Synthesis and structure of nanoparticles in intermetallic Al$_2$Au

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Abstract. The intermetallic compound Al$_2$Au has been obtained from gold powder and aluminum particles through mechanical alloying in ball mills. The intermetallic structure was investigated by the methods of scanning transmission electron microscopy and X-ray diffraction analysis. It was found that mechanical alloying resulted in the formation of micro and nano particles of Al$_2$Au. The powder obtained was compacted into tablets. X-ray diffraction analysis showed intermetallic lines and one line belonging to aluminum, within the compact. The structure of compacts after annealing was investigated. It was determined that compacting promoted the agglomeration of intermetallic particles. Further annealing led to the surface depletion in aluminum, cracking and refinement of structural elements. After heat treatment, a phase enriched in gold – AlAu – is registered in the samples.

1. Introduction

The intermetallic compound Al$_2$Au or “purple gold” was discovered in 1892. Its bright color is first of all attractive for jewelers, but the brittleness inherent in all intermetallic compounds makes it quite difficult to use the alloy. Another obstacle consists in the formation of the intermetallic within a narrow concentration range about 1060 °C. An alternative can be found in creating Al$_2$Au coatings. Film samples are easier to obtain, they are not so brittle. In addition, a thin film of Al$_2$Au is an optical filter [1]. The synthesis of this intermetallic compound followed by the investigation of its structure and properties is of interest both for research and for practical use.

To obtain fine powders, different technologies are used, including mechanical alloying (MA) in ball mills. The use of this method is quite successful in creating materials, which are difficult to obtain in the traditional way.

Earlier, we suggested obtaining the intermetallic compound Al$_2$Au by MA of nanosized gold and aluminum powders [2].

The purpose of this work is to investigate the microstructure of the intermetallic compound Al$_2$Au obtained by MA in accordance with our proprietary technology.

2. Experimental procedure

A fine powder was obtained using the gas-phase method, which consists in evaporation of a drop of molten and condensation of vapor in an argon flow [3]. To obtain Au powder, a wire with a diameter
of 0.6 mm of 99.99% pure gold was taken. The sizes of particle in the obtained powder were in the range of 30-50 nm [2]. Based on the results of previous research, it was concluded that the use of nanosized aluminum powder for MA was unreasonable due to the presence of an oxide film on its surface. That is why in this work the option of milling a mixture of nanosized gold with coarse (about 0.5 mm) aluminum filings was chosen. The test amounts of nanopowder of gold and aluminum filings were mixed in proportions corresponding to the composition of Al₂Au and dispersed by ultrasonication in toluene. MA was carried out in a planetary ball mill (PBM) Pulverisette-7 for 4 hours at a rotation speed of the milling pot of 800 rpm. The milling process was carried out in a hexane atmosphere; to ensure the most efficient running of the process, 15 balls with a diameter of 10 mm were used. The set of the planetary ball mill (milling pot and balls) was made of stainless steel. The ratio of the weights of the balls and source materials was 10:1 (the total weight of the balls was 60 g).

To carry out investigations, the powder obtained as the result of MA was compacted into tablets with a diameter of 11 mm and a thickness of 5 mm. The work included studies of compact samples after annealing in the temperature range from 300 to 600 °C. The compact was divided into 4 parts; each of them was annealed at a different temperature. Two samples with the most intense color were selected for the study. One was annealed at 350 °C for 30 minutes (mode 1). The other investigated sample was first soaked at 400 °C for 30 minutes and additionally treated at 600 °C, for 15 minutes (hereinafter – mode 2). The compacts were annealed in atmosphere of He.

The products of MA were studied using a JEM-200CX transmission electron microscope (hereinafter referred to as TEM study). The products of MA for the TEM study were placed between two copper grids. Microstructure evaluation was performed using a Philips SEM 515 scanning electron microscope (SEM). X-ray diffraction analysis was carried out using a Rigaku DMAX 2200 diffractometer.

3. Results and discussion
Figure 1 shows the results of the SEM study: it gives a general view of the synthetized powder and the elemental analysis data. Tiny particles of arbitrary shapes and agglomerations are well seen in figure 1a, b.

![Figure 1. Powder morphology (a); corresponding energy dispersive spectrum (b).](image)

The elemental analysis (figure 1b) of the powder showed good compliance with the intermetallic compound Al₂Au (as is known, it contains 79 wt% of Au and 21 wt% of Al). The size of the structural elements of the synthetized powder, which are seen through SEM, varies from 300 nm to 3 µm. Sometimes, there are cracks and defects on the surface of particles, which can be related to their high hardness and brittleness – properties inherent in all intermetallic compounds. The TEM study of the obtained powder showed the formation of nano- and micro-particles of the intermetallic compound
during MA (figure 2). Microdiffraction images are point-like for micro-particles and circular for nanograins, they correspond to the intermetallic compound \( \text{Al}_2\text{Au} \). There were found areas of the sample where no intermetallic compound formation took place with Au grains and \( \text{Al}_2\text{O}_3 \) particles being observed. During the study, the amorphous phase was registered.

