ENERGY-STORING SUBSTANCES IN HYDROGEN ENERGETICS

Goncharenko S. G, Volkov S. V, Kozin L. F*, Daniltsev B. I.
V. I. Vernadskii Institute of General and Inorganic Chemistry, Ukrainian NAS
prospect Palladina 32/34 03680 Kyiv, 03142.
Tel 8 (044) 424 0064 E-mail: kozin@ionc.kiev.ua

Introduction

In view of the fact that such convenient energy carriers as oil and natural gas will be practically completely exhausted in the XXIst century, special attention came to be paid in the world to the development of alternative energy sources, among which new methods for hydrogen production rank first. The development of new methods for hydrogen production from water plays an important role in modern science and technology since in contrast to organic fuel the water resources are unlimited and renewable [1]. We are developing new methods for hydrogen production with the aid of Energy-storing substances (ESS).

It is known that gallium is a good aluminium activator [2]. However, gallium belongs to rare disseminated elements, finds application in electronics and has therefore a high commercial value. The aim of this work is to develop new EESs based on aluminium activated by a metal-activator, which would be more readily available than gallium and have a much lower commercial value. This problem has been solved with the aid of such metal-activator as bismuth. Samples of activated-aluminiun alloys (systems Al-Ga, Al-Bi) were prepared in a aucible furnace in arson atmosphere under vigorous hydrodynamic stirring followed by crystallization under nonequilibirium conditions. The experimental procedure is described in detail in a patent [3]. The kinetics and mechanism of interaction between activated aluminium and water in the temperature rage 423-598 K were investigated in a high-pressure reactor. The investigations of the structure of a newly made fracture and the X-tay spectroscopic analysis were carried out on ZEISSEVO50XVP scanning electron microscope.

Results and discussion

Using kinetic p_i-τ и V_{H_2} - τ curves of dissolution of ESSs, based on bismuth-and gallium-activated aluminium in water, rates of hydrogen evolution from water, reaction rate constants have been calculated, and the time of reaching the maximum hydrogen evolution time has been determined. Figure 1(*a*) shows plots of hydrogen evolution rate against time in the case of interaction between aluminium, activated with 3 wt% gallium, and water at 423-573 ºK. The hydrogen evolution rate at 423; 473; 523 and 573 K is 148; 258; 631 and 984 l/m^2·min respectively. Figure 1(*b*) shows plots of hydrogen evolution rate against time in the case of interaction between aluminium, activated with 3 wt% bismuth, and water at 523-598 K. The kinetic curves in Fig 1(*b*) have a feebly marked

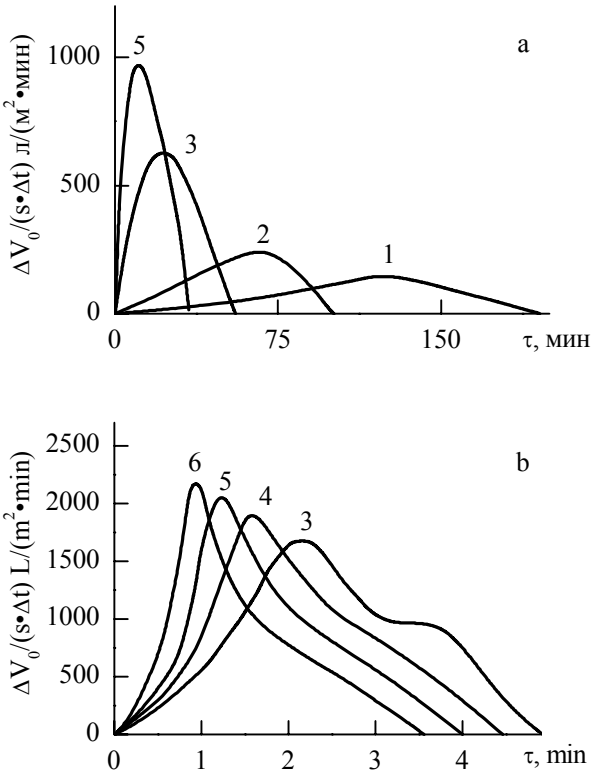
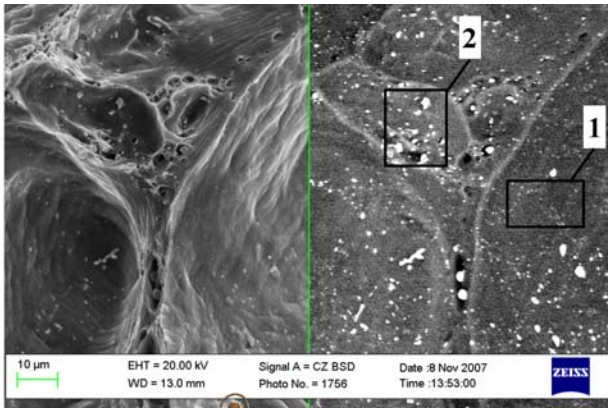


