

ON CORRELATION BETWEEN SURFACE STRUCTURE AND CATALYTIC ACTIVITY OF AMORPHOUS ALLOYS*

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Abstract

The present paper is a review summarizing our results gained in the field of catalysis over amorphous alloys. The route leading to the formation of the catalytically active phase is presented and the factors which may play a decisive role in this process is discussed. Following the surface characterization of amorphous alloys led to the constructions of a surface model its modifying effects are described. Their catalytic properties are further influenced by the structure and the morphology. These parameters are crucial to the formation of the active metal ensembles and to the behaviour of reactants over the surface. These factors are discussed in detail for the utilization of amorphous alloys, primarily as catalyst precursors.

Our investigations on amorphous alloys started in early 80-ies when a new area of the application of amorphous alloys or metallic glasses was opened by extending the catalytic research to this field (Yokoyama et al., 1981 and Brower et al., 1983).

Factors initiating the catalytic interest area are twofold:

I. In the basic catalytic research amorphous alloys can be considered as catalyst precursors with unique properties, such as: high concentration of surface low coordination sites (LCS), short range ordering (SRO), optionally changeable composition, planar morphologies being optimal for surface characterization, etc. (Cocke, 1986).

II. The other approach being in close relation to the industry is the applied catalytic approach. From its point of view the catalytic activity of amorphous materials is studied especially in comparison with the other forms of the catalysts, namely, the supported or the crystalline substrates with the same composition (Shibata and Masumoto, 1986).

Simultaneously, one must bear in mind that catalysis is a highly sensitive tool for surface characterization, therefore, it can be utilized for gathering knowledge about the surface.

The first important observation concerning the catalytic behaviours of amorphous alloys was that their catalytic activities are generally higher than

* Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

those of their crystalline counterparts. This fact stimulating the catalytic interest is clearly demonstrated by our results obtained over amorphous and crystallized FeB and FeNiB alloys in the $\text{CO} + \text{H}_2$ reaction (Kisfaludi *et al.*, 1985).

The surface of an amorphous sample is determined by the manufacturing process chosen. First the method applied is a crucial factor among all technical parameters involved. In addition, the gaseous environment during the manufacturing has also a great influence on the surface properties and, of course, the composition of starting materials is an essential factor, too.

As a consequence of the preparation technique (SRMS = Single Roller Melt Spinning) the two sides of the ribbons have different properties that can even be seen by visual inspection. The dull side was in contact with the copper disk and thus it was cooled more effectively than the shiny one. A pattern of air pockets can clearly be seen by SEM on it. The surface is severely oxidized, rather rough and porous in depth resulting in a decreased reflection of light. The other side far from the disk is shiny. It was in contact only with air and it is relatively smooth and homogeneous. As was revealed by XPS, the oxide layer is deeper on the dull side and consists mainly of iron oxide whereas on the shiny side, where because of the slower heat extraction there is time for boron segregation, an enrichment in boron oxide was detected.

The qualitative surface model constructed on the basis of these observations shows that the shiny side is mainly covered by a compact boron oxide layer with small amounts of iron oxide embedded in it while the dull side consists of two structures. One of them is the area of the air pockets resembling the shiny side while at the edges the air inclusions are trapped and so the large part of the dull side consists of iron oxide of porous structure.

As was found, there is metallic iron only in small amount as the catalytically active species in the as received state on the surface. The catalytic activity still showed can be explained by an initial reduction step by H_2 in the reaction mixture. Although H_2 cannot reduce boron oxide, iron oxide is transformed into metallic iron during this step hereby practically only the dull side shows catalytic activity.

The parameters determining the alloy surface give us the opportunity to modify it by their alteration (Kisfaludi *et al.*, 1987a and 1987b).

Our results with FeNiB alloys of different composition confirmed the assumption that though the bulk composition is not in a close correlation with the surface one, its changes should display similar trends to those of the bulk.

