Structure of Rapidly Solidified Al–(0.25–2.0) wt % Bi Alloys

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Abstract—This article describes study of the microstructure and texture of aluminum alloy foils containing 0.25–2.0 wt % Bi and manufactured by high speed solidification. The cooling rate of the melt is at least 10^5 K/s. Aluminum texture (111) is generated in the foils. The average chord of cross sections of bismuth spherical precipitates does not exceed 0.5 μm. The size of dispersed bismuth particles increases and their number per unit volume of aluminum matrix decreases with increase in the distance to the foil surface. The specific surface area of interface boundary at first increases and then decreases upon movement of solidification front. The alloy foils are dissolved in water at ambient temperature, forming hydrogen bubbles and amorphous powder of $Al_2O_3 \cdot 5(H_2O)$ and $Al_2O_3 \cdot 3(H_2O)$ aluminum hydrides.

Keywords: generation of hydrogen, aluminum alloy, texture, dispersed bismuth particles

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INTRODUCTION

Al–Bi alloys belong to the systems with limited solubility in the liquid state. At present, the microstructure formation and stability of such alloys have not been studied in detail [1]. However, there appeared reports [2, 3] about the use of aluminum alloys containing minor amount of bismuth for production of hydrogen from water, which is important for development of hydrogen power engineering, taking into account that this technology is environmentally safe. It is assumed that the heterogeneous distribution of dispersed bismuth particles in aluminum, as well as the particle size distribution, leads to formation of galvanic microelements. Their occurrence activates aluminum, initiating high reactivity of aluminum with regard to water, which promotes formation of aluminum hydrides and hydrogen evolution. It was established that the use of aluminum nanopowders facilitates hydrogen generation from water [3, 4]. Production of aluminum with dispersed phases of low melting metals is possible using high speed solidification and a less expensive low melting component, bismuth, as compared with gallium and indium, at which the cooling rate of the liquid phase exceeds 10^5 K/s, which has scientific and practical importance.

The aim of this work is to study the structure of rapidly solidified Al–Bi alloys containing 0.25–2.0 wt % Bi and their possible application for hydrogen generation from water.

EXPERIMENTAL

Binary aluminum alloys containing 0.25–2.0 wt % Bi were obtained by fusing components in quartz vessels. Bulk samples of the alloys were obtained by casting in a graphite mold. Then, a moderate lump of the alloy with the weight of ≈0.2 g was smelted and injected onto polished internal surface of rotating copper cylinder. A molten drop on the surface of solidification unit was solidified in the form of foil with the thickness of 30–90 μm [5].

X-ray diffraction analysis of the foil was carried out using a DRON-3 diffractometer. When analyzing the foil structure by the method of inverse pole figures, the diffraction lines 200, 220, 311, 222, 331, and 420 were used [6]. X-ray radiation fell onto the foil surface *A* contacting the solidification unit or onto its opposite surface *B* contacting the environment.

The microstructure of the alloy foils was analyzed using a LEO 1455 VP scanning electron microscope. The microstructure parameters were calculated using the methods of stereometric analysis [7]. The measurement error was ≈10–15%.

The produced rapidly solidified foils of Al–0.5 wt % Bi alloy are broken owing to corrosion in the environment containing water vapor in 8–12 h. Decrease in the bismuth content inhibits the corrosion. The gas evolved upon interaction between alloy foil and water at 20°C was collected into a test tube. Its combustion was instantaneous and was accompanied by sound characteristic of hydrogen combustion. In order to determine the phase composition of the white powder, aluminum doped to 0.3 wt % Fe was additionally used.

