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EFFECTS OF PRETREATMENTS ON THE STRUCTURE OF PALLADIUM-CONTAINING AMORPHOUS ALLOYS FOLLOWED BY DSC

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Abstract

Amorphous PdZr, PdCuZr and PdCuSi alloy ribbons and powders are characterized by DSC, XRD and XPS in the as-received state and after treatments with oxygen, hydrogen or dilute hydrogen fluoride solution. Zr-containing alloys are shown to undergo substantial structural changes resulting in palladium enrichment on their surface, whereas no apparent changes in the bulk structure are found for PdCuSi. Catalytic activity and selectivity of the pretreated samples were tested in the hydrogenation of phenylacetylene.

Keywords: amorphous palladium alloys, DSC, hydrogenation, mechanical alloying, phenylacetylene, structural characterization, X-ray diffractometry, X-ray photoelectron spectroscopy

Introduction

Amorphous metal alloys exhibit some unique properties that make them interesting materials in heterogeneous catalysis [1, 2]. They may be used in the as-received state or as catalyst precursor. The amorphous state is thermodynamically unstable: amorphous alloys are prone to crystallize. This low thermal stability is a severe limitation if they are to be used in the as-received state for catalysis. However, this is not necessarily the case if the alloys are used as catalyst precursors.

Continuing our work in the field of amorphous alloy catalysis here we report about the characterization of two- and three-component palladium-containing amorphous alloys by various physical methods and the properties of catalysts prepared from them in the selective hydrogenation of acetylenes.

Experimental

Materials

$Pd_{25}Zr_{75}$, $Pd_{22}Cu_{10}Zr_{68}$ and $Pd_{72}Cu_{10}Si_{18}$ amorphous alloy ribbons were prepared by the rapid quenching technique, whereas $Pd_{25}Zr_{75}$ and $Pd_{25}Cu_{10}Zr_{65}$ amorphous alloy powders were made by mechanical alloying (Spex Mixer Mill, Mod. 8000).

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Methods

Differential scanning calorimetry (DSC, Perkin-Elmer DSC-7, 20 K min^{-1} heating rate), X-ray diffraction (XRD, Siemens D500, CuK_α radiation), and X-ray photoelectron spectroscopy (XPS, Kratos XSAM 800) were used for characterization of the alloy samples.

Treatments of the alloy samples included treatment in oxygen (553 K, 3–12 h) or hydrogen (373–553 K), and dissolution with hydrogen fluoride (0.035 M, 10–60 min).

Hydrogenation of phenylacetylene was carried out in an all-glass apparatus at ambient temperature and pressure (0.020 g alloy, 100 µl phenylacetylene, 900 µl heptane as solvent). Product composition was determined by gas chromatography (Carlo Erba Fractovap Mod G, 1.5 m CWAX 1000 column, TCD detector).

Results and discussion

The DSC traces of all samples showed exothermic peak(s) indicating the presence of amorphous phase(s) (Fig. 1). In addition, all XRD patterns (not shown) were very similar exhibiting the broad band centered at around 40° characteristic of amorphous materials. The only exception is $Pd_{25}Zr_{75}$ ribbon prepared by melt spinning. Sharp signals in the XRD pattern of this specimen indicates the presence of $PdZr_2$ intermetallic compound in addition to the low intensity halo of amorphous materials. Amorphous $Pd_{25}Zr_{75}$ alloys are known to crystallize into a mixture of $PdZr_2$ and α-Zr [3]. The behavior of the two PdCuZr specimens is similar: primary crystallization into PdZr and $CuZr_2$ takes place (Fig. 2a). The single peak in the DSC trace of the $Pd_{72}Cu_{10}Si_{18}$ ribbon (707 K), in turn, indicates polymorphous or eutectic crystallization.

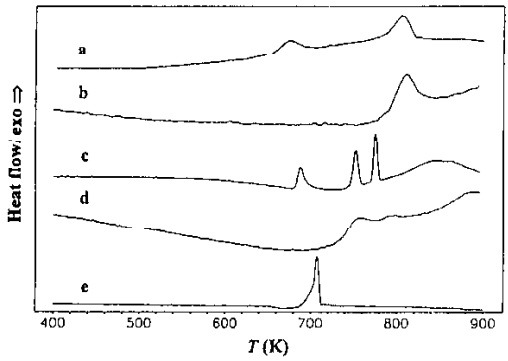

Fig. 1 DSC patterns of alloy samples in the as-received state. a) $Pd_{25}Zr_{75}$ ribbon, b) $Pd_{25}Zr_{75}$ powder, c) $Pd_{22}Cu_{10}Zr_{68}$ ribbon, d) $Pd_{25}Cu_{10}Zr_{65}$powder, e) $Pd_{72}Cu_{10}Si_{18}$ ribbon

Both the as-quenched ribbons and the as-milled powders exhibited rather low activity in the hydrogenation of phenylacetylene requiring long reaction time to achieve the consumption of 1 equivalent of hydrogen, i.e. the semihydrogenation of

the triple bond to yield the corresponding alkene (styrene). Various activation procedures, therefore, were applied to increase catalytic activities. On the basis of earlier literature observations [1, 2, 4–6] and our own experiences [7–9] treatments with oxygen or hydrogen, and with dilute hydrogen fluoride solution were employed.

