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Amorphous alloys as catalyst precursors

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Abstract

The most attractive characteristic of the amorphous alloy is the singlephase nature forming a solid solution exceeding the solubility limit at equilibrium. This characteristic enable to tailor new alloys with unique and useful properties.
The chemically homogenous single phase nature capable of forming a solid solution supersaturated with various elements added intentionally is the most important characteristic for obtaining the materials having new propietes.

Key words: *amorphous alloys, anode materials for electrolysis, catalysts.*

Introduction

Amorphous alloys have a potential to produce new catalysts or precursors of new catalysts for special reactions, because they form single-phase solid solutions containing various effective elements exceeding the solubility limit in the equilibrium state. In general, the alloying with effective elements changes the electronic state of the alloy-constituent elements. It is also known that different reactant species sometimes coordinate preferentially to different elements on the catalyst surface. Accordingly, for amorphous alloys, new synergistic effects of different elements and modification of the electronic state of the catalyst elements can be expected.

Recently, particular emphasis has been devoted to use amorphous alloys as catalyst precursors rather than catalysts themselves, because oxidation and reduction strongly affect their physical and chemical properties. Controlled oxidation of amorphous alloys is known as an interesting technique for preparing supported metal catalysts with unique structure and morphology. The metal-supported oxides can be formed by selective oxidation of one or more alloy constituents.

We tried to tailor new catalysts from amorphous alloys for the prevention of a concentration increase of the greenhouse gases and saving the ozone layer in addition to abundant energy supply. Based on these investigations, we proposed the "green" materials consisting of four subjects as shown in Fig.1 . All these problems can be solved by tailoring novel materials having attractive and unique properties such as catalytic, electrocatalytic and corrosion-resistant properties.

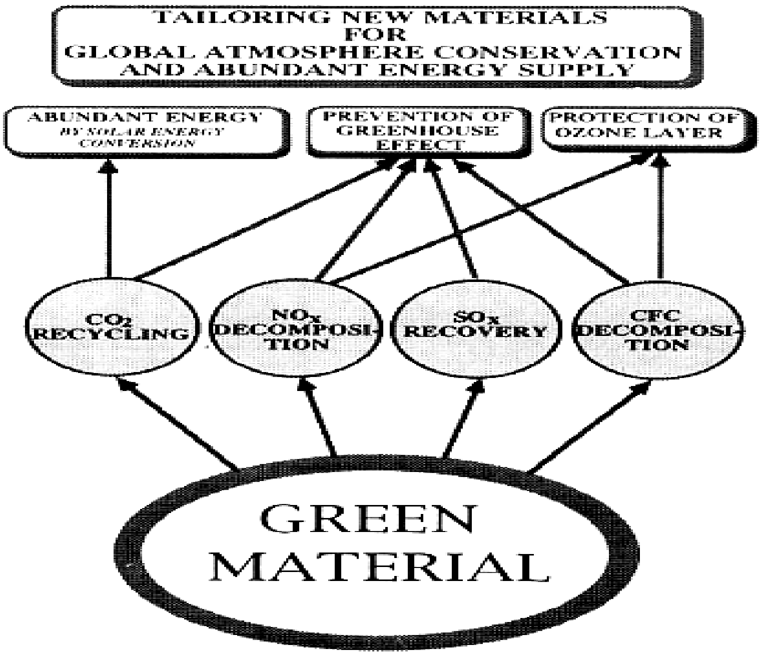

Fig.1. Schematic diagram of the green materials

CO_2 Recycling

There are a number of proposals to solve the CO_2 problem. However, since CO_2 is produced in energy-consuming processes, unless a new energy source is considered, the CO_2 problem cannot be solved. The proposal of CO_2 recycling not only provides the solution of the atmospheric problems but also supplies abundant energy, and it is based on the combination with solar-cell operation at deserts. When solar cells are operated with a 10 % efficiency for 8 h/d by using the solar constant of 2 $cal/cm^2 \cdot min$, in order to generate the electricity corresponding to the energy emitted by burning 6000 Mt/y of carbon in the whole world, we need 13.4 Mha of the area. This is only 0.83 % of the area of the main deserts on the earth. It is, however, impossible to supply electricity over 1000 km and hence, we need another energy carrier. We can transmit the electricity generated by the solar-cell operation on the deserts to the nearest coast and produce H_2 by electrolysis of seawater. H_2 thus produced can be liquefied and transported to fuel-burning plants by tankers. However, direct usage of H_2 has various disadvantages. Because of a lower energy content as the fuel, H_2 cannot be used directly for high-speed vehicles. Liquefaction consumes about one third of energy, and the energy content per volume is too low to be carried by liquefied H_2 tankers.