![Figure 2. TEM micrographs of mechanically alloyed powder \( \text{Al}_2\text{Au} \); a – bright field image and SAD pattern, b – dark field image in 220\( _{\text{Al}_2\text{Au}} \).](image)

To investigate the color change depending on the temperature of treatment, the synthetized powder was pressed into compacts. X-ray diffraction analysis (XDA) of a tablet pressed from MA powder defined in it the presence of intermetallic compound \( \text{Al}_2\text{Au} \) for the most part and a small amount of aluminum. The sizes of the coherent scattering regions were 25.2 \( \pm \) 1.6 nm, the microstrain values: 0.29 \( \pm \) 0.02 %. To study the dependence of the powder color on the treatment temperature, the compact was divided into four parts, each of which was annealed. For the studies, two samples with the most intense color were selected. After annealing, all the samples changed their color, but did not acquire the bright purple color characteristic of the intermetallic \( \text{Al}_2\text{Au} \) (figure 3).

![Figure 3. Surface view of \( \text{Al}_2\text{Au} \) compact; a – mode 1, b – mode 2, optics.](image)

The surfaces of the compacts, processed in two modes, were studied using SEM. Particles in heat-treated samples have arbitrary shapes; sharp edges and brittle chips are observed. Elemental analysis revealed that annealing causes a deviation in the ratio of components from the desired composition. The content of Al (13-16%) and Au (83-86%) in both samples would rather correspond to the AuAl phase. This indicates that in the process of heat treatment, the composition of the material is enriched with gold due to evaporation of some part of aluminum.

The study showed that after heat treatment in accordance with mode 1, the particle size is 0.5 \( \div \) 5 \( \mu \text{m} \). On the surface of the particles there are multiple defects (cracks, chips). It can be assumed that
during compacting and subsequent hydrostatic pressing, deformation hardening processes take place [4]. Recall that in the initial state, the synthesized powder had particle sizes from 0.3 to 3 µm (figure 1). It is obvious that agglomeration of particles occurred during this heat treatment. In turn, the particle sizes of the sample after heat treatment in mode 2 decreased to 0.2 ÷ 2 µm. Such a refinement of the grains with increasing annealing temperature is rare and requires an explanation. To obtain a more general picture of the processes taking place in compacts during annealing, X-ray diffraction studies were carried out. On the diffractograms of compacts, after annealing, lines appear from the AuAl phase along with the intermetallide Al₂Au. With an increase in the annealing temperature, the intensity of reflections from the AuAl phase goes up slightly, the number of X-ray peaks corresponding to the equiatomic intermetallic compound also increases (from two to three). In contrast to the diffractogram for the initial compact, no aluminum reflections are observed after annealing. The sizes of coherent scattering regions for mode 1 and mode 2 are: 78.5 ± 2.5 nm and 108.0 ± 4.5 nm, and the microstrain values are 0.15 ± 0.01% and 0.12 ± 0.01%, respectively. Thus, the X-ray diffraction study did not reveal an anomalous dependence of the grain size on the processing temperature. Consequently, the refinement of the structure in the compact treated in mode 2, as shown in figure 3, can be explained by the fracture of particles along cracks and defects caused by Al depletion of the surface layer of the material at a higher annealing temperature. Electron microscope studies showed that submicro- and nanocrystalline structures are formed in the sample after annealing in mode 2, the average grain size does not exceed 100 nm. Microdiffraction patterns contain rings from the Al₂Au phase. TEM study of the structure in the modes of bright and dark fields showed that a structure with high-angle boundaries is formed in the sample. In some grains of the intermetallic compound, an increased dislocation density and uneven contrast are observed.

On the basis of the data obtained, it can be assumed that the color change of the intermetallic phase of Al₂Au after annealing is caused by defects of different natures that occurred in the surface layer of the compacts as a result of heat treatment.

4. Conclusions
It is shown that it is possible to obtain a sufficiently pure powder of the intermetallic compound Al₂Au by the MA method. The formation of various intermetallic grains, ranging from nanostructures to microcrystallites, takes place. During MA, an amorphous phase is formed.

Pressing and heat treatment promote the agglomeration of intermetallic particles. Additional annealing at the temperature of 600 °C leads to cracking and refinement of structural elements in the surface layer. The composition of the samples after annealing changes: the AuAl phase appears.

Compacting and subsequent heat treatments lead to a change in color. The change in color is associated with the appearance of new phases, the crushing of particles and the increase in their defectiveness on the surface of the samples.

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References
[1] Supansomboon S, Maaroof A and Cortie M B 2008 Gold Bull. 41 296
[2] Volkov A Yu, Uimin M A, Mysik A A, Novozhonov V I, Volkova E G, Shchegoleva N N, Kniazev Y V and Kozlov K A 2011 Inorg. Mater. 47 465
[3] Popov V V, Stolbovskii A V, Uimin M A and Ermakov A E 2013 Phys. Metals Metallogr. 114 77
[4] Nes E 1997 Progr. Mater. Sci. 41 129