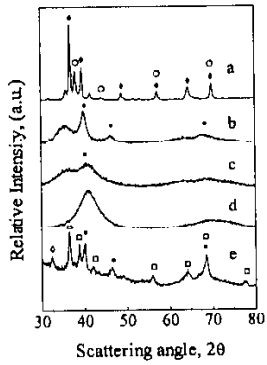

Fig. 2 X-ray diffractograms of selected alloy specimens. a) amorphous $Pd_{25}Cu_{10}Zr_{65}$ powder after DSC ♦ – $CuZr_2$ (JCPDS 18-466), o – PdZr (JCPDS 16-432), b) $Pd_{25}Zr_{75}$ ribbon after treatment with HF solution. • – Pd (JCPDS 5-681), c) $Pd_{22}Cu_{10}Zr_{68}$ ribbon after treatment with HF solution. • – Pd (JCPDS 5-681), d) $Pd_{72}Cu_{10}Si_{18}$ ribbon after treatment with HF solution, e) $Pd_{25}Zr_{75}$ ribbon after treatment with HF solution, after DSC • – Pd (JCPDS 5-681), □– $PdZr_2$ (JCPDS 18-962), ◊ – ZrH_2 (JCPDS 17-314)

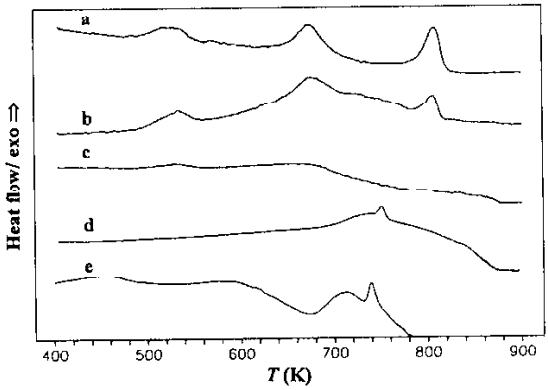

Fig. 3 DSC patterns of the $Pd_{25}Zr_{75}$ ribbon after various pretreatments. Treatment in oxygen at 553 K for a) 3 h, b) 6 h, c) 12 h; HF treatment for d) 15 min, e) 60 min

Treatment in oxygen of the $Pd_{25}Zr_{75}$ ribbon results in oxidation of the constituent elements and, therefore, the intensity of the exothermic DSC signals gradually decreases (Fig. 3, a–c). After a short, 3 h treatment at 553 K the sample is still amorphous, whereas after a 12 h treatment in oxygen the amorphous phase almost com-

pletely disappears. The broad peak appearing at about 750 K (Fig. 3b) is attributed to the reaction between PdO and Zr in the solid state [5]. The oxidation of both palladium and zirconium under these conditions is evidenced by XPS (Fig. 4A. a and b. Fig. 4B, a and b).

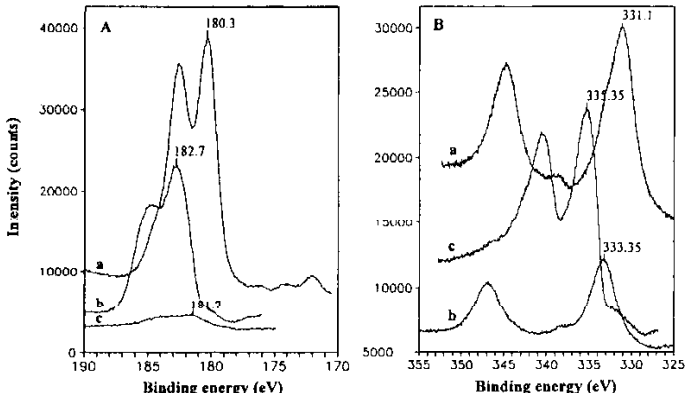

Fig. 4 Zr3d (A), and Zr3p and Pd3d (B) regions of the XPS spectrum of the $Pd_{25}Zr_{75}$ alloy ribbon. a) as-received, b) after treatment in oxygen at 553 K for 3 h, c) after treatment with HF for 15 min

Since HF is known to bring about dissolution of zirconium, this treatment is expected to result in marked structural changes (Fig. 3, d and e, Fig. 5). Two significant features are common in all HF-treated Zr-containing alloys. According to XRD the activation with HF induces Pd segregation from the matrix (Fig. 2, b and c). On the other hand, a new ZrH_2 phase always appears during crystallization. The peaks in the DSC curve of the HF-treated $Pd_{25}Zr_{75}$ ribbon correspond to crystallization into Pd, $PdZr_2$ and ZrH_2 (Fig. 2, c). The two PdCuZr specimens, in turn, crystallize into

