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Spontaneous Oxidization of an Amorphous $Zr_{70}Au_{30}$ Alloy in Air*

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Synopsis

An amorphous $Zr_{70}Au_{30}$ alloy prepared by the melt-quenching technique was found to possess an extremely high oxidization tendency in air even at room temperature, even though the other Zr-based amorphous alloys remain unchanged in the same environment. Upon oxidization, the amorphous structure changes into a duplex crystalline structure consisting of a monoclinic ZrO_2 matrix including fcc Au particles with a size as fine as about 2 nm at an inter-particle spacing of about 4 nm. The oxidization tendency depends strongly on the humidity in air and becomes remarkable with increasing humidity. Furthermore, the oxidization causes a spontaneous pulverization of the ribbon into fine powders consisting of ZrO_2 and Au. The reason for the exceptionally high oxidization only for the $Zr_{70}Au_{30}$ amorphous alloy was inferred to be due to a combination effect of a weak attractive bonding nature between Zr and Au and a great catalytic ability of Au.

I. Introduction

Since an amorphous phase is thermodynamically nonequilibrium, an atomic configuration on the surface layer is in a high energy state and hence an amorphous alloy is thought to possess a highly active reactivity against various kinds of environmental gases. As a typical example, high catalytic activities for CO hydrogenation are known for the amorphous alloys of Fe-Ni-P-B[1], Ni-Zr[2], Pd-Zr[3] and Cu-Zr[4] systems. From these studies, in the view to produce a good catalytic material with high reactivity, it has been pointed out that it is very important to find amorphous alloys which oxidize easily, accompanied with a self-breaking action of the surface oxide layer. Most recently, the present authors have found that zirconium-rich Zr-Au amorphous

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alloys oxidize very actively during room temperature aging in air and pulverize into fine powders. The aim of this paper is to present the changes in the microstructure and alloy component of the oxidized $Zr_{70}Au_{30}$ amorphous alloy upon room temperature aging in air with different humidities.

II. Experimental Procedure

A mixture of 99.6 wt% pure zirconium and 99.99 wt% pure gold was melted under a purified and gettered argon atmosphere on a water-cooled copper mould in an arc furnace. The ingot was repeatedly turned over and remelted to ensure homogeneity. The composition of alloy reported is the nominal one since the loss during melting was negligible. An amorphous $Zr_{70}Au_{30}$ ribbon specimen with about 0.02 mm thickness and about 1 mm width was prepared from the mixed alloy under a purified argon atmosphere using a single roller melt spinning apparatus. The amorphous nature of the as-quenched ribbon was confirmed by X-ray diffractometer using Cu-K α radiation and with a differential thermal analyzer. The changes in the structure, alloy component and morphology of the amorphous ribbon during room temperature (R.T.) aging in air with different relative humidities ranging from ≈ 0 to 100 % were examined as a function of aging time by X-ray diffraction and optical, transmission and analytical scanning electron microscopies.

III. Results

Figure 1 shows the optical micrographs revealing the change in the surface structure of $Zr_{70}Au_{30}$ amorphous ribbon upon R.T. aging in air with a relative humidity of about 62 %. In as-quenched state, no contrast indicating the existence of any precipitates in the amorphous matrix is seen, even though a high density of concavities caused by the inlet of argon gas are observed on the ribbon surface which was contacted with roller (Fig. 1d). A dark contrast which looks like a precipitate begins to appear for the sample aged for 2 to 3 days and its region grows gradually with aging time. As exemplified in Fig. 1, such dark regions appear more easily at the edge of the ribbon sample and on the roller surface with concavities, probably because of the ease of an inhomogeneous nucleation of the precipitate. Additionally, it is seen that the morphology of each precipitate is spherical at the initial stage and then changes to a caterpillar-like shape by incorporation with proceeding aging.

