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Hydrogenation under high pressure enhancing catalytic activity of Cu–Zr amorphous alloys

A Szummer¹, M Janik-Czachor², Á Molnár³, I Marchuk², M Varga³ and S M Filipek²

¹ Faculty of Material Science, Technical University, Warsaw, Poland

² Institute of Physical Chemistry, Polish Academy of Sciences, Kaprzaka 44/52, 01-224 Warsaw, Poland

³ Department of Organic Chemistry, University of Szeged, Dóm tér 8, H-6720 Szeged, Hungary

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Abstract

High pressures of hydrogen up to 3.0 GPa and temperatures up to 373 K were used as a pretreatment to introduce structural changes in the bulk and on the surface of Cu–Zr amorphous alloys which then were examined by means of x-ray diffraction and microscopy. The hydrogenative pretreatment of high hydrogen fugacity followed by annealing at 623 K, aimed at causing desorption of hydrogen, and an eventual exposure of the samples to air at room temperature to oxidize Zr, resulted in a distinct increase of catalytic activity in the dehydrogenation of 2-propanol. A tentative mechanism to account for the enhancement of the catalytic activity induced by the above combined pretreatment is discussed.

1. Introduction

Recently, zirconium-containing amorphous alloys (AA) have attracted significant attention as precursors of efficient and durable catalysts for a number of technically important chemical reactions [1–3]. Various procedures of activation aimed at transforming the original amorphous ribbons of low surface area into efficient and stable catalysts have been developed. Among these, the most effective techniques are ageing in air, etching, i.e. partial dissolution of Zr with dilute HF solution [4–7], and *in situ* activation occurring during alcohol dehydrogenation over Cu–Zr [5] or exposure of Zr-containing alloys (Cu–Zr, Au–Zr, Ni–Zr, Pd–Zr) to CO₂ hydrogenation [9, 10] or CO oxidation conditions [11, 12]. As our own experience with Cu–Zr AA ribbons has shown, electrochemical modification is also an efficient pretreatment which significantly increases catalytic activity in the dehydrogenation of alcohols [13–15].

In contrast, the effect of gaseous hydrogen at atmospheric pressure on the catalytic activity is found to be moderate even after prolonged application at elevated temperature [5, 16, 17]. Studies using such hydrogenative pretreatment have indicated significant changes in both the bulk and the surface structure [17–20]. However, the effect of high-pressure hydrogenation

of zirconium-containing amorphous ribbons on their catalytic performance has not been investigated. Hydrogen treatment at high pressure is known to bring about significant structural changes in the bulk and on the surface [21–23]. Moreover, the high-pressure hydrogen treatment of Cu–Zr AA markedly reduces the temperature of crystallization. Naturally, the crystallization products differ significantly when the crystallization process is carried out during high-pressure hydrogenation or in an inert gas atmosphere. Such a pretreatment, therefore, may be of interest as a useful process for inducing the necessary transformations leading to the development of catalytically active materials.

The aim of this work, therefore, is to examine the effects of a high-pressure hydrogenative treatment of Cu–Zr amorphous ribbons on their structure and catalytic properties.

2. Experimental procedure

2.1. Materials and microscopic examinations

The Cu–Zr AA ribbons (60Cu–40Zr or 50Cu–50Zr) produced by the melt-spinning method were 4 mm wide and $\sim 40 \mu\text{m}$ thick. Two kinds of ribbon were used for the investigations: freshly cast, or aged in air for from eight months to twelve years, with a visible partial devitrification.

X-ray diffraction (XRD) analysis was carried out by a RIGAKU diffractometer using Cu $K\alpha$ radiation. The samples were examined with an optical microscope, and an electron microprobe CAMECA SEMPROBE SU30 instrument equipped with WDS/EDS (wavelength/energy-dispersive spectrometry).

The following surface corrosion/devitrification products were analysed:

- (a) the surface oxide zone on both sides of the ribbon;
- (b) the red islands formed on the wheel side of the ribbons;
- (c) carefully polished cross-sections of the surface zone of the ribbon; to obtain such a cross-section a piece of the ribbon was mounted into epoxy to protect the peculiar structure of the wheel side, and then carefully polished to reveal the structure of the cross-section.

