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OF  $Fe_{1-x}B_x$  METALLIC GLASSES

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ELECTROCHEMICAL CORROSION OF  $Fe_{1-x}B_x$  METALLIC GLASSES

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#### АННОТАЦИЯ

Потенциостатическим методом исследовалась электрохимическая коррозия металлических стекол Fe-B, полученных быстрым охлаждением расплава. Ток коррозии определяется по кривым анодной и катодной поляризации. Найдено, что ток коррозии зависит как от содержания бора, так и от скорости охлаждения. На обеих сторонах образцов измерялась отличающаяся скорость коррозии. Изучалось также влияние структурной релаксации и кристаллизации на скорость коррозии.

#### KIVONAT

Olvadékok gyorsűtésével előállított Fe-B féművegek elektrokémiai korrózióját vizsgáltuk potenciosztatikus módszerrel. A korróziós áram, amit anód- és katódpolarizációs görbék segítségével mértünk, a bór-tartalomtól és az előállítás körülményeitől egyaránt függ. Egymástól eltérő korróziós áramot mértünk a minták két ellentétes oldalán is. Relaxáló és kristályosító hőkezelések hatására a korrózió sebessége növekszik.



## ABSTRACT

Electrochemical corrosion of  $\text{Fe}_{100-x}\text{B}_x$  / $x=11.7-21.6$ / metallic glasses was studied by the potentiostatic method. The corrosion current was determined from the anodic and cathodic polarization curves. It was found that the corrosion current varied with the quenching rate and was also influenced by the boron content in the range investigated. The rate of corrosion was also different on the two sides of the as-quenched specimens. The influence of structural relaxation and crystallization on the corrosion rate was also studied.

## INTRODUCTION

Despite of the relatively good corrosion quality of the metallic glasses which is the consequence of their chemically homogeneous single phase structure, the rate of corrosion of simple binary, iron based glasses is remarkable. Significant improvement is achievable by alloying with other transition metals /Cr, Mo, W/ but the mechanism of corrosion is not well understood at present [1, 2]. In this paper we deal with the following problems:

- How does the corrosion resistance of the as-quenched ribbons change with boron content;
- How corrosion resistance is influenced by quenching conditions;
- What is the connection between structural relaxation and corrosion behaviour?



Basic processes of corrosion

The spontaneous dissolution of metals takes place in the presence of electrochemically active materials /depolarizers such as oxygen or H<sup>+</sup> ions/. In the process of dissolution at least two parallel-coupled electrode processes are involved:



where M and M<sup>z+</sup> are the metal atoms and ions, respectively; O is depolarizer and R is the product arising from the depolarizer; k<sub>a</sub> and k<sub>k</sub> are the rate constants of the partial processes in question depending exponentially on the electrode potential. If the rates of reactions I and II do not change significantly during the experiment, the j current density of corrosion can be described as:

$$j = \frac{k_{a_1} - k_{k_1} c_{M^{z+}}}{1 + \frac{k_{k_1}}{zX_{M^{z+}}}} - \frac{k_{a_2} c_R - k_{k_2} c_O}{1 + \frac{k_{a_2}}{nX_R} + \frac{k_{k_2}}{nX_O}} \quad /1/$$

which is the equation of the polarization curve shown in Fig. 1. In this equation X<sub>R</sub> and X<sub>O</sub> are the "rate constants" of diffusion, c<sub>M</sub> and c<sub>O</sub> represent the concentration of the components. The rate of corrosion can be determined on the basis of polarization curves by the extrapolation to the corrosion potential (from the high polarization region), or by calculation using the modified form of Eq. 1 [3] and the slope of polarization curves as the "polarization resistance" R<sub>p</sub> (in the vicinity of zero-current state).



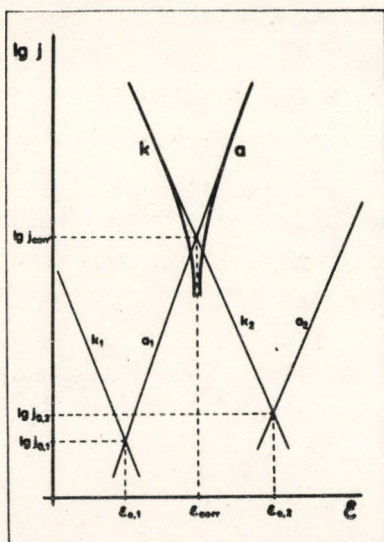


Fig. 1. Polarization curves for electrochemical corrosion of metals.  $\epsilon$ : electrode potential;  $j$ : current density;  $a_i, k_i$ : polarization curves for the partial processes;  $a, k$ : the resulting /anodic and cathodic/ polarization curves;  $j_{corr}$ : rate of corrosion.