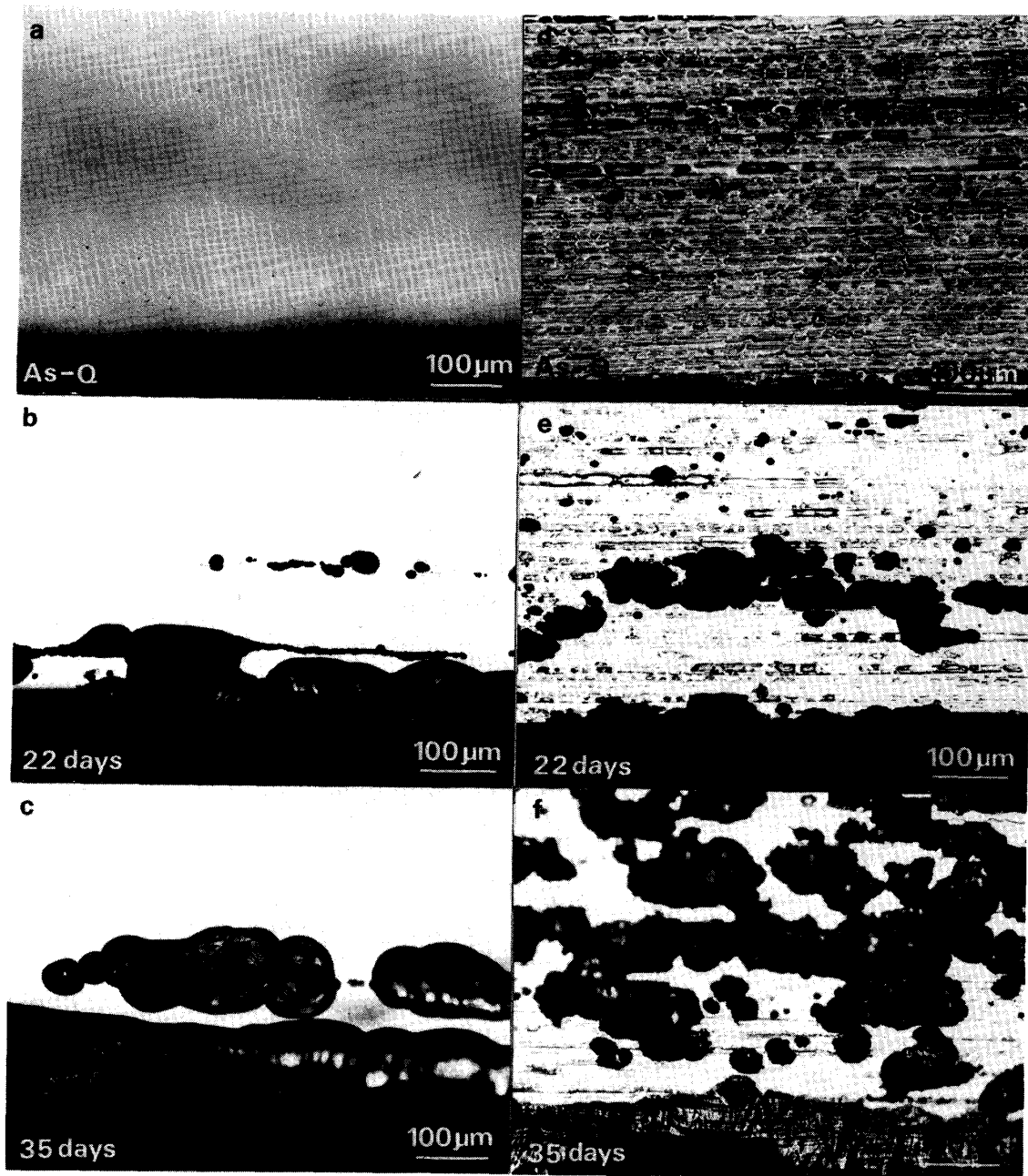


Fig. 1

Optical micrographs showing the change in the surface structure of an amorphous $Zr_{70}Au_{30}$ ribbon upon R.T. aging in air with a relative humidity of about 62%. (a to c) Freely solidified surface and (d to f) surface contacted with roller.

