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Alloying of Yb–Cu and Yb–Ag utilizing liquid ammonia metal solutions of ytterbium

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Abstract

In the course of the studies on preparation of novel compounds using the dissolution of Eu or Yb metals in liquid ammonia, the formation of Yb–Cu and Yb–Ag intermetallic films has been found. When Cu or Ag metal powders were placed in a reactor containing a solution of Yb metal in liquid ammonia, the dissolved Yb readily react with the Cu or Ag metal particles to form surface alloy compounds. X-ray diffraction of Yb–Cu showed that upon thermal treatment above 673 K, the Yb metal deposited on the Cu particles reacted together to be transformed into the $YbCu_{6.5}$ intermetallic compound. A characteristic endothermic peak at 749 K, due to alloying of Yb–Cu, was observed by the differential scanning calorimeter measurements. By use of the high reactivity of liquid ammonia metal solutions of ytterbium, it was found that the ytterbium intermetallic films were readily formed under mild conditions. Yb–Cu and Yb–Ag exhibited enhanced catalytic activity for the hydrogenation of ethene as a result of alloying.

Keywords: Alloying; Rare-earth; Ytterbium; Copper; Silver; Intermetallics; Catalyst; Liquid ammonia; Hydrogenation; Ethene

1. Introduction

Europium and ytterbium metals readily dissolve in liquid ammonia to yield a homogeneous solution [1]. By the use of such dissolution of Eu and Yb metals, we have developed methods for the preparation of novel Eu or Yb-containing materials (rare-earth-doped oxides, rare-earth intermetallics). Much attention has been directed toward their surface properties, especially catalysis [2]. It has been shown that they exhibit unexpected activity and selectivity for various reactions.

Since rare earth (R) elements have specific electron configurations based on $4f$ orbitals, they are expected to catalyze many intriguing reactions that cannot be realized with d-block transition metals. Recently there has been a growing interest in heterogeneous catalysis of rare-earth elements and their related compounds [3].

In this paper, Cu and Ag metal powders readily react with Yb metal solutions in liquid ammonia to form the intermetallic surface compounds. Their surface properties are characterized by the catalysis for the hydrogenation of ethene.

2. Experimental

Yb (99.9%) was obtained from Santoku Co. Ammonia produced by Iwatani Ind. Ltd. was dried through calcium oxide and subsequently through a sodium hydroxide column. Cu powders (grade: FMP) were obtained from Fukuda Metal Film and Powder Ind. Ltd., and further reduced with hydrogen at 423 K. The surface areas of Cu thus treated were $1.9\,m^2\,g^{-1}$ according to nitrogen adsorption at 77 K. Ag powders were conventionally prepared by an incipient wetness technique; i.e., the $AgNO_3$ salt decomposed in basic solutions, forming precipitates of AgOH. The resulting precipitate was filtered off, washed with distilled water, dried, calcined and reduced at 423 K with hydrogen.

Cu or Ag powers were placed in a Schlenk tube, cooled by a dry ice/methanol bath, and then, purified ammonia gas was liquefied. Yb metal was added to react with Cu or Ag. After the reaction, the vessel was allowed to warm to room temperature and the excess ammonia

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was removed leaving Yb–Cu or Yb–Ag. All operations were carried out without exposure to air.

3. Results and discussion

In a typical preparation of a 10 at% Yb–Cu sample, the reduced Cu powders were placed in liquid ammonia and Yb turnings were added in limited amounts with stirring around 195 K. Upon dissolution of Yb metal in liquid ammonia, the solution was colored blue, which is characteristic of the ammoniated electrons [1]. Subsequently the blue color gradually disappeared presumably as a result of the reaction of Cu particles with the Yb metal dissolved in liquid ammonia. X-ray diffraction (XRD) of the Yb–Cu samples thus prepared was taken (Fig. 1). For Yb–Cu as prepared, the host Cu showed no XRD changes in lattice parameters of its cubic structure, while there were no diffraction peaks derived from ytterbium. However, the XRD pattern of Yb–Cu changed upon thermal treatments with evacuation to ca.10^{-4} Torr with an oil diffusion pump. Upon heating around 673 K, diffraction peaks corresponding to the hexagonal structure of $YbCu_{6.5}$ [4] were first observed, and further heating led to an increase in the peak intensity. This was consistent with differential scanning calorimeter (DSC) measurements: the DSC traces exhibited a characteristic endothermic peak at 749 K, due to alloying of Yb–Cu. In XRD of Fig. 1, the Cu metal phase was still observed in substantial quantity. Thus the Yb–Cu samples may be those in which the Yb metal spreads over the Cu surface and reacts when heated to form a surface intermetallic phase [5–7]. When the amount of Yb added in Yb–Cu was changed, the Yb addition of more than 10 at% led to clear diffraction peaks due to $YbCu_{6.5}$ as shown in XRD (Fig. 2).

