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Influence of the Elemental Composition of the Amorphous Metallic Alloys Fe-Me-Si-B on the Catalytic Activity in the Red/Ox Reactions

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The catalytic activity of the series of the Fe-based amorphous metallic alloys (AMA) in decomposition processes of hydrogen peroxide is studied. Presence this alloys in the reaction system reduced of the activation energy in H_2O_2 decomposition by 2-3 times. Catalytic activity of amorphous alloys has been renewed by means of magnetization in the alternating magnetic field with frequency 50 hertz.

Key words: amorphous metallic alloy, H_2O_2, catalytic activity.

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Introduction

The nature of active centers on the surface of amorphous alloys is not completely studied but the concentration of active centers on the surface of amorphous alloys is higher than in crystalline ones. It was suggested that active centers in amorphous and crystalline catalizators are identical because a splitting of C-O bonding energy in both case equals to 100 kJ/moll being independent on the composition and thermodynamical state of alloy. Certainly the selection of any chemical composition of amorphous alloy and the condition of further activation process is the reason of active centers of high density [1-3].

Most probably that catalytic activity is connected with exited state of electron in atoms of amorphous matrix under influence of other kind neighbor atoms. Beside electron structure, the activity of amorphous catalizator depends also on microgeometry of surface [2,3].

Microregions of surface of some definite geometry and electron structure, different equilibrium complexes, which are formed at interaction of amorphous alloy with any component of chemical process and passivity films, appearing as a result of chemical and electrochemical processes can be considered as catalysis centers. Two mechanism of CO absorption (both as molecules and products of their dissociation) on amorphous alloy is the evidence of no equal valuation of their active centers.

Passivity films are of significant interest. Due to high chemical activity of amorphous alloy such films are formed in surroundings of mean chemical activity even. In amorphous alloys it is possible to vary the chemical composition and properties of passivating films. The search of amorphous alloys, which are able to catalyze the chemical processes due to their passivating protecting films, is one of the most promising for practical use. We suggest that some features of amorphous state of matter - high density of active centers, significantly different catalitical activity in comparison with corresponding crystalline materials, higher both specific surface square, viscosity and strength make possible to regulate the catalytic activity and corrosion resistivity.

Starting of crystallization process in amorphous alloy is accompanied by increase of structurally nonequilibrium centers in amorphous matrix, what is the one of reason in growing of their catalytic activity. It should be noted also that starting of crystallization of amorphous alloy decreases the resistivity to chemical corrosion. On that reason amorphous-crystalline catalisators can be used in such processes, where their corrosion resistivity is sufficiently enough.

We have carried the comparative analysis of catalytic activity for Fe-based AMA and for crystalline iron in reaction of H_2O_2 deposition. Results on reduce of catalytic activity of amorphous samples magnetized in alternative magnetic field are also presented.

I. Experimental methods

Amorphous alloys in the form of ribbons 35 μm of thickness and 20 mm of width and different composition were choose for studies:

$Fe_{80,0}Si_{6,0}B_{14,0}$ (AMA-1),
$Fe_{80,0}Ni_{1,0}Mo_{0,5}Si_{6,0}B_{14,0}$ (AMA-2),

Table 1

The decomposition velocity (V) of H_2O_2 in $1{,}06\cdot10^{-4}$M aqueous solution at 333K under presence of AMA at different stages of reaction.

AMA	$V\times10^{6}, \frac{M}{min}$ 0-50 min	$V\times10^{6}, \frac{M}{min}$ 50-150 min	$V\times10^{7}, \frac{M}{min}$ 150-250 min	P, %
1	3,96	1,96	7,14	100
2	4,46	2,45	5,80	100
3	5,98	1,43	3,12	100
4	6,51	0,45	0,45	80

Table 2

Velocities of H_2O_2 decomposition in $1{,}06\cdot10^{-4}$M aqueous solution at 313K under presence of AMA before and after renewing of catalytic activity of surface by means of magnetization.

AMA	$V\times10^{6}, \frac{M}{min}$ 0 - 50 min	τ, min	P, %	$V\times10^{6}, \frac{M}{min}$ after magnetiz.	P,%
1	2,43	140	6,5	1,92	87
2	3,03	67	6,8	2,23	92
3	2,59	210	8,4	2,01	83
4	3,21	80	4,2	1,65	68