In order to identify the structure of the precipitate with dark contrast, the X-ray diffraction analysis was made for $Zr_{70}Au_{30}$ samples in as-quenched and aged states. As shown in Fig. 2, the as-quenched sample shows two broad peaks which are typical of an amorphous structure, but the sample aged for 37 days exhibits a superposition of amorphous and crystalline peaks. As identified for the X-ray diffraction peaks of the sample aged for 215 days, the precipitate is composed of an fcc gold and a monoclinic ZrO_2 , and their lattice spacings are found to be the same as the previously reported values of $a=0.408$ nm for gold[5] and $a=0.522$ nm, $b=0.527$ nm, $c=0.538$ nm and $\beta=80^\circ 32'$ for ZrO_2 [5]. In order to reconfirm the alloy component in the spherical precipitates, X-ray fluorescence images of oxygen, gold and zirconium were examined for the sample aged for 2 days in air with a relative humidity of 100 %. Figure 3 shows the scanning electron topological image (a) and X-ray images showing the distribution of oxygen (b), gold (c) and zirconium (d) elements. Additionally, Fig. 4 shows the composition distribution of oxygen, gold and zirconium elements along the line marked in Fig. 3 (a). The features of Figs. 3 and 4 are summarized as follows; (1) The spherical precipitates contain oxygen content much higher than that of the amorphous matrix phase. (2) The concentrations of zirconium and gold in the precipitates are lower by about 18 % and 26 %, respectively, as compared with those in the amorphous matrix phase. Accordingly, these results allow us to reconfirm that the aging-induced products are mainly composed of two phases of ZrO_2 and gold. The reason why the intensity of oxygen and zirconium decreases rapidly around a central region in Fig. 4 is due to the result that the detection of X-ray is distributed by the upheaval of the precipitate. In addition to the topological image shown in Fig. 3 (a), the disturbance also demonstrates clearly that the precipitate protrudes from the ribbon surface.

Additionally, the microstructure of the precipitate consisting of ZrO_2 and gold was examined by TEM for the $Zr_{70}Au_{30}$ sample aged for 100 days in air. As exemplified in Fig. 5, the bright field image reveals that the structure consists of two phases and the size of the second phase corresponding to a number of small black contrasts is as fine as about 2 nm. The selected area diffraction pattern also indicates that the duplex phases produced upon oxidization consist of fcc gold and monoclinic ZrO_2 , in accordance with the result (Fig. 2) obtained by X-ray diffraction. Considering the facts that the alloy component is zirconium-rich and the transparent ability of accelerated electrons is much lower for gold than for ZrO_2 , it is reasonably concluded that a

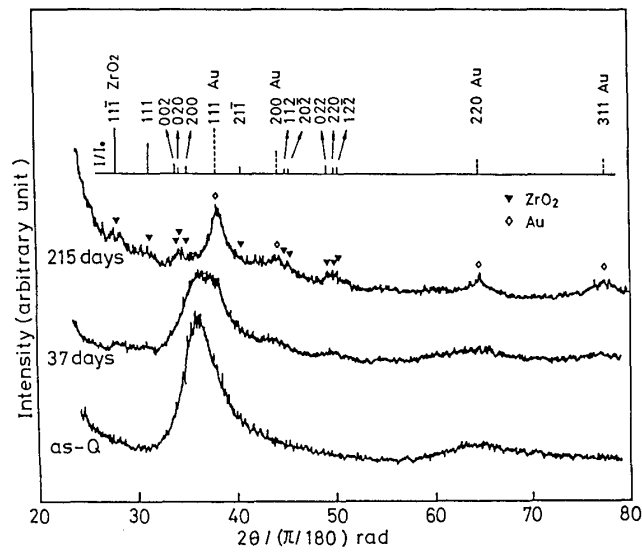


Fig. 2 X-ray diffraction patterns showing the change in the structure in an amorphous $Zr_{70}Au_{30}$ alloy upon R.T. aging in air with a relative humidity of about 62 %.

