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Journal of Alloys and Compounds 234 (1996) 251–255

Journal of
ALLOYS
AND COMPOUNDS

Oxidation of hydrogen and carbon monoxide on the catalyst surfaces obtained from iron- and cobalt-based amorphous alloys

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Received 23 June 1995; in final form 31 August 1995

Abstract

Amorphous alloys with compositions $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{60}Co_{25}B_{15}$ and $Co_{70}Fe_5B_{10}Si_{15}$ were applied as catalysts for the oxidation of hydrogen and carbon monoxide. The samples were activated by etching with hydrofluoric acid and oxidation at 750 K. The catalytic activity was measured in a standard static-circular apparatus at 500–650 K. The rate constants and the activation energies of the processes were determined.

The results showed that the untreated alloys displayed catalytic activity. Preliminary oxidation, treatment with hydrofluoric acid and subsequent oxidation of the alloys altered the catalytic activity. The effects were lower for hydrogen oxidation than for carbon monoxide oxidation, for which they were considerable.

Keywords: Catalytic activity; Amorphous Fe- and Co-based alloys; Hydrogen oxidation; Carbon monoxide oxidation

1. Introduction

It is known that in heterogeneous catalysis on metal-based catalysts, the chemical surface properties, the local arrangement of atoms or clusters on the surface play an important role. They can be modified by alloying and new catalytic activities can be generated. Much work has been done on catalytic reactions over crystalline surfaces of metal alloys, whereas little research has been performed on catalytic reactions over amorphous alloys (metallic glasses). The amorphous alloys may be of metal–metal or metal–metalloid composition. Metal–metalloid alloys are the more important group, containing typically 80% metal(s) (Fe, Ni, Co, Pd, Cu) and 20% metalloid(s) (B, P, Si, C). Melt-spinning has evolved as a convenient laboratory method for making them. It is important to note that the alloys used so far in catalysis have mainly been produced by melt-spinning.

The amorphous alloys can present unique and original compositions and surface structures to reacting molecules with respect to conventional crystalline metals and they may be an ideal model for studying elementary catalytic reactions. They also exhibit some unique properties, such a high density of low-coordination sites and defects, ideal chemical homogeneity and structural isotropy, and high reactivity owing to their metastable structure, which make them interesting materials in catalysis.

Earlier studies demonstrated catalytic properties of amorphous alloys [1,2]. Fe-, Ni-, Pd- and Cu-based amorphous alloys have been the most tested with respect to their catalytic properties in reactions of CO hydrogenation [3–7], hydrogenation of olefins [8–11], oxidation of CO [12,13], oxidation of methanol [14] and synthesis of ammonia [15,16]. Two different types of investigations can be distinguished: catalytic studies on untreated surfaces of alloys, and studies centered on the role of pretreatment and its influence on the catalytic properties. It is noted that the surface of an as-prepared amorphous alloy is covered with an inactive oxide layer. This oxide layer has to be removed by a pretreatment procedure to expose the active metal sites. Therefore, several activation procedures are applied to improve the catalytic activity of the amorphous alloys, such as reduction in hydrogen or in other reducing-gas atmospheres, treatment with acid (HCl, HF, HNO_3) followed by oxidation, and reduction.

The present work studies the catalytic activity of the iron- and cobalt-based amorphous alloys with respect

SSDI 0925-8388(95)02052-7

to the oxidation of hydrogen and carbon monoxide. Correlation is sought between the composition and the catalytic activity of the alloys, on the one hand, and the influence of the different pretreatment procedures on the catalytic activity, on the other.