2.2. Hydrogenation under high pressure

A high-pressure piston–cylinder apparatus described elsewhere [21, 24] was used for hydrogen or deuterium compression up to about 3.0 GPa. The temperature of the apparatus was controlled up to 373 K; for higher temperatures samples were heated in a special small electric furnace placed in the pressure vessel. H/CuZr ratios were determined by elemental analysis or by mass spectrometry.

2.3. Heat treatment/air exposure

Some of the hydrogenated samples were additionally heat treated in helium at 623 K to cause hydrogen to desorb. The resulting material was then exposed to air at room temperature for controlled time intervals in order to allow Zr to oxidize.

2.4. Catalytic test

Dehydrogenation of 2-propanol was chosen to test the changes in the catalytic activity of the Cu–Zr ribbons. About 15 mg of the as-received, the aged or the pretreated ribbon sample was loaded into a glass microreactor. 2-propanol was fed by a microfeeder into a stainless steel evaporator, where it was mixed with hydrogen (used in order to activate Cu–Zr ribbons).

Then the gas mixture (2-propanol /hydrogen = 0.018) was introduced into the reactor kept at 573 K. The total flow rate was 10 ml min⁻¹.

The Cu(0) surface area of the samples was measured by N₂O titration at 363 K based on the reaction of nitrous oxide with Cu(0) species using the GC pulse method. A short hydrogen treatment (30 min at 563 K) was applied before measurements.

3. Results and discussion

Examinations of the as-received ribbons confirm the findings of the previous investigations [15, 23, 25]; specifically, the freshly fabricated Cu–Zr AA are covered by a thin (0.6–0.8 nm) ZrO₂ layer [15, 25]. When the ribbon is kept in air (aged), oxidation proceeds with a concomitant Cu segregation. This devitrification process results in the development of a ‘sandwich structure’ of crystalline Cu/ZrO₂ bilayer or multilayer on the wheel side. The bulk of the ribbon, however, remains amorphous; compare [15, 25].

The hydrogen treatment at 302 K of ribbons with the devitrified zone on top resulted in an extremely slow absorption kinetics even at pressures as high as 2.7 GPa. For example, after 100 h of exposure the H/CuZr ratio for 50Cu–50Zr was as low as 0.07. It was found that after the mechanical removal of the thin (2–3 μm) devitrified surface layer, the hydrogen absorption process accelerated considerably [23].

For 50Cu–50Zr alloy a 75 h exposure to 1.1 GPa hydrogen at 373 K resulted in the attainment of an atomic ratio of H/CuZr = 1.2, whereas at 302 K this ratio was only about 0.3.

The samples undergoing hydrogen treatment became brittle. The high brittleness of these samples provided an easy way to obtain a material with a high specific surface area, since they disintegrate into small pieces at a simple touch. However, new surface areas open up for further oxidation of Zr resulting in devitrification with concomitant Cu segregation.

Typical XRD patterns of 50Cu–50Zr amorphous ribbons, with no devitrified surface layer on top, showed only a broad maximum, characteristic of an amorphous phase. The XRD pattern after hydrogenation under a high pressure (e.g. at 373 K, P_{H_2} = 1 GPa, three days) differed distinctly from those of the amorphous samples. Hydrogen charging has shifted the broad amorphous peak to lower angles, thus indicating an increase in the interatomic distances within the alloy due to hydrogen absorption. Moreover, distinct diffraction lines from crystalline Cu appeared, suggesting a partial crystallization of copper. Similar changes were observed for the other alloy with a different Cu content

Figure 1 shows micrographs of a hydrogenated sample (393 K, P_{H_2} = 0.12 GPa, 70 h) which was additionally annealed for 30 min at 623 K to cause hydrogen to desorb. Apparently, absorption and desorption of hydrogen resulted in partial devitrification on both sides of the ribbon. Distinct particles (red) of Cu are visible. On the free side they are smaller by a factor of 2–3 than those on the wheel side.