Table 3

Composition (mas.%) of elements on the ribbon surface

Elem.		$Fe_{80,0}Si_{6,0}B_{14,0}$	$Fe_{80,0}Ni_{1,0}Mo_{0,5}Si_{6,0}B_{14,0}$	$Fe_{81,0}Ni_{1,0}Mo_{0,5}Nb_{0,5}Si_{3,0}B_{14,0}$	$Fe_{73,1}Cu_{1,0}Nb_{3,0}Si_{6,5}B_{7,4}$
Fe	1	93,33	91,33	92,10	82,65
	2	78,71	69,30	65,12	73,60
	3	90,20	90,22	82,10	76,60
Ni	1	-	1,22	1,20	-
	2	-	0,92	1,04	-
	3	-	1,33	1,35	-
Cu	1	-	-	-	1,27
	2	-	-	-	1,05
	3	-	-	-	1,22
Mo	1	-	1,00	0,98	-
	2	-	0,26	0,35	-
	3	-	0,42	0,85	-
Nb	1	-	-	0,93	3,65
	2	-	-	0,43	0,94
	3	-	-	0,26	1,25
Si	1	3,51	3,50	1,70	8,80
B	1	3,15	3,14	3,07	1,63

1-initial composition, 2-after catalytic decomposition H_2O_2, 3-after catalytic decomposition H_2O_2 and magnetization

Table 4

Activation energy of decomposition H_2O_2, catalyzed AMA

AMA	-	1	2	3	4
E_a, kJ/mol	75,0	21,2	16,9	36,4	30,3

$Fe_{81,0}Ni_{1,0}Mo_{0,5}Nb_{0,5}Si_{3,0}B_{14,0}$ (AMA-3),
$Fe_{73,1}Cu_{1,0}Nb_{3,0}Si_{6,5}B_{7,4}$ (AMA-4).

These alloys consist chemical elements which are active in the ox-red processes.

Samples were prepared using a single roller melt-spinning device with a copper wheel rotating at a velocity of 30 m/s.

Electrochemical measurements of potential and corrosion current were carried out in termostated cell at temperature $293 \pm 0{,}5$K by means of Jaissle Potentiostat/Galvanostat IMP 88PC-R equipment. Composition of elements on the ribbon surface was measured along 400 μm scanning line and was determined as a mean value for few points. Microphotography of samples surface were obtained with using of WDX-125 electronic microscope with increase by 5000.

II. Results and discussion

In order to obtain the activities of Fe-based amorphous alloys in catalytic red-ox reactions the reaction of deposition in hydrogen peroxyde was chosen [4]. This reaction is widely studied and on that reason the attention is attracted to catalytic action of AMA as a new kind of heterogeneous catalysators with possibility of controlled rout of red-ox process and periodic renewing of catalytic action [5,6].

Fig. 1. represents the deposition kinetics in H_2O_2 at 333K. As it can be seen all amorphous alloys studied in this work reveal the catalytic action. In respect to the acceleration of starting stage of deposition of H_2O_2 at 333K studied in this work amorphous alloys can be arranged in such series:

AMA-2 < AMA-1 < AMA-3 < AMA-4.

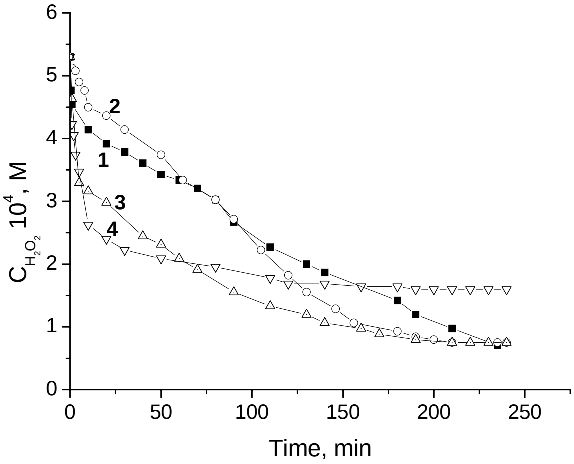


Fig. 1. The catalytic decomposition H_2O_2 in the $1{,}06\cdot10^{-4}$M aqueous solution at 333K under presence of AMA:
1 – $Fe_{80,0}Si_{6,0}B_{14,0}$;
2 – $Fe_{80,0}Ni_{1,0}Mo_{0,5}Si_{6,0}B_{14,0}$;
3 – $Fe_{81,0}Ni_{1,0}Mo_{0,5}Nb_{0,5}Si_{3,0}B_{14,0;}$
4 – $Fe_{73,1}Cu_{1,0}Nb_{3,0}Si_{6,5}B_{7,4}$.

Nevertheless, presence of AMA-catalizator in system no influence the completeness of H_2O_2 decomposition beside AMA-4 containing 1 at.% of copper. This alloy significantly promotes the starting stage of peroxyde decomposition (Tabl. 1.) but already upon 20 min it lacks activity. The decomposition reaction retards and completeness of peroxyde (P) transformation in such case is only 80%.