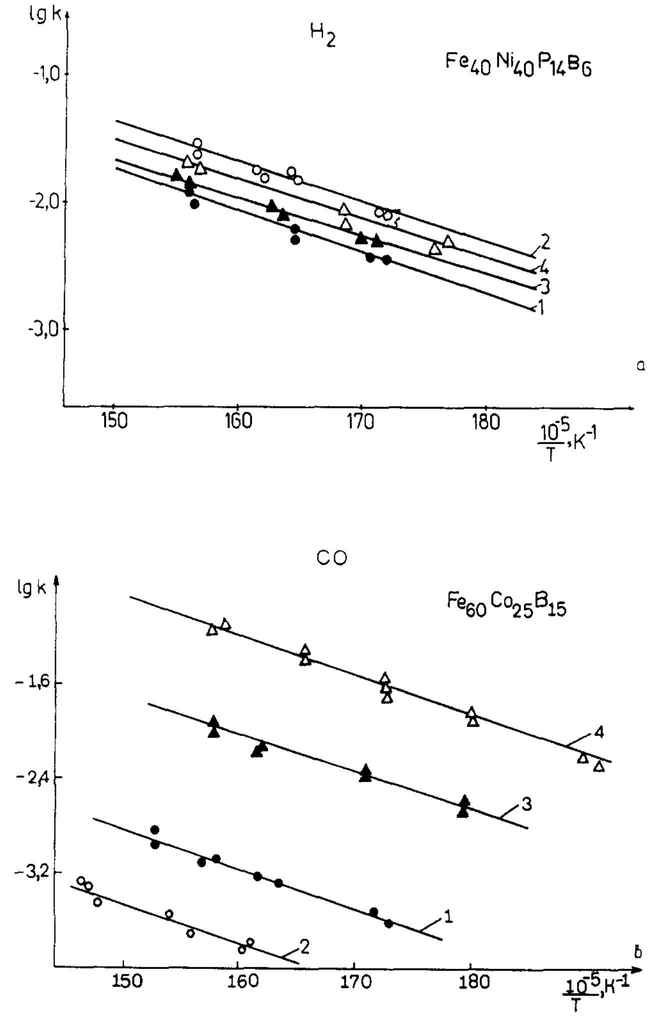

Fig. 1. Catalytic activity of alloys in Arrhenius coordinates. (a) $Fe_{40}Ni_{40}P_{14}B_6$ for hydrogen oxidation. (b) $Fe_{60}Co_{25}B_{15}$ for carbon monoxide oxidation: ● untreated alloy; ○ oxidized alloy; ▼ treated with HF; △ treated with HF and oxidized.

2. Experimental

The amorphous alloys were prepared using the melt-spinning technique. Their amorphous structure was found by X-ray diffraction and differential scanning calorimetry, and morphological changes by scanning electron microscopy (SEM). The compositions of the alloys were $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{60}Co_{25}B_{15}$ and $Co_{70}Fe_5B_{10}Si_{15}$. They were activated by treatment with HF and oxidation at 750 K. The samples studied were: untreated alloys; those treated with 40% HF; those treated with HF followed oxidation; and those preliminarily oxidized. The oxidation of the alloys was carried out at 750 K in air for 2 h. After alcoholic treatment the samples were immersed in 40% hydrofluoric acid for 5 min and then washed with distilled water.

The catalytic activity was measured in a standard circular apparatus at temperatures 500–650 K. The oxygen detector, constructed on an electrochemical principle, allowed for a continuous high accuracy (0.005%) in monitoring the oxygen concentration. The initial gaseous mixtures contained 98% hydrogen and 2% oxygen, or 96% carbon monoxide and 4% oxygen. The experiments were carried out at atmospheric pressure. The samples were dried in the reaction atmosphere for 2 h at 550 K. The rate constants k (m^{-2} s^{-1}) and the activation energies E_a (kJ mol^{-1}) of the processes were determined.

3. Results

3.1. Hydrogen oxidation

The results must be interpreted in the light of the fact that the Arrhenius law predicts an exponentially increasing reaction rate with increasing temperature. Fig. 1(a) presents the catalytic activity of the $Fe_{40}Ni_{40}P_{14}B_6$ alloy in Arrhenius coordinates. Curve 1 shows the activity of the untreated alloy which is the lowest. An increase of the activity is observed if the alloy is preliminarily oxidized (curve 2). The etching of the sample with hydrofluoric acid leads to a slight increase of the activity (curve 3) than that of the untreated alloy. The activity increases even more if the alloy, treated with acid, is oxidized afterwards (curve 4). The results received with the $Fe_{60}Co_{25}B_{15}$ alloy are similar. The replacement of Ni with Co does not lead to significant changes in the catalytic activity. The difference in the observed catalytic activities of the untreated and the treated alloys is relatively small and it is not connected with the considerable changes in the activation energy (Table 1).