On the contrary, CH_4 has a 3.32 times higher energy per volume than H_2, and CO_2 is easily converted to CH_4 by the reaction with H_2. Figure 2 shows the proposal of the CO_2 recycling. The electric power is generated by the solar-cell operation at deserts and transmitted to the nearest coast. Using this electricity H_2 can be generated by the electrolysis of seawater. On the other hand, CO_2 is recovered at fuel-burning plants, liquefied and transported by tankers to the coast closest to the deserts. CH_4 can be produced by the reaction of CO_2 and $H_2$and liquefied. The liquefied CH_4 can be transported by tankers to fuel-burning plants.

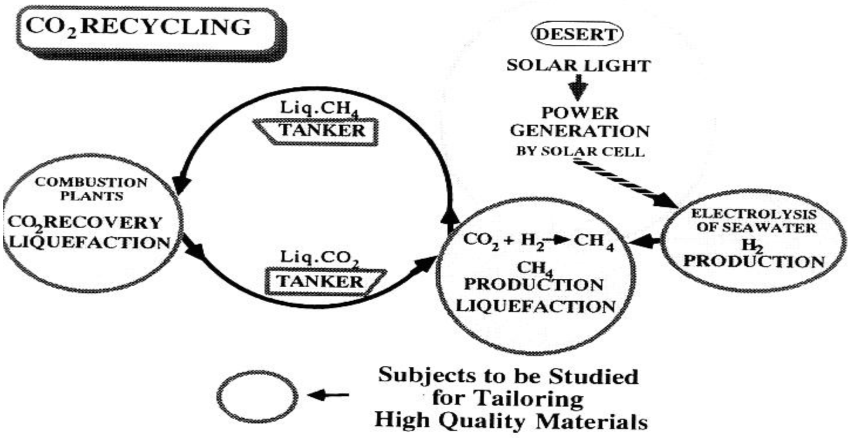

Fig.2. Schematic diagram of CO_2 recycling

The problems which must be solved by material scientists in the CO_2 recycling are electrodes for electrolysis of seawater and catalysts for conversion of CO_2 to CH_4 by the reaction with H_2. In order to utilize the electricity generated in deserts where water is not available, not fresh-water but seawater must be used for the production of hydrogen by the electrolysis at the nearest coast to the desert. The electrolysis of seawater gives us a new problem. A large amount of H_2 is required for the conversion of CO_2 emitted in the whole world to CH_4. However, a large amount of chlorine release by reaction (1) is not allowed for the production of H_2. Therefore, the electrode which is capable of evolving oxygen without chlorine evolution must be tailored. Oxygen evolution is the reverse reaction of reaction (2).

$$2Cl^{-} = Cl_2 + 2e^{-} \tag{1}$$

$$O_2 + 2H_2O + 4e = 4OH^{-} \tag{2}$$

Investigations in tailoring amorphous-alloy anodes and cathodes for the electrolysis of seawater are in progress.

Because of large-scale production of CO_2, the catalytic reaction for CO_2 conversion must be very fast under ambient pressure on a catalyst without containing any platinum-group element. CH_4 formation is the only possible reaction to be used, since reactions to form other hydrocarbons are too slow to be used in addition to usually requiring high pressure. Amorphous alloys are very effective catalyst precursors for the conversion of CO_2 by the reaction (3).

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{3}$$

Figure 3 shows the rate of CO_2 conversion to form CH_4 on various catalysts prepared from amorphous alloys. In the atmosphere of reaction (3), valve metals are oxidized, but nickel is in the metallic state. Therefore, these amorphous alloys are at first oxidized in air and then reduced in a hydrogen atmosphere. The catalyst thus formed consists of fine grains of valve-metal oxides on which nickel in the metallic state is finely dispersed. The single-phase nature of amorphous alloys is very suitable for forming this kind of catalyst which cannot be prepared by any other methods.