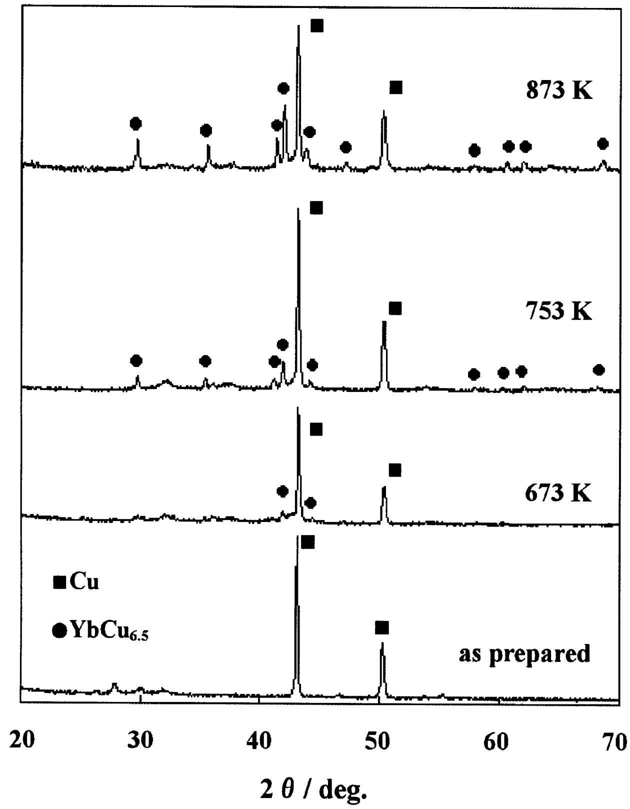

Fig. 1. Changes in the X-ray diffraction patterns of 10 atomic % Yb–Cu with the thermal treatments. The thermal treatments were carried out in a vacuum (ca. 10^{-4} Torr) at each temperature for 2 h.

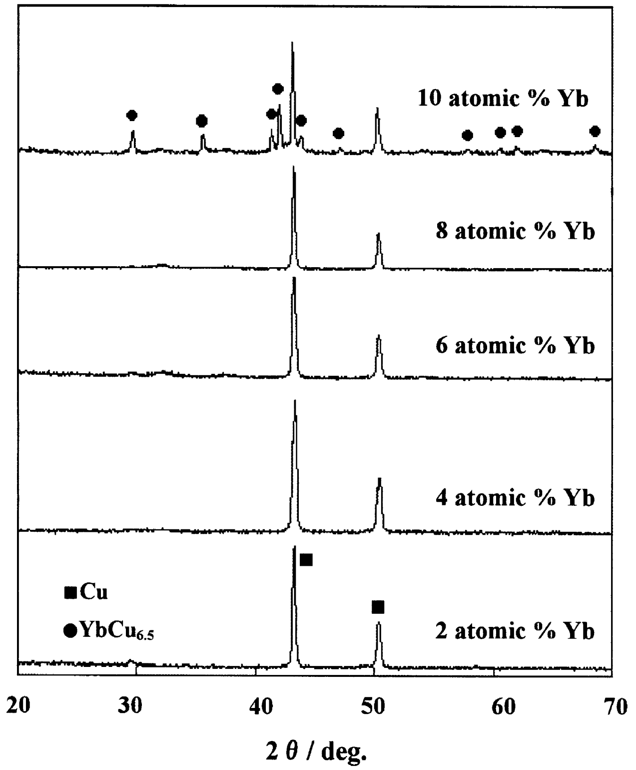

Fig. 2. XRD of Yb–Cu with different Yb contents. The Yb–Cu samples were pretreated with evacuation at 873 K for 2 h.

The changes in structure with the thermal treatment of Yb–Cu markedly reflected the surface property, especially in the catalytic property which was evaluated by the hydrogenation of ethene as a test reaction. The catalytic reactions were examined using a conventional gas circulation system with a reaction space of about 221 cm^3. As shown in Fig. 3, the catalytic behavior of Yb–Cu also varied markedly with the heat treating temperatures. A maximum activity was obtained when Yb–Cu was treated in the range of about 573–750 K. These temperatures were close to those causing the alloying of Yb–Cu. In particular, catalytic activity increased by over two orders of magnitude with a change in temperature from 293 to 573 K. This is probably due to the reconstruction of surface morphology with increasing heat treating temperatures. For the characteristics of adsorption, Cu alone adsorbed a negligible amount of hydrogen at room temperature,