Considering the effect of the cooling rate the XPS depth profiles revealed that the slower the cooling rate the deeper and more porous the oxide structure on the dull side. Regarding this a simple explanation arises for the reaction rate vs. disk surface velocity curve: since the initial reduction step is necessary

for the catalytic reaction increasing the porosity the amount of the accessible iron oxide, hereby the catalytic activity, increases.

The other possibility is the chemical etching. After a pretreatment of FeB alloy by HCl the XPS measurements revealed that beside the removal of the boron oxide layer from the shiny side iron is deeply oxidized. Simultaneously, on the dull side the originally porous mixed oxide structure is converted into a compact oxide layer thereby further decreasing the accessible metal sites and so the catalytic activity. This example clearly demonstrates that the chemical etching can play a significant role in modifying the catalytic activity of amorphous alloys not only by removing the original surface layers but also by forming new surface structures.

Nevertheless, one must notice that these modifications alter not only the composition but the structure of the alloy surface, too.

Between the two extremes of morphology, i.e. the fully amorphous and crystalline states the partially crystalline material turned out to have the highest catalytic activity (Guczi et al., 1987).

With the amorphous materials being thermodynamically unstable they are transforming into crystalline form (Köster and Herold, 1981). These crystallizations lead to different types of crystallites for different compositions as was measured by XRD.

After the crystallization FeB alloy contains α -iron particles whereas they do not occur in crystallized FeNiB. Regarding the XRD pattern of the partially crystallized FeNiB sample it represents microcrystallites embedded into the amorphous matrix.

Further investigation of the structural effect was performed by chemisorption experiments over previously cleaned alloy surfaces. During the $\text{CO} + \text{H}_2$ reaction three different types of surface carbon and trapped surface oxygen could be distinguished by XPS among which the surface carbide is the catalytically active form (Wesner et al., 1985).

The results obtained by XPS after CO adsorption at room temperature, by which the different surface structures can be characterized, revealed that beside carbidic carbon graphitic species are also present over all surfaces except on the partially crystallized sample where instead of this inactive form molecularly bound CO occurs. Simultaneously, only one type of surface oxygen appears representing the so-called "B—O—M" oxygen trapped on the iron-boron interface (Zsoldos et al., 1988). From these experiments carried out at room temperature it could be concluded that the partially crystallized FeNiB sample must have a special surface structure because of which the formation of inactive carbon is suppressed.

Similar XPS measurements carried out after CO adsorption at the reaction temperature resulted in the bulk or subsurface oxidation of boron on each alloy surface. The XPS spectra of the C1s region showed that carbidic

carbon is the prevailing form on all samples but its relative amount displayed in the shapes of the spectra is different.

To explain the different behaviours of the different structures on the small metal ensembles of the amorphous samples the bulk carbide formation is hindered and a part of the large amount of surface carbon can be agglomerated forming inactive, graphitic species. On the other hand, on large crystallites of the crystallized samples surface carbon can migrate into the bulk and carbide in the subsurface layers can be formed. However, on the partially crystallized surface, beside the hindered bulk carbide formation, the occurrence of graphitic species is also diminished. The surface carbidic species then the prevailing form to which the high catalytic activity can be attributed.

Conclusion

I. The surface composition and thus the catalytic activity of amorphous materials can be changed either chemically or by altering some manufacturing parameters.

II. Their stabilization processes, the crystallizations lead to proper kinds and sizes of the crystalline phases which can also be a controlling factor for the difference in activity.

III. During the catalytic reaction a reduction of the metallic and the oxidation of the metalloid components proceed. While the zerovalent metal formed is responsible for the catalytic activity the oxidized metalloid may serve as a stabilizing matrix surrounding the small metallic microcrystallites developed. This process can assist to coming into existence of the unique high catalytic activity of partially crystallized alloy in the $\text{CO} + \text{H}_2$ reaction.

IV. Concerning the future utilization of amorphous alloys in catalysis
— alloys with high specific area
— and stabilized and highly active materials seem to be promising (Armbruster *et al.*, 1986).

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