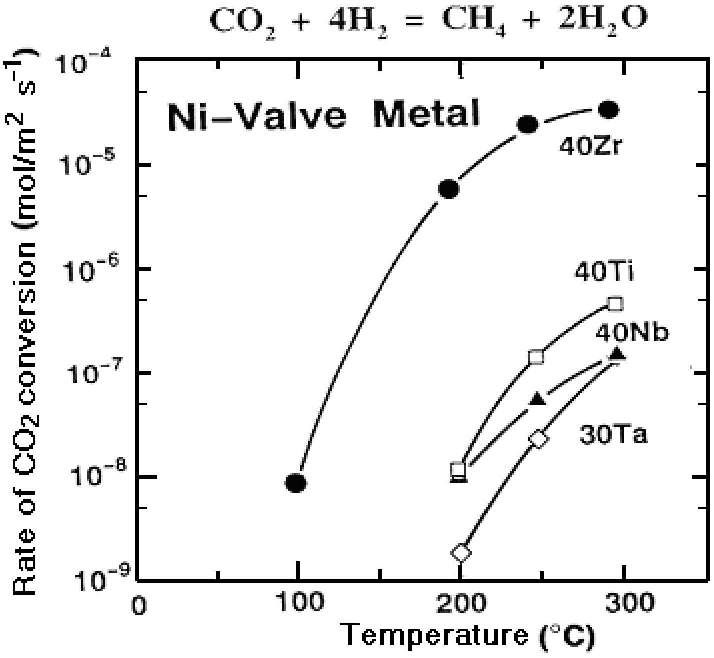

Fig.3. Rates of CO_2 conversion on oxidation-reduction treated Ni-valve metal alloys as a function of reaction temperature

Since effective anode and cathode for electrolysiss of seawater and catalysts for conversion of CO_2 into CH_4 have been tailored, the global CO_2 recycling plant has been built on the roof of the Institute for Materials Research, Tohoku University [1]: the plant consists of solar cells for power generation at a desert, an electrolytic cell for H_2 production and a reactor for conversion of CO_2 into CH_4 at a coast closest to the desert, and a CH_4 combustion and CO_2 recovery plant at an energy consuming district. The performance of the global CO_2 recycling plant utilizing these novel electrodes and catalyst has substantiated that the solar energy at deserts can be used in the form of CH_4 without emitting CO_2 at an energy consuming district such as Japan.

Catalysts for the Decomposition of NO_x

NO_x, is formed at temperatures higher than 1000^{0}C but is unstable at lower temperatures. Accordingly, the direct decomposition of NO_x, into 0_2 and N_2 is thermodynamically feasible at lower temperatures, such as $2NO=N_2+O_2$.

Some amorphous iron-group metal-valve metal alloys containing a very small amount of platinum-group elements were used for the direct decomposition of NO. When the alloys were used as the heterogeneous catalyst for the decomposition of NO, oxidation of the alloys initially occurred, releasing N_2. After almost complete oxidation of the alloy specimens, direct decomposition of NO into O_2 and N_2 took place. The activities for the direct decomposition are illustrated in figure 4. The catalyst prepared from the palladium-containing alloy has the highest catalytic activity for NO decomposition which was higher than that of palladium black powder. When amorphous Ni-Ta and Ni-Nb alloys rate was further increased. In particular, Ni-Ta-Pd alloys showed a high activity in the temperature range from 500 to 900^{0}C. This high activity in the wide temperature range has never been shown by other known catalysts. It was found that the catalysts consisted of a double oxide of nickel and valve metal on which metallic palladium was finely dispersed [2].