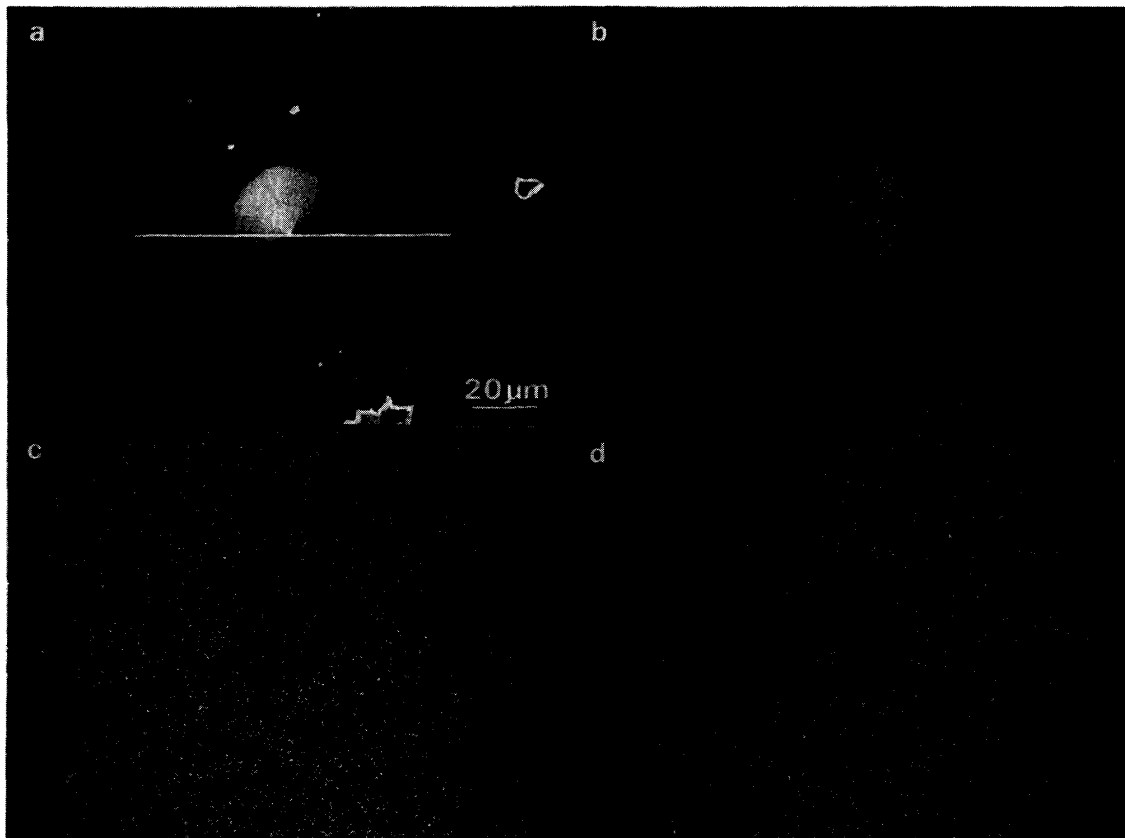


Fig. 3 Scanning electron micrographs showing the topological state (a) on the freely solidified surface and X-ray images showing the distribution of oxygen (b), gold (c) and zirconium (d) elements for an amorphous $Zr_{70}Au_{30}$ alloy aged for 2 days at R.T. in air with a relative humidity of 100 %.