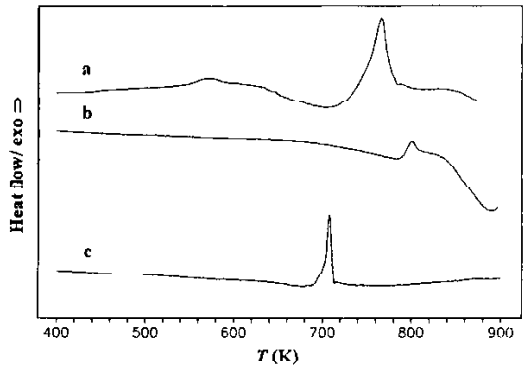

Fig. 5 DSC patterns of various alloy samples after HF dissolution (15 min). a) $Pd_{22}Cu_{10}Zr_{68}$ ribbon, b) $Pd_{25}Cu_{10}Zr_{65}$ powder, c) $Pd_{72}Cu_{10}S_{18}$ ribbon

PdZr, $CuZr_2$ and ZrH_2. In sharp contrast, no apparent changes in the bulk structure of the $Pd_{72}Cu_{10}Si_{18}$ ribbon are induced by HF treatment (Fig. 2, d).

Due to Pd segregation and zirconium dissolution the surface after HF treatment of the Zr-containing alloys becomes depleted in zirconium and rich in palladium as evidenced by XPS (Fig. 4A, c and Fig. 4B, c).

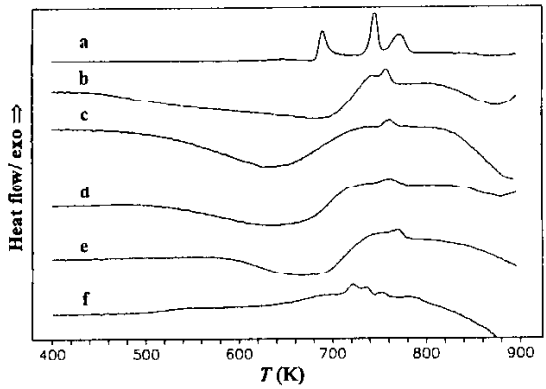

Fig. 6 DSC patterns of the $Pd_{22}Cu_{10}Zr_{68}$ ribbon after combinative treatments. a) treatment in oxygen (3 h), b) treatment in oxygen (3 h) then in hydrogen (40 min), c) treatment in oxygen (3 h) then in hydrogen (3 h), d) treatment in hydrogen (3 h), e) treatment in oxygen (3 h) then with HF (15 min), f) HF treatment (15 min) then treatment in oxygen (3 h)

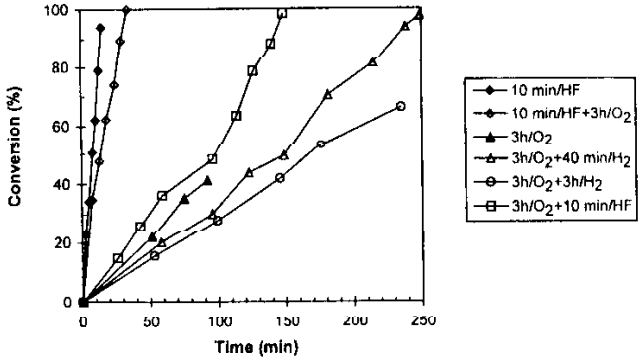

Fig. 7 Activity of the $Pd_{22}Cu_{10}Zr_{68}$ ribbon after various pretreatments in the hydrogenation of phenylacetylene

The DSC results observed with specimens, which were exposed to the combinations of the above pretreatments, are presented in Fig. 6. Most of the DSC traces testify to marked changes relative to the as-received state. It is seen that a 3 h oxidation

of the PdCuZr ribbon alone causes only minor changes (Fig. 6, a), whereas a treatment in hydrogen (Fig. 6, d) or the combination of oxidation with any other treatment results in the complete loss of the original DSC pattern (Fig. 6, b, c, e and f). DSC patterns of the PdCuZr alloy powder (not shown) are similarly rather complex. The $Pd_{72}Cu_{10}Si_{18}$ ribbon, again, appears to be stable under any pretreatments.

Most of the pretreatments proved to be highly beneficial with respect to the activity of the alloy specimens in the hydrogenation of phenylacetylene. Representative results of catalytic studies using the $Pd_{22}Cu_{10}Zr_{68}$ ribbon are given in Fig. 7. The most dramatic effect is brought about by HF treatments either alone or combined with oxidation. Apparently, the highly increased activity of the pretreated samples is accounted for by surface Pd enrichment evidenced by the physical characterization techniques discussed above. Moreover, selectivities are also enhanced significantly (the best results, about 96% styrene at 50% hydrogen uptake, were achieved with the specimens treated with HF). This observation, however, needs further clarification.

Conclusions

Amorphous PdZr and PdCuZr alloy ribbons and powders were shown by DSC, XRD and XPS to undergo substantial structural and surface changes after treatments in oxygen, hydrogen or with dilute hydrogen fluoride solution. Surface palladium enrichment accounts for their high catalytic activity in the hydrogenation of phenylacetylene.

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