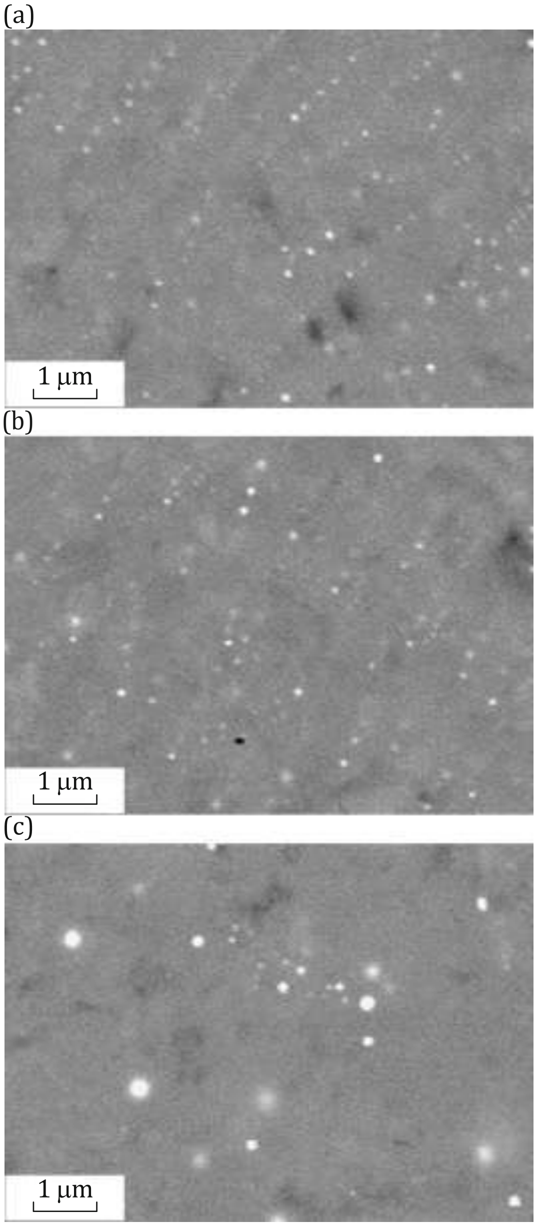

Fig. 1. Microstructure of cross section of Al–1.0 wt % Bi alloy foil adjacent to surface *A* (a) and *B* (c) and in the middle (b).

It is known that the rapidly solidified foils of such alloy contain dispersed particles of the $AlFe_3$ stable phase and the $AlFe_6$ metastable phase, which upon the heterogeneous mechanism of nucleation promote formation of solidification centers of new phases as a result of interaction between foil and water, which makes it possible to determine the crystalline phases generated in the powder using X-ray diffraction analysis.

RESULTS AND DISCUSSION

The images of cross sections of Al–1.0 wt % Bi alloy foil are illustrated in Fig. 1. Light dispersed spherical precipitates of bismuth on dark aluminum background are observed. As the solidification front moves from the surface *A* to its opposite surface *B*, the average length of chords of random secants on the cross sections of bismuth particles monotonically increases, which is due to a decrease in supercooling of the liquid phase because of heat evolution during solidification of previous layers.

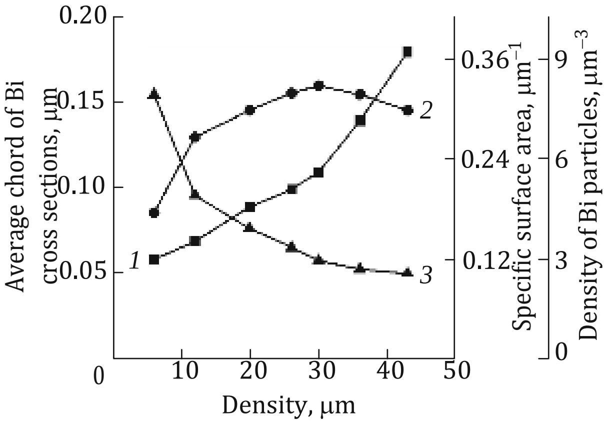

Fig. 2. Average length of chords at the cross section of bismuth particles (*1*), specific surface area of the interface boundaries (*2*), and average number of particles per unit volume (*3*) as a function of distance to the foil surface *A* of Al–1.0 wt % Bi alloy.

Analysis of the microstructure of foil cross section between the surfaces *A* and *B* demonstrated that the bismuth particles in aluminum are distributed heterogeneously. The parameters of the microstructure of Al–1.0 wt % Bi alloy foil as a function of distance x counted from the surface *A* of foil with the thickness 56–60 μm are illustrated in Fig. 2.

The average length of chords on the cross section of bismuth particles monotonically increases and their amount per unit volume monotonically decreases with the distance to surface *A*. The specific surface area of the aluminum–bismuth interphase boundary is characterized by a weakly pronounced diffused maximum.

The histogram in Fig. 3 illustrates the distribution of chords on cross sections of bismuth particles of Al–0.25 wt % Bi. Fine precipitates with the chord length less than 0.01 μm are predominantly localized in the volume adjacent to the surface *A*. The coarsest precipitates are in the size group from 0.02 to 0.03 μm and mainly located in the layer (*B*) adjacent to the foil free surface.