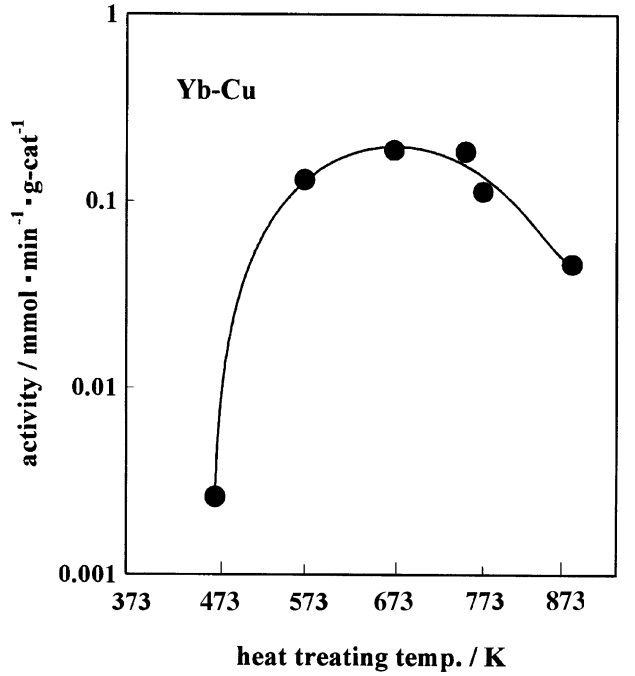

Fig. 3. Catalytic activity of 10 at% Yb–Cu with the thermal treatments. The hydrogenation of ethene was carried out at 413 K (C_2H_4 = 30 Torr; H_2 = 60 Torr). The Yb–Cu sample was evacuated at elevated temperatures for 2 h prior to the reaction.

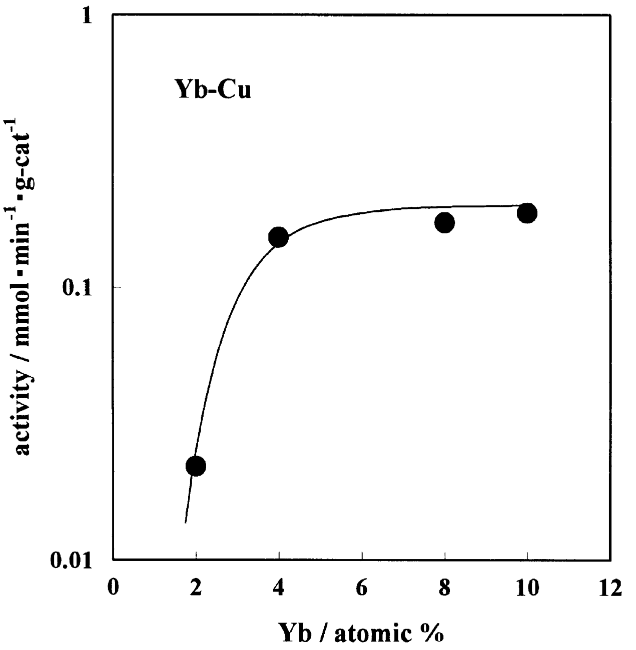

Fig. 4. Effects of addition of Yb to Cu powders on the catalytic activity. The hydrogenation of ethene was carried out at 413 K (C_2H_4 = 30 Torr; H_2 = 60 Torr).

while the Yb-added Cu exhibited the hydrogen adsorption of 42.1 μmol g^{-1} when pretreated at 673 K.

The catalytic behavior of Yb–Cu varied markedly with the amount of Yb added (Fig. 4). Cu showed negligible activity, and it was used more efficiently when doped with Yb metal. The first-order rate constant k was used as an index of the activity; the activity for the Yb–Cu system increased by over one order of magnitude with increasing Yb content. The catalytic activity was not monotonically proportional to the Yb addition; it increased abruptly with the addition of 2–4 at% Yb, but less progressively for further addition. As shown in Fig. 2, the formation of intermetallic surface compound was not detected in XRD in such a low Yb content (2–4 at%). When once the surface Yb intermetallics layer is formed on the Cu particles, the activity shows no great change. Such dependence of the Yb addition on the activity indicates that the existence of some synergetic effects between the copper and ytterbium rather than individual metals constitutes active sites. This synergy is a complex effect which depends upon many factors including the electronic effect of Yb metals and the geometrical effect of surface structure. Studies on rare earth-transition metal intermetallics have made it abundantly clear that there is electron transfer from the rare-earth to the transition metal [8].

Upon the addition of Yb to Ag, Yb–Ag exhibited behavior essentially similar to the Yb–Cu system. XRD and DSC of Yb–Ag showed the formation of alloys upon heating around 745 K. Ag was catalytically inactive, but alloying of Yb–Ag resulted in enhanced activity for the hydrogenation of ethene. It has been shown that by use of the high reactivity of Yb dissolved in liquid ammonia solutions, the Yb–Cu and Yb–Ag intermetallic films on Cu and Ag, respectively, were readily formed under mild conditions. Alloying of Yb–Cu and Yb–Ag in the surface layer led to drastic changes in catalysis at the same time.

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