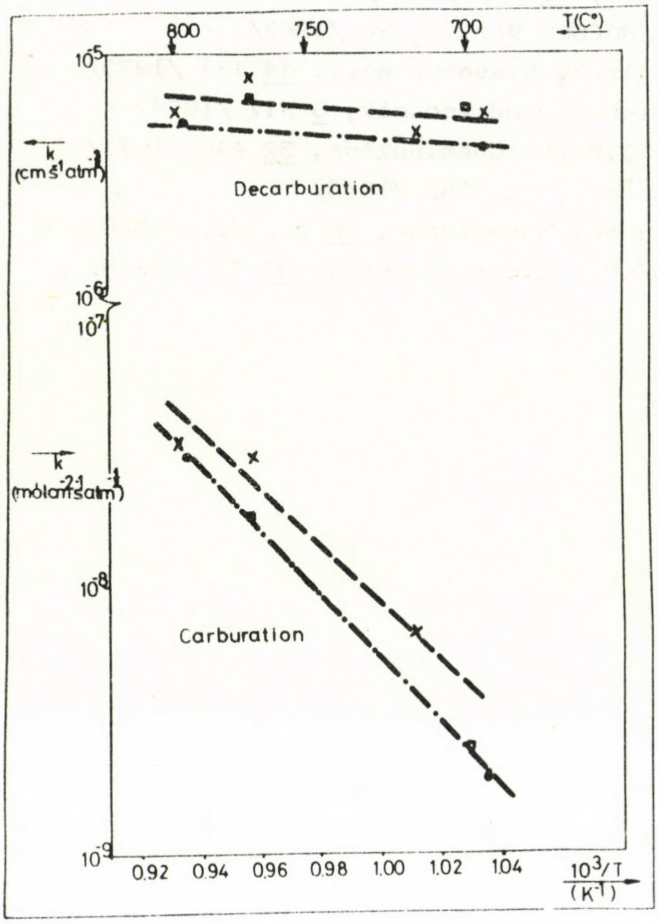

Fig. 2. Temperature dependence of rate constants of carburization and decarburization

o Fe, 15 ppm $O_2$
x Fe, 4o ppm $O_2$
□ Fe-Mn, 4o ppm $O_2$

The rate constants calculated from these measurements are near to results of other investigations [3] . We obtained for the activation energy of reaction /1/ the following values:

$Q_{decarb.}$ = 9.2 kcal/mol and $Q_{carb.}$ = 5o kcal/mol.

Finally, an observation on the change in the specific resistivity increment of carbon in the iron-manganese alloy is mentioned, namely: that in an experiment at 695 °C the value of this increment was twice as great /1.6 μohm cm/ at% C/ in the case of the iron manganese alloy as that in the pure iron.

ACKNOWLEDGEMENT

This work was sponsored by Csepel Metalworks, Budapest.

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Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Vasvári Béla
Szakmai lektor: Krén Emil
Nyelvi lektor: Harvey Shenker
Példányszám: 320 Törzsszám: 1977-690
Készült a KFKI sokszorositó üzemében
Budapest, 1977. julius hó