EXPERIMENTAL

Sample preparation and the details of measurements has been described elsewhere [3-5]. The electrolytes used in this experiment can be divided into two categories: electrolytes containing "active" anions  $Cl^-$  and those containing "inactive" anions  $SO_4^{2-}, ClO_4^-$ . The shape of the polarization curves varies depending on the type of anion used /Fig. 2/.

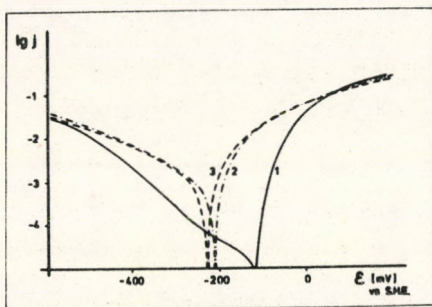


Fig. 2. Polarization curves plotted in different types of electrolyte solutions  
 /1/ 1 mol/dm<sup>3</sup> HCl  
 /2/ 1 mol/dm<sup>3</sup> HClO<sub>4</sub>  
 /3/ 0,5 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>

Curve 1 plotted in Fig. 2 was measured in the solution of 1 mol/dm<sup>3</sup> HCl, curves 2 and 3 were determined in the solutions of 1 mol/dm<sup>3</sup> HClO<sub>4</sub> and 0.5 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> solutions, respectively. It is clear that the shapes of the curves with inactive anions /2, 3 curves!/ are the same within the limits of experimental error.



RESULTS AND DISCUSSION

Corrosion rate and the content. The corrosion current decreases with increasing boron content as Table I shows.

Table I

Corrosion current for as-quenched ribbons with different boron content

Fe <sub>100-x</sub> B <sub>x</sub>	j <sub>corr</sub> x 10 <sup>5</sup> [A cm <sup>-2</sup> ]	
	x	from "extr"
11.7	5.9	5.7
16.6	2.7	2.9
21.6	1.6	1.6

where "extr" and "R<sub>p</sub>" indicates the two procedures described above

The role of processing parameters. Recently it was pointed out that several physical properties of the as-quenched ribbons change sensitively with the processing conditions [6-8]. The cooling rate and melt superheat are especially important among these parameters. In this paper their influence have been examined at constant boron-content /c<sub>B</sub> = 16.3 at%/. In agreement with other results [9] it was found that melt superheat has no measurable influence on the corrosion current /Table II/.

Table II

Corrosion current for Fe<sub>83.7</sub>B<sub>16.3</sub> eutectic amorphous alloys quenched from different melt temperatures

Fe <sub>83.7</sub> B <sub>16.3</sub>	j <sub>corr</sub> x 10 <sup>5</sup> [A cm <sup>-2</sup> ]	
	T [K]	from extr.
1550	1.8	1.8
1630	2.1	2.1
1720	1.8	1.7
1770	2.2	2.0



The plausible explanation for this independence is that the structure of the eutectic Fe-Bmelt does not change with temperature, or to a slight degree only. On the other hand, the corrosion current changes significantly with the cooling rate, i.e. the rotation speed of the disc and shows a minimum at about 6000 r.p.m. /Fig. 3/. The sudden increase in the range of the low cooling rate may be connected with the small amounts of crystalline embryos, however the presence of any crystalline phase was not detectable by the usual X-ray diffraction. The higher corrosion rate in the high speed range of the disc may be caused by

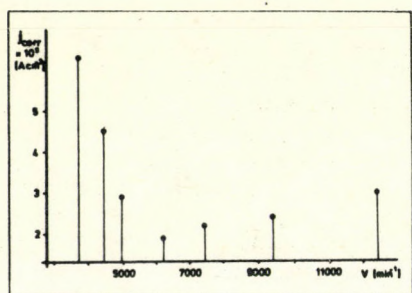


Fig. 3. Corrosion current versus the rotation speed of the disc /i.e. cooling rate/

the quenched-in stresses. Another possible interpretation is the postulation of extended defects or chemical inhomogenities though these have not, as yet, been specified in the literature. The presence of inhomogenities is supported by the fact that a change in the corrosion rate is especially pronounced if "inactive" anions of  $\text{ClO}_4^-$  are used. It is mentioned that the trend of the change in the corrosion rate shows similar characteristics as was found during the measurements of  $H_C$  /coercive force/ in these alloys. Such a trend was found by Luborsky [10] when investigating the connection between  $H_C$  and the thickness of ribbons. The polarization curves measured on opposite sides of the ribbons are also different /Fig. 4/. These results were obtained by masking of either