Fig 1**.** Dependence of hydrogen evolution rate on time the case of interaction between aluminium, activated with additions of 3.0 wt% gallium (a) and additions of 3.0 wt% bismuth (b), at 423 K (*1*), 473 K (*2*), 523 K (*3*), 548 K (*4*), 573 K (*5*), 598 K (*6*).

sigmoid trend, which is due to the ability of Al-Bi alloys to from a broad miscibility gap of the constituents in the liquid [4]. The immiscibility of the large difference in the surface tension of aluminium (σ_{Al}) (851-930 mN/m in the temperature range 933-1823 K) and bismuth (σ_{Bi}) (375 mN/m in the temperature range 544÷773 K) [5]. The evolution rate at 523; 548; 573 and 598 K is 1678; 1898; 2061 and 2188 l/m^2·min respectively, which is a factor of 2.5 higher then that in the case of aluminium activation

by gallium. Reaction activation energies (E_a) for aluminium-based ESSs with 1.0; 3.0; 5.0; 7.5; and 10 wt% Bi have been calculate from rate constants of reactions and interaction between activated-aluminium alloys and water. The E_a values obtained are 6.3; 6.9: 24.7; 10.5 and 10.6 kJ/mol respectively; it follows that they pass through a maximum, which falls at 5.0 wt. % Bi. These *E*a values indicate that the rate of interaction between EESs based on aluminium, activated by 1.0; 3.0; 7.5; and 10 wt% Bi, and water is limited by diffusion restrictions and for aluminium alloy with 5.0 wt% Bi by kinetic restrictions.

Fig. 2 shows the microstructure of a newly made fracture of ESS based on aluminium activated by 3 wt% bismuth, photographed on a ZEISSEVO50XVP, microscope, in secondary(Fig 2(*a*)) (SEI) and reflected (Fig 2(*b*)) (BEI) electrons at X 1000 magnification. In



a b

Fig 2. Microstructure of a newly fracture of ESS based on aluminium activated by 3 wh% Bi in secondary (a) (SEI) and (b) reflected (BEI) electrons at X1000 magnification:
(*1*)- bismuth nanoparticles, (*2*)- bismuth globules.

Fig 2(*b*), one can clearly see a grey background, denoted by numerals 1 and *2*. The region 1 is inclusions of bismuth nanoparticles (50-100 nm) and nanoclusters consisting of 4-10 bismuth and alumunium nanoparticles. The 1.2–1.5 µm white spots which are in the region *2*, correspond to bismuth globules is due to the fact that the force of interaction between atoms, Al-Al and Bi-Bi, exceeds greatly that of interaction between different atoms in the system Al-Bi, owing to a great difference between the radii of aluminium and bismuth atoms, which about 16% [6]. According to the data of X-rey spectroscopic analysis (INCA 450), bismuth globules contain 60-80 wt% bismuth and 40-20 wt% aluminium. It follows that globule formation in Al-Bi alloys affects adversely the rate of hydrogen avolution from water

Conclusions

1) The kinetics and mechanism of interaction between gallium and bismuth-activated aluminium and water in the temperature range 423–598 °C have been studied. The kinetic parameters of reaction have been calculated and a mechanism of hydrogen production from water with the aid of ESSs has been proposed.

2) It has been shown that such aluminium activator as bismuth is a factor of 2.5 more efficient that gallium.

3) Using a ZEISS EVO 50XVP alectron microscope, it has been found that in the Al-Bi alloy matrix, bismuth separates out as nanoparticles and nanoclusters, which ensure high rates of hydrogen evolution from water.

References

1. L. F. Kozin, S. V. Volkov, Modern Energetics and Ecology: Problems and prospects (in Russian), aukova dumka, Kyiv (2006).

2. . USSR inventor's certificate №618920 cl. CO 1B 1/07. 14,04,78

3. Ukrainian patent № 35192, IPC C01B 3/02. A method for hydrogen production, S. V. Volkov, L. F. Kozin, S. G. Goncharenko, B. I. Daniltsev.

4. N.P. lyakishev, Diagrams of binary metal systems in 2 volumes (in Russian) Mir, Moscow, 1996.

5. V. I. Nizhenko, L. I. Floka, Surface tension of Liquid Crystals and Alloys, a handbook (in Russian), Metallurgiya, Moscow (1981).

6. I. S. Kulikov, Isotopes and properties of Elements, a handbook (in Russian) Metallurgiya, Moscow, 1990.