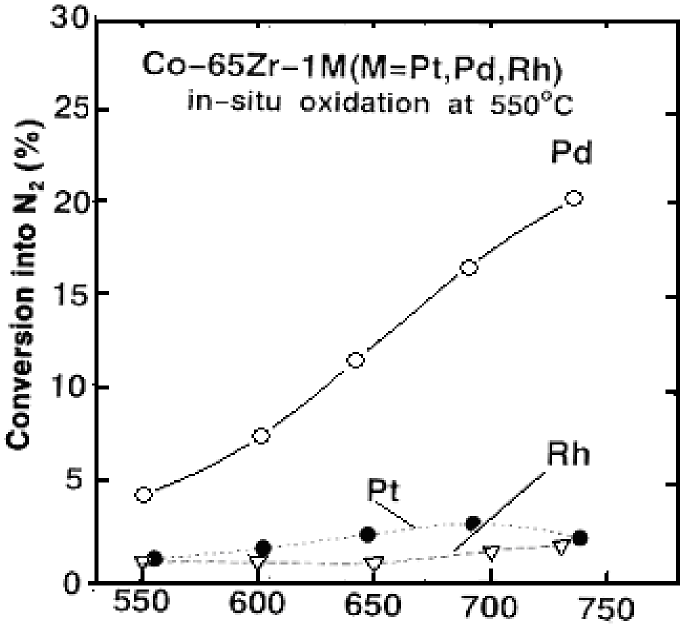

Fig.4. Conversion of NO into N_2 after oxidation of Co-65Zr-1wt% platinum grpoup element alloy specimen after in-situ oxidation at 550^0C; 0.5vol5 NO in He was passed through 0.08g of the alloys fixed in a length of about 40 mm in a quartz tube of 8 mm inner diameter.

Catalysts for the Decomposition of Chlorofluorocarbons

A leakage of stored ChloroFluoroCarbons (CFCs) leads to the destruction of the ozone layer. Accordingly, the CFCs produced so far must be converted into safe and usable substances. Various procedures have been proposed. First of all, CFCs must be decomposed not into chlorine-containing organic compounds but completely into inorganic substances. The simplest, easiest and cheapest method for the complete decomposition of CFCs is catalytic hydrolysis, i.e., the reaction of CFCs with H_2O to form $C0_2$, HCl and HE This type of reaction is exothermic. For example CFC-12 decomposes as: $CCl_2F_2 + 2H_2O = CO_2 + 2HCl + 2HF$.
When humid CFC-12 was passed through amorphous iron-group metalvalve metal alloys, catalytic decomposition occurred at a high rate. Amorphous Fe-Zr and Ni-Zr alloys were particularly effective as the precursor of the catalyst, although they suffered oxyhalogenation to form a mixture of oxides, chlorides, fluoride, oxychlorides and oxyfluorides. When chromium, molybdenum and/or tungsten, which have a higher resistance against oxychlorination than iron and nickel do, were added to the alloys, the durability of the catalyst was significantly increased.

Anode Materials for Electrolysis

Anode Materials for Electrolysis of Hot Concentrated NaCI Solutions

In the chlor-alkali industry, electrolysis of hot concentrated NaCl solutions produces chlorine on the anode and sodium hydroxide and hydrogen on the cathode. Both chlorine and oxygen evolution occurs on the anode in sodium chloride aqueous solutions.

$$2Cl^- = Cl_2 + 2e$$

$$H_2O = 0_2 + 4H + + 4e$$

These are both anodic oxidation reactions. Thus the anode materials must have preferentially high catalytic activity for chlorine evolution and low activity for oxygen evolution, in addition to a high corrosion resistance against highly oxidizing environments containing nascent chlorine. Palladium among platinum group metals which are only the candidates for the electrode materials, has the highest electrocatalytic activity and selectivity for the chlorine evolution but has the lowest corrosion resistance. Accordingly, the corrosion-resistant materials were designed by alloying of palladium and vitrifying for improvement of the corrosion resistance without deteriorating high electrocatalytic activity and reaction selectivity of palladium.

As shown in table 1, the corrosion resistance of amorphous palladium-based alloys is extremely high under anodic polarization conditions where palladium metal dissolves very rapidly without producing chlorine. The amorphous palladium-based alloys are spontaneously passive in the hot concentrated NaCl solution, and chlorine evolution takes place on the passive film. The electrolysis of the NaCl solution produces both chlorine and oxygen on the anode, while that of the Na2SO4 solution produces only oxygen. It is clear that various amorphous palladium-base alloys possess significantly high activity for chlorine evolution and very low activity for oxygenn evolution, and hence can be expected as energy-saving anode materials.