Figure 2 represents the results of the catalytic tests (activities in the dehydrogenation of 2-propanol) for a 60Cu–40Zr amorphous ribbon. The catalytic efficiency of the samples without hydrogenative pretreatment is negligible. Figure 2 gives also the results of catalytic tests for the hydrogen-treated samples. The catalytic efficiency of the hydrogenated ribbon is distinctly higher than that without any preceding hydrogenation (compare plots (a) and (b)). Yet, the rather homogeneous Zr–Cu–H ternary AA with the expanded interatomic distances between the metal atoms and the small clusters of partly crystallized Cu embedded therein is not an efficient catalyst for the test reaction.

However, after further pretreatment—specifically, after the hydrogen is made to desorb at 623 K and the subsequent exposure to air—the catalytic efficiency of the material gradually increases (compare plot (b) with plots (c) and (d) in figure 2).

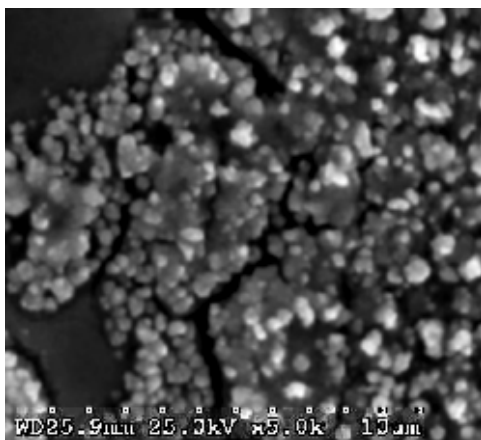


Figure 1. The morphology of a 50Cu–50Zr glassy ribbon after hydrogenation at 323 K, $P_{\text{H}_2} = 0.10$ GPa, 14 days. Visible particles of crystalline Cu are clearly distinguishable at the surface (wheel side).

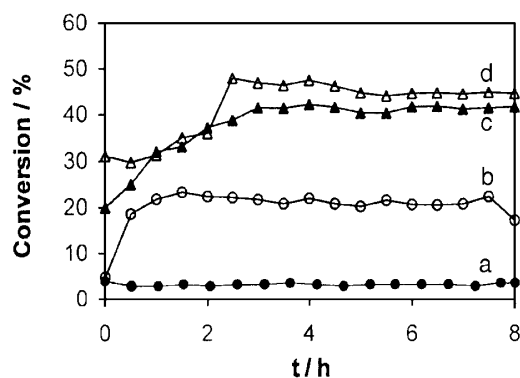


Figure 2. The efficiency for the conversion of 2-propanol as a function of reaction time over a one-year-old amorphous 60Cu–40Zr alloy: (a) before any pretreatment (●); (b) the ribbon additionally modified by hydrogenation (393 K, $P_{\text{H}_2} = 0.12$ GPa, 70 h) (○); (c) pretreated as in (b) followed by annealing at 623 K for 5 h in flowing helium and additionally exposed to air for two days (▲); (d) pretreated as in (c) and additionally exposed to air for seven days (△).

These results indicate the beneficial role of oxidation of Zr in the overall catalytic process. One may suggest that at least a partial oxidation of a large, freshly developed surface of a rather brittle Cu–Zr material leads to the segregation and, eventually, precipitation of copper to the surface and a suitable arrangement of the Cu active centres on a ZrO_x support (compare also figure 1). This surface rearrangement certainly should include the coalescence of Cu crystallites—that is, an increase in particle size.

4. Conclusions

Hydrogenation of Cu–Zr AA under high pressures and at temperatures up to 373 K results in an expansion of the interatomic distances in the bulk of the Cu–Zr AA, brittleness of the bulk material and formation of some surface microcracks where a partial Cu crystallization

can start. This material exhibits low catalytic activity in the dehydrogenation of 2-propanol in spite of a large specific surface area developing additionally in the catalytic reaction. However, after the hydrogen has desorbed at 623 K and the subsequent air exposure at room temperature, the catalytic activity increases with exposure time. This points to the role of Zr oxidation in generating active Cu centres with suitable size and arrangement on a ZrO_x support for the catalytic process.

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