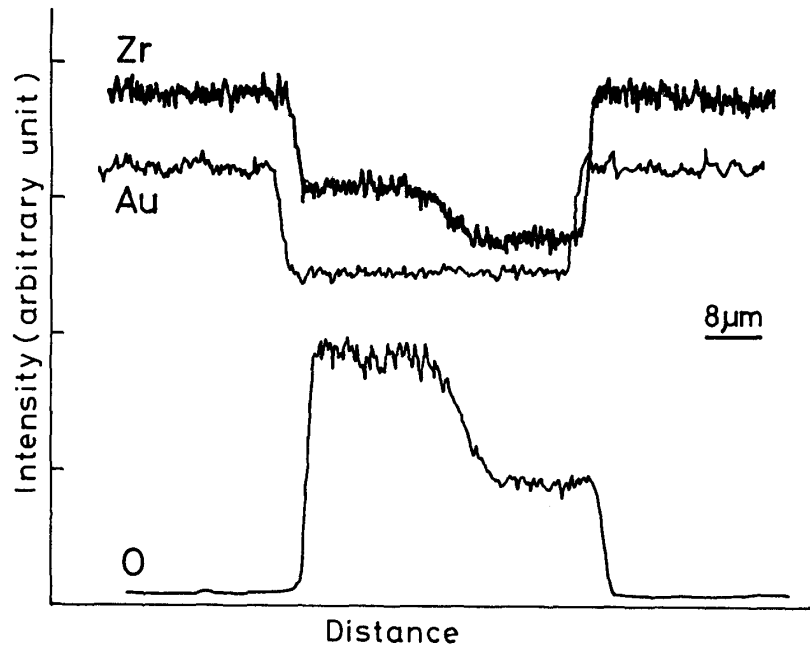


Fig. 4

Normalized intensity profiles of zirconium, gold and oxygen elements as a function of distance analyzed along the line marked in Fig. 3 (a) for an amorphous $Zr_{70}Au_{30}$ alloy.

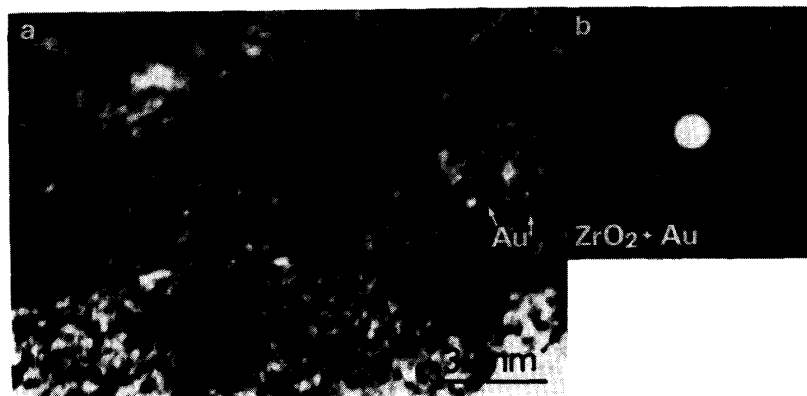


Fig. 5

Transmission electron micrograph and selected area diffraction pattern showing the completely oxidized structure in an amorphous $Zr_{70}Au_{30}$ alloy aged for 100 days at R.T. in air with a relative humidity of 62 %.

small area fraction of precipitates with black contrast corresponds to gold and the matrix phase is ZrO_2 .

Thus, the $Zr_{70}Au_{30}$ amorphous alloy changes into the very fine duplex crystalline phases consisting of monoclinic ZrO_2 matrix and gold particles with a size as small as about 2 nm upon room temperature aging in air. It appears important to point out that such a fine duplex structure is formed only through the oxidization of the highly unstable amorphous phase and is not obtainable by the conventional solidification and heat-treatment techniques. Most recently, the fine duplex alloy consisting of ZrO_2 and gold prepared by aging the $Zr_{70}Au_{30}$ amorphous alloy at R.T. in air has been found[6] to exhibit an excellent catalytic activity for hydrogenation of carbon monoxide and the main reason for the achievement of the good catalytic property has been thought[6] to be due to a high reactivity of ultra-fine gold particles dispersed isolately and densely in ZrO_2 matrix.

Additionally, the ductile ribbon sample was found to pulverize spontaneously together with the oxidization-induced structural change of the amorphous phase to the duplex phases of ZrO_2 and gold. Figure 6 shows the scanning electron micrographs revealing a spontaneously pulverizing process from the $Zr_{70}Au_{30}$ amorphous ribbon into the crystallized powders. The photographs may allow us to infer the following pulverizing process; (1) The oxidization from amorphous to ZrO_2 and gold is preferentially generated at the ribbon edge and proceeds into the central area, accompanied with a significant change in volume. (2) The change in the volume due to the structural change results in the initiation of a number of microcracks, probably because of an extremely poor resistance of the resultant duplex phases against a rather high internal stress caused by the volume change. Accordingly, the spontaneous pulverization of the amorphous ribbon into powders upon oxidization may be concluded to result from a large volume change through the structural change and an extremely brittle nature of the resultant duplex phases. Figure 7 shows the surface morphology of the $Zr_{70}Au_{30}$ powders prepared by the spontaneous pulverization through the R.T. oxidization. The as-pulverized powders have a morphology of irregularly shaped polygons, but a slight trace of the original ribbon shape is seen.