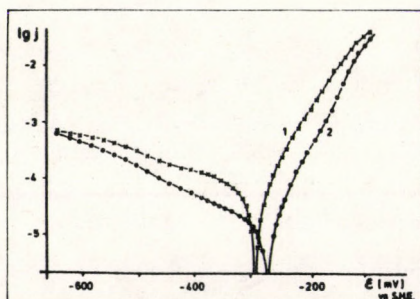


Fig. 4. Polarization curves plotted on the opposite side of specimens  
/1/ surface near quenching wheel  
/2/ free surface

the "top" or the "bottom" surface of the specimens before the measure-



ments. Fig. 4 shows, that mainly the hydrogen overvoltage is different on the opposite-side surfaces.

Change of corrosion rate after isothermal heat treatments

The role of isothermal heat treatment on the corrosion rate is summarized in the Table III.

Table III

Corrosion current measured after isothermal treatments

Fe <sub>83.4</sub> B <sub>16.6</sub>	TOP (SHINY) SURFACE		BOTTOM (DULL) SURFACE		
	Nº	$j_{\text{cor}(a,b)} \times 10^5$ (A cm <sup>-2</sup> )	$j_{\text{cor}(a,b)} \times 10^5$ (A cm <sup>-2</sup> )	$j_{\text{cor}(a,b)} \times 10^5$ (A cm <sup>-2</sup> )	$j_{\text{cor}(a,b)} \times 10^5$ (A cm <sup>-2</sup> )
	0	1,9	2,1	1,5	1,7
	1	3,0	3,1	1,9	2,0
	2	6,0	6,2	3,6	3,7
	3	8,9	9,3	5,6	5,7
	4	4,5	4,7	4,5	4,7

The rate of corrosion was also measured on both sides of the ribbon. Designations 0, 1, 2, 3 and 4 represent the thermal history of the specimens:

- 0 as-quenched ribbons
  - 1 after 470 K/3 h
  - 2 after 570 K/3 h
  - 3 after 670 K/3 h
  - 4 after 1070 K/1 h
- } "relaxed state"
- crystallized to Fe<sub>3</sub>B + αFe
- crystallized to Fe<sub>2</sub>B + αFe

The corrosion rate is higher at the top /shiny/ surface of the eutectic, as-quenched ribbons. This may be understood because of the lower cooling rate at this side. The rate of corrosion increases at this composition during the relaxation, and reaches its maximum in the state of crystallization to Fe<sub>3</sub>B + αFe.



After the heat treatment at 1070 K, when the equilibrium  $\text{Fe}_2\text{B} + \alpha\text{Fe}$  phase mixture is reached, the rate of corrosion decreases again however it remains about two-times higher than it was in the amorphous state. The difference in the corrosion rate measured at the opposite surfaces disappears after the heat treatment at high temperature. The fact, that corrosion current rapidly increases during the relaxation, even in the amorphous state, suggests that it must be connected with extended defects which do not disappear during the structural relaxation used. This conclusion is supported by the observation that the formation of holes took place during the low temperature, long-term aging processes in these ribbons [11].

#### SUMMARY

1. The electrochemical corrosion of  $\text{Fe}_{1-x}\text{B}_x$  as-quenched amorphous ribbons decreases with increasing boron content.
2. The corrosion current is changed by the cooling rate, but the influence of melt overheating was not detectable. The sudden increase of the corrosion current at low cooling rate may be the consequence of the small amounts of crystalline embryos, however the presence was not detectable by the usual X-ray diffraction scans.
3. The rate of corrosion for eutectic Fe-B ribbons was found to increase during the structural relaxation and during the crystallization to  $\text{Fe}_3\text{B} + \alpha\text{Fe}$ , but decreased again when the equilibrium  $\text{Fe}_2\text{B} + \alpha\text{Fe}$  structure is reached.
4. The corrosion currents were different at the opposite sides of the as-quenched ribbons.



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