The results are different for the $Co_{70}Fe_5B_{10}Si_{15}$ alloy where Co is a basic component and there is a new component, Si. In this case the activity of the untreated sample is the highest and the different treatments slightly diminish it (Table 1).

3.2. Carbon monoxide oxidation

The catalytic activity of the $Fe_{60}Co_{25}B_{15}$ alloy is shown in Fig. 1(b). The acid treatment and particularly the following oxidation lead to a considerable increase in the activity (curves 3 and 4), while only oxidation of the sample decreases the activity (curve 2). The results obtained with the $Co_{70}Fe_5B_{10}Si_{15}$ composition are

Table 1
Catalytic activity (log *k*) of the alloys at 625 K and the activation energy (E_a, kJ mol^{-1}) of the catalytic reactions

Sample	Untreated	Oxidized	Treated with HF	Treated with HF and oxidized
H_2 oxidation				
log *k*				
Fe60Co25B15	−2.10 ± 0.02	−1.80 ± 0.02	−1.80 ± 0.06	−1.90 ± 0.06
Fe40Ni40P14B6	−2.00 ± 0.06	−1.70 ± 0.02	−2.00 ± 0.02	−1.80 ± 0.04
Co70Fe5B10Si1	−1.40 ± 0.02	−1.60 ± 0.02	−1.70 ± 0.02	−1.60 ± 0.02
E_a				
Fe60Co25B15	69.0 ± 0.4	65.0 ± 0.4	65.0 ± 0.4	65.0 ± 0.4
Fe40Ni40P14B6	61.0 ± 0.5	58.0 ± 0.2	54.0 ± 0.4	58.0 ± 0.5
Co70Fe5B10Si15	69.0 ± 0.2	73.0 ± 0.2	75.0 ± 0.2	73.0 ± 0.2
CO oxidation				
log *k*				
Fe60Co25B15	−3.10 ± 0.06	−3.90 ± 0.05	−2.00 ± 0.04	−1.10 ± 0.06
Co75Fe5B10Si15	−3.40 ± 0.03	−3.60 ± 0.04	−1.80 ± 0.04	−1.00 ± 0.06
E_a				
Fe60Co25B15	67.0 ± 0.5	69.0 ± 0.4	53.0 ± 0.7	69.0 ± 0.4
Co70Fe5B10Si15	57.0 ± 0.8	57.0 ± 0.8	54.0 ± 0.5	52.0 ± 0.6

analogous (Table 1). It is interesting that the maximum catalytic activity is the same for the two compositions. The values of E_a change within the range 52–70 kJ mol^{-1} and do not differ considerably from those determined for CO oxidation of oxides of iron and cobalt.

4. Discussion

The untreated alloys reveal catalytic activity showing that the surface is not completely covered with an inactive oxide layer or that part of it is easily removed during the catalytic reaction. This activity is comparatively high for the hydrogen oxidation.

The catalytic behavior of amorphous alloys observed in the as-received state could be easily altered by using chemical pretreatment. In most catalytic applications treatment of the as-received alloys is crucial to obtain high catalytic activities. It is interesting to note that in most studies the amorphous samples have been found to exhibit improved catalytic behaviour, i.e. higher activity or selectivity, compared with their crystalline counterparts. Several factors, such as degree of ordering and dispersion of the active component, electronic properties, formation a new phases, nucleation and growth of crystalline domains, segregation phenomena and textural properties, will be influenced in different ways during pretreatment.