By stamp milling the spontaneously pulverized powders for a time as short as 1 min, the powder size decreases drastically from about 10 μm to about 1 μm as exemplified in Fig. 8, because of the highly brittle nature of the oxidized alloy, and the morphology of the milled powders is that of polygons without any trace of the original ribbon shape. The further increase in the stamp milling time resulted in a

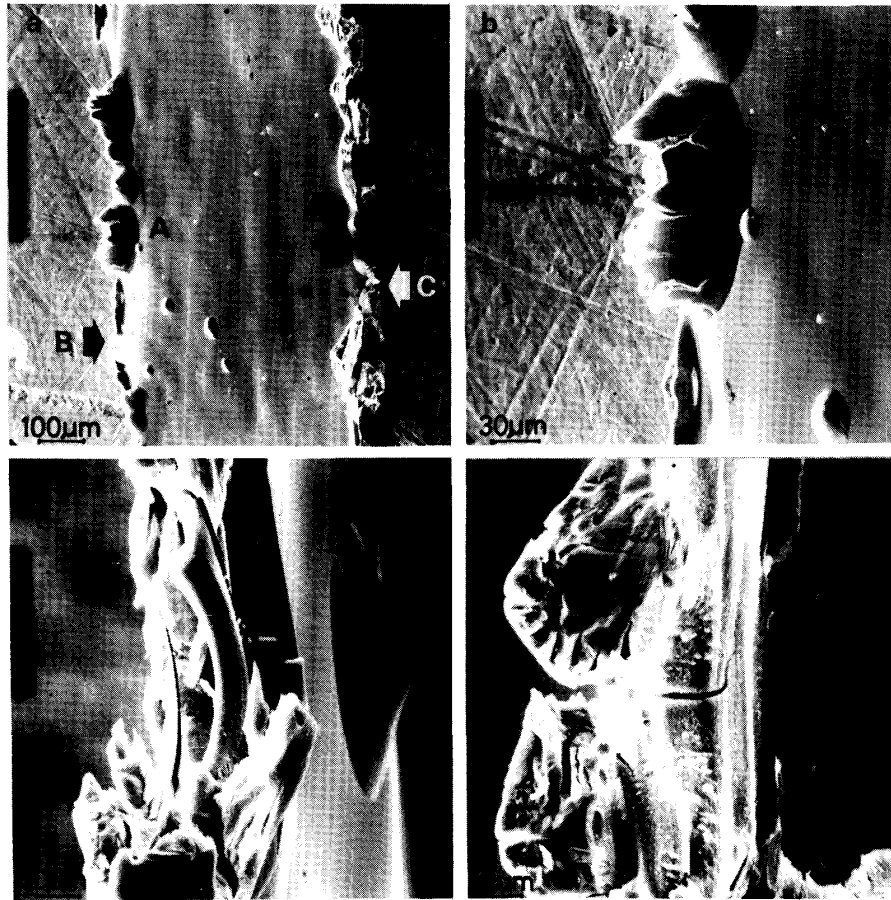


Fig. 6 Scanning electron micrographs showing the morphology of the ribbon sample at the initiate stage of oxidation for an amorphous $Zr_{70}Au_{30}$ alloy aged for 2 days at R.T. in air with a relative humidity of 100 %. (b) is an enlarged micrograph taken from the region A in (a), and (c) and (d) present enlarged micrographs taken from the directions of the arrows B and C, respectively, marked in (a).



Fig. 7

Scanning electron micrograph showing the morphology of $Zr_{70}Au_{30}$ alloy powders pulverized spontaneously during R.T. aging for 20 days in air with a relative humidity of 62 %.

further decrease in the powder size, e.g., to about 100 nm after milling for 5 min, but simultaneously the fine powders began to incorporate with each other during milling probably because of a highly unstable energy state on the surface and an increased specific surface area, and the decrease in the powder size tends to be saturated. Anyhow, it appears important to note that the chemically active powders with a size as fine as about 100 nm can be obtained by milling the spontaneously pulverized powders consisting of ZrO_2 and gold phases for a time as short as several minutes.