Table 1. Corrosion rate during galvanestatic polarization at 100 A m^{-2} in 4 kmol m^{-3}s NaCl solution at pH 4 and 353 K.[3]

	Anode material	**Corrosion rate (g $m^{-2}h^{-1}$)**
Amorphous	Pd-20Rh-19P	0.00
	Pd-30Rh-19P	0.00
	Pd-30Pt-19P	0.02
	Pd-40Pt-19P	0.01
	Pd-401r-19P	0.18
Crystalline metal	Ru	0.18
	Rh	0.02
	Pd	2027.08
	Ir	0.02
	Pt	0.03

Anode Materials for Electrolysis of Seawater

In industrial plants using seawater as a coolant, sodium hypochlorite NaClO is injected into the coolant at the intake of the cooling system for the sake of protection against the marine life such as barnacle which decreases the cooling efficiency and sometimes clogs the system. Sodium hypochlorite is produced by the reaction of chlorine with sodium hydroxide as follows:

$$C1_2+2NaOH = NaClO+NaCl+H_2O$$

These two reactants are products of electrolysis of seawater on the anode and cathode, respectively. Accordingly, the anode for electrolysis of seawater also produces chlorine, but is required to have far higher activity in comparison with the anodes for the ehloralkali industry because competitive oxygen evolution easily occurs in neutral seawater of ambient temperature whose chloride concentration is about one eighth as high as the solutions used in the chlor-alkali industry. Therefore, an activation treatment was applied to the amorphous palladium-based.

Activation of alloys for the sake of increase in the catalytic activity is generally based on surface roughening along with accumulation of catalytically active elements in the alloy surface by using preferential dissolution of alloy constituents unnecessary for the electrocatalytic reactions from the alloy surface into aqueous solutions. However, there have been found no methods for selective dissolution of alloy constituents such as phosphorus from the palladium-base alloys, and hence an idea adopted for surface activation is based on alloying with a low melting point element which is easily diffused into alloy at relatively low temperatures and is easily dissolved in acids or alkalis: The surface activation treatment consists of (1) electrodeposition of zinc on the amorphous palladiumbase alloys, (2) diffusion of zinc into the amorphous alloy by heat treatment at temperatures below crystallization temperatures of the amorphous alloys, and (3) leaching of zinc from the alloy surfaces into a hot alkali.[4]

Even if their activity is extremely high they consist of precious metals. Another attempt to obtain active anode materials composed mainly of transition metals was made by utilizing the characteristics of amorphous alloys. Amorphous nickel-valve metal alloys such as Ni-40Nb and Ni-30Ta alloys containing a few at% platinum group elements are spontaneously passive showing a high corrosion resistance during anodic polarization in seawater, although their activity for chlorine evolution is about four orders of magnitude lower than that required for the anode for electrolysis of seawater. Since valve metals are known to be dissolved easily in HF solutions, the activation treatment consisting of immersion in HF solutions has been carried out. The immersion of nickel-valve metal alloys containing small amounts of platinum group elements in HF solutions leads to preferential dissolution of not only valve metals but also nickel with a consequent surface enrichment of platinum group elements. The increase in surface concentration of platinum group element to 80-90 at% and more than two orders of magnitude increase in the effective surface area due to the HF immersion treatment result in about four orders of magnitude increase in the electrocatalytic activity of the amorphous nickel-valve metal alloys containing a few at% platinum group elements.

Conclusion

Various unknown, attractive and useful properties of amorphous alloys have been found. As has been shown already, the formation of a single-phase solid solution supersaturated with various alloying elements exceeding the solubility limits at equilibrium is quite suitable in obtaining novel materials with specific functions. The global atmospheric and energy problems can be solved by tailoring new materials by using unique properties of amorphous alloys such as catalytic, electrocatalytic and corrosion-resistant properties as well as the metastability itself. Studies of the chemical properties of amorphous alloys have not been widely performed.

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Aliaje amorfe ca precursori catalitici

Rezumat

Cea mai atractivă caracteristică a aliajului amorf este natura sa de a avea o singură fază şi de a forma o soluție solidă foarte solubilă la limita de echilibru. Această caracteristică permite formrea de noi aliaje cu proprietăți unice şi folositoare.
Omogenitatea chimică a fazei singure, este capabilă a forma soluție solidă suprasaturată cu elemente variate adăugate intenționat şi reprezintă caracteristica importantă pentru obținerea materialelor având proprietăți noi.