The experiments of other workers [3–8,12,17] have shown that acid treatment is effective in removing the inactive oxides, leaving thinner surface oxides of the metal and metalloid components, increasing the porosity and surface area of the as-produced alloys. We suppose that the catalytic activity depends on certain changes on the surface. The untreated amorphous alloys are not porous and have exposed surface areas of about 0.05–0.15 m^2 g^{-1}, after acid treatment and oxidation the surface area increases about ten-fold. Results from SEM study of the $Fe_{60}Co_{25}B_{15}$ surfaces are shown in Fig. 2, indicating that the morphology of the untreated alloy (Fig. 2(a)) is altered following treatment. The surface becomes significantly porous after acid treatment and subsequent oxidation (Fig. 2(b)). Accordingly, the acid treatment and oxidation are effective in enhancing the activity, presumably, in part, as a result of the increase in surface area of the untreated alloy. It is apparent that this change is connected with the increased catalytic activity of the alloys in the reaction of hydrogen oxidation, but does not explain the result for CO oxidation where increasing of catalytic activity of the alloys occurs to a greater extent.

The values of E_a are not very different, suggesting the same nature of the active sites on the untreated and the treated samples. The acid treatment and oxidation lead to larger surface area and greater number of the active sites per unit area. In the case of CO oxidation, the difference in the activity could be due to a rise both in the number of active sites per unit area and the surface area. The additional formation of active sites is probably related to the presence of an oxide phase. Hydrogen oxidation increases only the surface area at a constant number of active sites.

The slight diminution of the activity for the preliminarily oxidized $Fe_{60}Co_{25}B_{15}$ and $Co_{70}Fe_5B_{10}Si_{15}$ alloys could be due to the covering of the surface by solid oxide layer, which adsorbs CO more steadily preventing the oxidation of CO. Partial crystallization is possible by the oxidation at 750 K and it is also connected with changes in the activity (Fig. 2(c)).

At present, the relationship between the catalytic

(a) (b) (c)

Fig. 2. SEM image of $Fe_{60}Co_{25}B_{15}$ surfaces: (a) untreated; (b) treated with HF and oxidized; (c) treated in air at 750 K.

activity and the structural changes is not clear and the more detailed studies will need to be undertaken to achieve a better knowledge of the surface structure. The thermal stability is a severe limitation if the amorphous alloys are to be used in the as-quenched state for catalysis, however. This is not necessarily the case if the alloys are used as catalyst precursors. In the present case the amorphous alloys should be considered as catalyst precursors.

5. Conclusion

The results show that the Fe- and Co-based amorphous alloys display catalytic activity with respect to the oxidation of H_2 and CO. The treatment of the alloys with HF acid and oxidation at 750 K changes the activity. The effects are less apparent for H_2 oxidation than for CO oxidation, where they are considerable. It seems that the original surface structure of the amorphous alloys is altered and the alloys should be considered as catalyst precursors.

The preliminary oxidation of the alloys, the treatment with HF acid and subsequent oxidation all increase the catalytic activity of the $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{60}Co_{25}B_{15}$ and decrease that of the $Co_{70}Fe_5B_{10}Si_{15}$ in H_2 oxidation. For CO oxidation the catalytic activity of $Fe_{60}Co_{25}B_{15}$ and $Co_{70}Fe_5B_{10}Si_{15}$ increases after acid treatment and subsequent oxidation, while only the oxidation of the alloys decreases the activity.

The values of the activation energies are almost the same, suggesting that the active sites on the untreated and the treated samples are of the same type. Treatment with acid and oxidation of the alloys leads to larger area and greater number of active sites per unit area in the case of CO oxidation, and to a strong increase of the surface at constant number of active sites upon oxidation of hydrogen.

There are many problems in the application of amorphous alloys as catalysts, such as their low surface areas, high prices and the presence of an inactive surface oxide layer. Efforts to increase the surface area by making ultra-fine particles, oxidation or reduction should be continued. The pretreatments for removing surface oxide layers by mechanical or chemical methods so as to expose the active surface should be improved. However, the amorphous alloys seem to be a new class of catalyst systems offering new possibilities in catalytic activity and selectivity.

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