In general, the ease of oxidization depends on atmosphere as well as aging temperature. Therefore, the influence of the humidity in air on the oxidization behavior of the $Zr_{70}Au_{30}$ amorphous alloy was examined as a function of relative humidity at R.T. As typical examples, the optical micrographs shown in Fig. 9 reveal that the increase in the humidity accelerates remarkably the oxidizing reaction into ZrO_2 and gold phases and results in an enhanced formation of the very fine pulverized powders. On the other hand, the decrease in the relative humidity to below 20 % suppresses very drastically the oxidizing tendency and the $Zr_{70}Au_{30}$ amorphous alloy remains unchanged even after an aging time as long as 200 days. The drastic effect of the humidity on the oxidizing tendency of the $Zr_{70}Au_{30}$ amorphous alloy suggests that the reaction of the amorphous to ZrO_2 and gold phases is mainly dominated by the concentration of H_2O in air.

IV. Discussion

In this section, we shall discuss the reason why the $Zr_{70}Au_{30}$ amorphous alloy exhibits a strong oxidization tendency even at a low temperature of about 293 K, accompanied with the spontaneous pulverization into powders. It is well known[7] that an amorphous single phase is formed at a number of alloy compositions in binary Zr-X (X=Fe, Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Pt or Au) systems. However, the alloy system which exhibited the strong oxidization tendency during R.T. aging in air was limited only to Zr-Au system despite the fact that the gold is the most noble metal. The amorphous structure in the other systems remains unchanged even after the R.T. aging for a time as long as about 6 months[8], except that the surface of copper-rich Cu-Zr amorphous alloys changed into a copper-like red color. Thus, the oxidizing tendency of the amorphous phase depends strongly on the alloy component and the coexistence of gold and zirconium is concluded to enable to promote the structural change to ZrO_2 and gold through the oxidization. Furthermore, the existence of H_2O

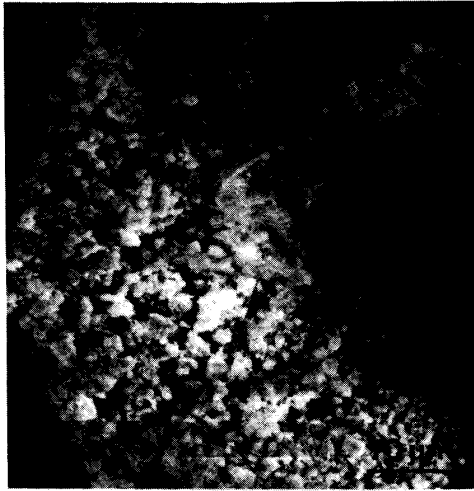


Fig. 8

Scanning electron micrograph showing the morphology of $Zr_{70}Au_{30}$ alloy powders produced by comminuting the spontaneously pulverized powders shown in Fig. 7 for 1 min.



Fig. 9

Optical micrographs showing the influence of the humidity in air on the pulverized process of an amorphous $Zr_{70}Au_{30}$ alloy. (a) R.T. aging for 5 days in air with a relative humidity of 100 %, and (b) R.T. aging for 200 days in air with a relative humidity below 20 %.

accelerates the oxidization.

Considering the fact[9] that gold is noblest among the X metals, it is concluded that the reactivity of the X elements against oxygen is not related to the ease of the oxidization of the Zr-X binary amorphous alloys. As a peculiar nature only for the Zr-Au amorphous phase as compared with the other Zr-X amorphous alloys, one may point out the following three results; (1) The amorphous formation range is limited to a very narrow range in the vicinity of $Zr_{70}Au_{30}$ [7] and the amorphous-forming tendency is inferred to be lowest among the Zr-X amorphous alloys even though its formation ability is not quantitatively measured, (2) the atomic size of the X metals is largest for gold[10], and (3) the reactivity of the X metals against oxygen is lowest for gold[9], implying that the relative difference against zirconium for the reactivity with oxygen is largest for gold. Additionally, the duplex ZrO_2+Au phases have been reported[6] to be an active catalyzer for CO hydrogenation. The low amorphous-forming tendency of the Zr-Au alloy suggests that the attractive interaction between zirconium and gold is not always strong and the phase separation of zirconium and gold is apt to occur on the microscale of atomic size. Furthermore, the short-range dense random-packing structure in the amorphous Zr-Au alloy contains rather large holes because of the largest atomic size of gold and hence it appears easy for the Zr-Au amorphous phase to catch oxygen atoms which are essential for the oxidization. Also, the coexistence of gold and zirconium in the amorphous phase is inferred to enhance the dissociation of H_2O to oxygen and hydrogen on the surface layer of the amorphous phase.