Rapidly solidified foils of the considered alloys have microcrystalline structure. They are characterized by predominant orientation of aluminum grains. Table 1 summarizes the values of pole densities of aluminum diffraction lines for the layer contacting the surface of the solidification unit. The diffraction line 111 is characterized by the maximum pole density,

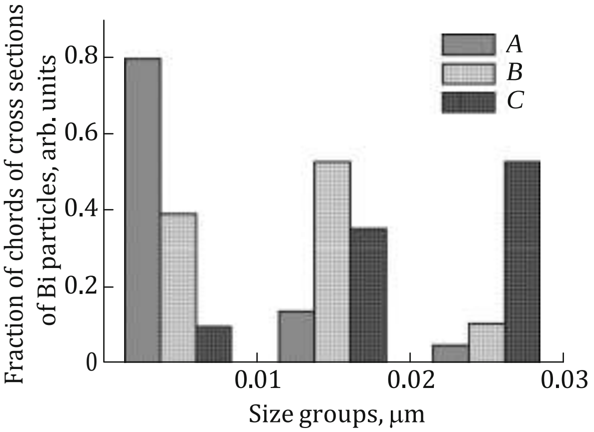

Fig. 3. Distribution of chords of random secants at cross sections of bismuth particles of Al–0.25 wt % Bi alloy by size groups in the *A*, *B*, and *C* foil layers.

which indicates formation of the texture (111). Similar texture was also observed in foils of pure aluminum and its alloys [5]. Formation of the texture (111) is related to the highest packing density of crystallographic planes {111} of aluminum, which promotes predominant grain growth with such orientation in the direction of heat flow [6, 8].

Holding the considered alloys in the environment containing water vapor leads to corrosion along the grain boundaries and occurrence of microcracks in the foils, initiating their breakage and transformation into black powder.

In addition, the behavior of rapidly solidified Al–0.5 wt % Bi alloy foil in water was analyzed. The foil placed in water at 20°C disappeared in 2 h, resulting in occurrence of floating hydrogen bubbles. Upon evaporation of water from the vessel, at first a nebulous liquid was formed, and then dispersed white powder was formed upon further evaporation of water. Using X-ray diffraction analysis, it was established that the black powder has crystalline structure. The X-ray pattern (Fig. 4, curve *1*) illustrates diffraction reflections corresponding to the $Al_2O_3 \cdot 5(H_2O)$ and AlO(OH) compounds. The diffraction pattern of the white powder (Fig. 4, curve *2*) does not contain diffraction peaks, which indicates its amorphous structure. However, on the diffraction pattern of the white powder obtained using aluminum with 0.3 wt % Fe, the diffraction peaks corresponding to $Al_2O_3 \cdot 5(H_2O)$ and $Al_2O_3 \cdot 3(H_2O)$ aluminum hydrides were observed. Therefore, it is possible to consider that the white powder obtained using foils of undoped aluminum is also composed of the same amorphous phases.

Table 1. Pole densities of diffraction lines of aluminum alloy foils containing 0.25, 0.5, 1.0, and 2.0 wt % Bi

Bi concentration, wt %	Diffraction lines					
	111	200	220	311	331	420
0.25	2.7	0.6	0.8	0.8	0.4	0.7
0.5	2.2	1.0	1.2	1.2	0.8	0.5
1.0	2.1	0.6	1.1	1.3	0.5	0.4
2.0	2.0	0.8	0.9	1.1	0.6	0.5

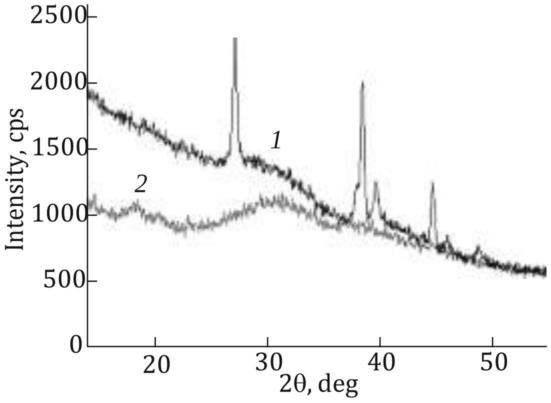

Fig. 4. Diffraction patterns of black (*1*) and white (*2*) powders.

Hydrogen evolution during interaction between water and rapidly solidified Al–Bi alloy foils takes place under normal conditions (t = 20°C, $P = 1 \times 10^5$ Pa) even without additional reagents, which is of practical importance for development of hydrogen power engineering and makes it possible to use the obtained data for development of energy storing substances and technical means on their basis.

CONCLUSIONS

Dispersed bismuth precipitates are formed in rapidly solidified aluminum alloy foils with 0.25–2.0 wt % Bi. They have spheroid shape; the average length of chords of cross sections of bismuth particles does not exceed 0.5 μm. A weakly expressed aluminum texture (111) is formed in the foils. In the case of existence of dispersed bismuth particles in aluminum foil at ambient temperature and normal pressure, without use of additional reagents, the water molecules are broken with formation of hydrogen and $Al_2O_3 \cdot 5(H_2O)$ and $Al_2O_3 \cdot 3(H_2O)$ amorphous aluminum hydrides, which is of practical importance for development of technical means using hydrogen.

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