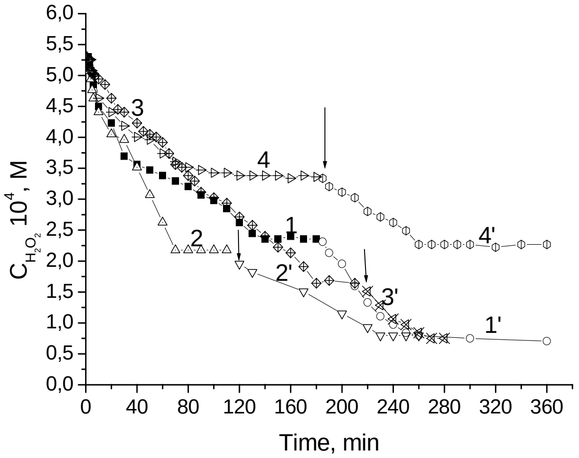


Fig. 2. The catalytic decomposition H_2O_2 in the $1{,}06\cdot10^{-4}$M aqueous solution at 313 K under presence of AMA:
1,1'-$Fe_{80,0}Si_{6,0}B_{14,0}$;
2,2'-$Fe_{80,0}Ni_{1,0}Mo_{0,5}Si_{6,0}B_{14,0}$;
3,3'-$Fe_{81,0}Ni_{1,0}Mo_{0,5}Nb_{0,5}Si_{3,0}B_{14,0;}$
4,4'-$Fe_{73,1}Cu_{1,0}Nb_{3,0}Si_{6,5}B_{7,4}$ before (1, 2, 3, 4) and after (1', 2', 3', 4') renewing of catalytic activity of surface by means of magnetization.

The formation of interphase HOOH complex on the metal surface is the first stage of catalytic decomposition. There are of kinetic nature proofs of such complexes formation and it is shown that dissociation velocity of O-O bonds has a limited behaviour depending on relation substate concentration – active surface of catalyzator (S).

The activation of peroxyde at presence of catalizator is caused by shift of electron density along O-O bouding. Presence of electron donors (D) on a catalizator surface (S) lead to increase of H_2O_2 decomposition velocity, whereas presence of acceptor (A) decrease the activity of catalyzator. Therefore, reduce in time of H_2O_2 transformation occurs due to deactivation of surface what is caused by its oxidation. On that reason the method of renewing of catalyzator by magnetization was evaluated.

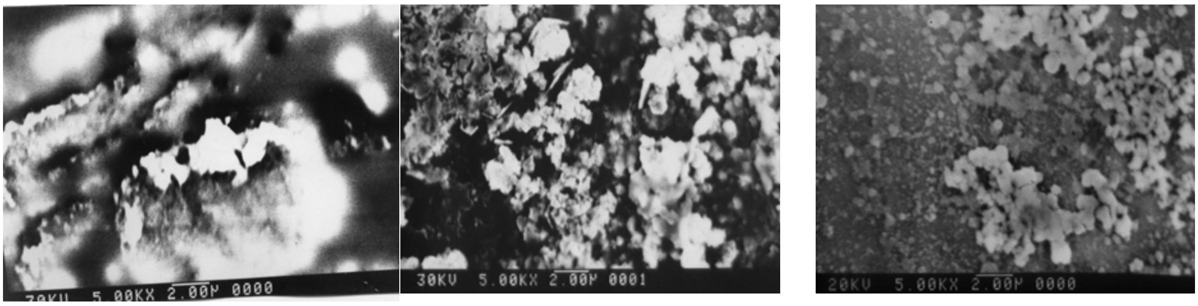
The catalytic decomposition of H_2O_2 performed at temperature 313 K. The values of starting velocity of H_2O_2 decomposition and renewing of catalyzator by magnetization after deactivation are listed in table 2 and figure 2.

Temperature of decomposition reaction of peroxyde decrease low to 313 K leads to changes in order of catalytic activity series. Most active before and upon magnetization now are AMA-2 and AMA-1. Alloys with Nb at lower temperature are of less activity:

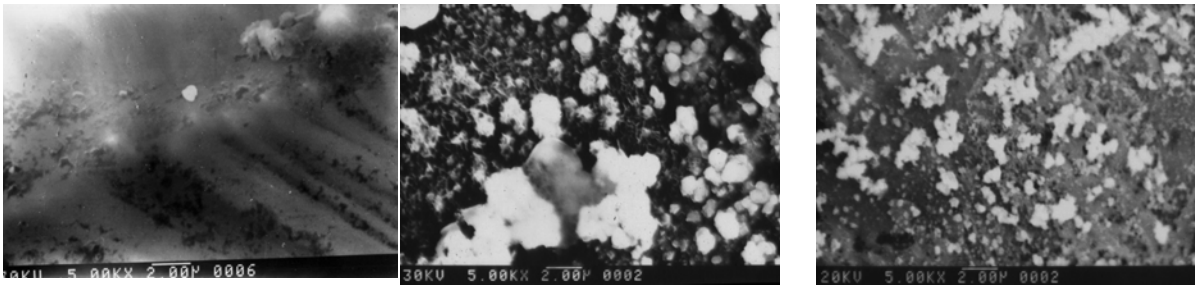
AMA-3 < AMA-4 < AMA-2 < AMA-1.