From the above discussion, the structural change of the Zr-Au amorphous phase into ZrO_2 and gold upon oxidization may be summarized to occur through the following processes; (1) Absorption of H_2O . The absorption occurs preferentially at the ribbon edge and on the rough surface with concavities. (2) Dissociation of H_2O to H_2 and O by the assist of gold or gold+zirconium which is inferred to have an effective catalytic action. (3) Easy dissolution of H_2 and O into the Zr-Au amorphous phase because of the existence of large holes through the largest atomic size of gold. (4) Preferential reaction between zirconium and oxygen to form ZrO_2 , resulting from the high tendency of the phase separation to zirconium and gold on the atomic scale due to a weak attractive interaction, the large negative free energy for the formation of ZrO_2 and the highest resistance of gold against oxidization. (5) Progress of the phase decomposition of the amorphous phase into ZrO_2 and gold through the increase in the supplied amount

of oxygen, i.e., with increasing aging time.

The spontaneous pulverization of the amorphous ribbon into fine powders was pointed out to be closely related to the volume expansion caused by the oxidization. However, the hydrogen which was generated by the dissociation of H_2O is also thought to play an important role on the spontaneous pulverization. Accordingly, the pulverization phenomenon is considered to occur by a combination effect of the large expansion of volume by the structural change of the amorphous into ZrO_2 and gold phases, a highly brittle nature of ZrO_2 phase and the accumulation of a high concentration of hydrogen.

In conclusion, the information that only the Zr-Au amorphous alloy among a number of amorphous alloys in Zr-X binary systems exhibits an extremely strong oxidization accompanied with a spontaneous pulverization into powders during R.T. aging in air is very important in the view of the production of highly active catalytic materials. The catalytic characteristics of the fine powders consisting of ZrO_2 and gold prepared by oxidizing the $Zr_{70}Au_{30}$ amorphous ribbon have presently been studied in various kinds of chemical reactions and the outstanding catalytic activity will be presented elsewhere in near future.

V. Summary

The oxidization behavior of an amorphous $Zr_{70}Au_{30}$ alloy during room temperature aging in air was examined by various means of optical microscopy, X-ray diffraction and transmission and analytical scanning electron microscopies etc. The results obtained are summarized as follows:

(1) The oxidization at R.T. takes place preferentially at the ribbon edge and on the rough ribbon surface with a high degree of ruggedness and progresses gradually into the central area with aging time.

(2) The oxidization-induced product consists of a monoclinic ZrO_2 and an fcc gold and hence the oxidization is concluded to result in the structural change from the amorphous single phase to the duplex crystalline phases of ZrO_2 and gold. The particle size and inter-particle spacing of gold phase are as fine as about 2 nm and 4 nm, respectively.

(3) The ease of the oxidization is significantly affected by the humidity in air and there is a distinct tendency that the higher the humidity the greater is the oxidizing tendency. Also, the oxidization is completely suppressed in air with a relative humidity below 20 %.

(4) The ductile Zr-Au amorphous ribbon was spontaneously pulverized

to fine powders during the structural change caused by the oxidization. The pulverized powders were easily comminuted to powders with a size as fine as about 100 nm by a milling treatment for several minutes.

(5) From the result that the easy oxidization occurs only for the $Zr_{70}Au_{30}$ amorphous alloy among a number of zirconium-transition metal amorphous alloys, the oxidization was interpreted to result mainly from a combination effect of a weak attractive interaction between zirconium and gold and a high catalytic ability of gold element.

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