The change of structural state in surface of AMA-catalizator after interaction with hydrogen peroxyde in comparison to initial surface and after magnetization are presented in figure 3.

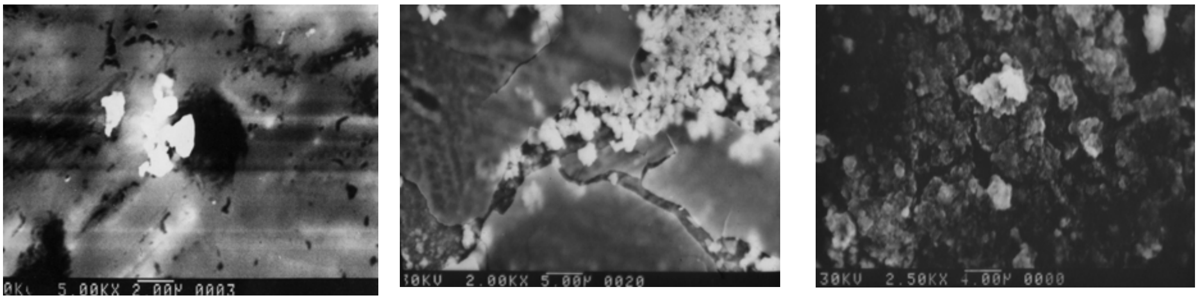
Appearance of contact between catalizator and H_2O_2 solution leads to significant decrease in number of metallic components (D) i surface layers of AMA (Tabl. 3.). Formation of oxides on surface inhibits the recombination of hydroxide radicals, in result of which the extraction of O_2 occurs. The magnetization promotes the enriching of surface with active metals and renewing of catalytic reaction of peroxyde decomposition (Tabl. 3). Activation energies of H_2O_2 decomposition under presence of AMA are listed in table 4.



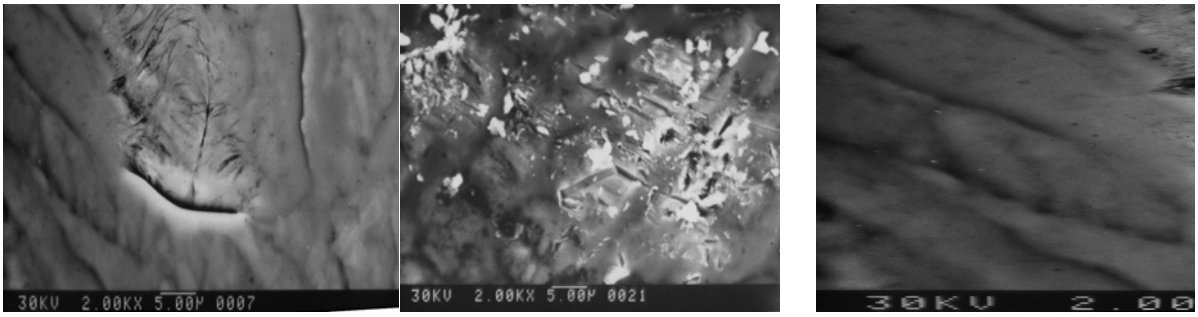
$Fe_{80,0}Si_{6,0}B_{14,0}$ **1** **2** **3**



$Fe_{80,0}Ni_{1,0}Mo_{0,5}Si_{6,0}B_{14,0}$ **1** **2** **3**



$Fe_{81,0}Ni_{1,0}Mo_{0,5}Nb_{0,5}Si_{3,0}B_{14,0}$ **1** **2** **3**



$Fe_{73,1}Cu_{1,0}Nb_{3,0}Si_{6,5}B_{7,4}$ **1** **2** **3**

Fig. 3. Microphotographs of the surface AMA: 1-before, 2-after chemical process and 3-after renewing of catalytic activity of surface by means of magnetization.

Conclusions

Mechanism of catalytic action can be considered as interaction between AMA activated surface with peroxyde what promotes the heterolytic breaking of O-O bonds [2]:

$$[D^{\delta+}...S^{\delta-}]+HOOH \rightarrow [D^{\delta+}...S...HOOH^{\delta-}] \rightarrow$$
$$\rightarrow HO^{\bullet+}+[HO^{-}...S...D].$$

Therefore the decomposition process of peroxyde depending on nature of multicomponent catalytic system can occur in heterogeneous-homogeneous way with formation of free radicals on the surface of catalyzator and their further transformation in volume [1]. In the case of AMA-catalizator, doped with Cu, it is most probably that heterogeneous decomposition without output of radicals in volume occurs.

Acknowledgements

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