EFFECTS OF GERMANIUM (GE) ON HARDNESS AND MICROSTRUCTURE OF AL-MG, AL-CU, AL-MN SYSTEM ALLOYS

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Abstract - This article presents researches conducted on samples obtained by micro alloying aluminum alloys with germanium oxide. Experiments were carried out on aluminum-magnesium, aluminum-copper and aluminum-manganese aluminum alloys, and the hardness and microstructure of the samples obtained by casting were studied. The samples were melted in the open air in a resistance furnace and poured into sand-clay molds. Germanium oxide was added to the charge in a rolled state using a special aluminum coating. Depending on the weight of the charge and the oxide's germanium concentration, between 0.1 and 0.3 percent of germanium oxide was added to aluminum alloys. An optical metallographic microscope was used for microscopic analysis of cast samples. Studies have shown that the germanium addition significantly destroys the microstructure of an aluminum alloy with intermetallic granules. Moreover, the hardness of the researched samples was studied. The authors outlined their recommendations and conclusions at the end of the article.

Keywords: Germanium oxide, Hardness, Microstructure, Micro alloying, Aluminum, Mechanical properties.

1. Introduction

Today, aluminum alloys are widely used in various industries, including mechanical engineering, automotive, shipbuilding, aircraft engineering and others. As the demand for aluminum alloys increases, so does the number of studies aimed at changing their properties [1-4]. One of the popular ways to improve the properties of aluminum alloys is to include other elements in their composition. In particular, Serbian researchers Vesna Maksimovic, Slavica Zec, Velimir Radmilovic, and Milan Jovanovic conducted experiments in their research work "The effect of micro alloying with silicon and germanium on the micro structure and hardness of industrial aluminum", aimed at increasing its properties by introducing various alloying elements into aluminum alloy [5]. In the experiments of scientists above cited, a commercial aluminum alloy 2219 (fully compliant with the ASTM standard) manufactured by Kaiser Aluminum was used as the starting material. At the next stage, the chemical composition of this alloy was changed, adding to the composition of aluminum alloy with a total concentration of Si and Ge at 0.5%. With this micro alloying process, two experimental alloys were produced, namely one alloy with a higher concentration than the Standard ASTM alloy, and another alloy with Si and Ge additives. The microstructure and hardness variations of the alloys obtained have been studied.

Gulov S., Ganiev I., et. al. studied the effect of germanium and strontium on the structure of an aluminum alloy AK9M2 and it's mechanical parameters. They studied the change in the aluminum properties when Germanium is added in the above-mentioned aluminum alloy. According to their research, adding germanium to the sample alloy improved its fluidity property by up to 30% and reduced the porosity in the intake by 10–12% [6]. In addition, scientists from the School of Materials Science and Engineering, University of Science and Technology Beijing Zhi-wei NIU, Ji-hua HUANG, Shu-hai CHEN, Xing-ke ZHAO also added germanium into the aluminium-silicon alloy and studied its microstructure. In their studies, researchers conducted experiments by introducing 99,999% germanium into an aluminum-silicon alloy [7].

In addition, studies aimed at increasing its properties by adding germanium element to non-ferrous alloys as a microalloyer have been conducted. A. M. El-Taher and others introduced germanium into Sn–Ag–Cu system alloy and studied mechanical properties such as tensile strength and relative elongation.

These properties improved by 56.5% when adding 0.5% germanium in tensile strength, and the specific elongation changed by 58.3% [8]. In experiments using germanium as a microalloyer, it can be seen that the microstructure and mechanical properties of its alloy are improved [9-13].

From the above experiments, in this paper, the microstructure and changes in hardness of aluminum by the influence of germanium oxide on Al-Mg, Al-Cu, Al-Mn alloys is analyzed.

2. Materials and Methods

The Germanium substance is a gray-white intermediate optic, shiny like metal [14]. Germanium is often extracted as a semi-metallic combination from ores containing nickel and tungsten. Additionally, silicates are a source of it. Germanium oxide is liberated as GeO_2 following extremely intricate ore processing procedures. In the experimental research, aluminum alloys were obtained by melting in a resistance furnace in a state in which germanium oxide was added [15].

Figure 1: Sand-clay mold

In the experimental studies on aluminum alloys such as Al-Mg, Al-Cu, Al-Mn, germanium oxide was added into the composition of a charge (mixture) with a special coating. The composition of the alloys is shown in Tables 1, 2, 3.

Figure 2: Processed samples

Samples were first put into aluminum alloys for comparison during the experiments, but germanium oxide was not added. Subsequently, the alloys of the chosen grade were supplemented with germanium in the form of germanium oxide, with the addition occurring in the range of 0.1 to 0.3 percent of charge. The compound's introduction causes the germanium in the alloy to absorb the oxygen it contains.

Alloy samples of three distinct compositions were cast from each chosen brand. The samples were poured into sand-clay molds at 750°C in a resistance oven [16] (Figure 1). The composition of the mixture used in pouring the samples consists of 85% quartz sand, 11% bentonite clay, and 4% water. The cast samples were cut and processed in the desired size and shape on a lathe. The machined samples are shown in Figure 2.

Table 1. Alloy in aluminum-magnesium system

№	Name	Percentage of elements in mass accounting, %										
		Al	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Ti**	**Be**	**Zn**	**Ge**	**Cr**
1	**Al-Mg**	91,9-94	0,5	0,5	0,1	0,3-0,8	4,8-5,8	0,1	0,005	0,2	-	-
2	**Al-Mg**	91,9-94	0,5	0,5	0,1	0,3-0,8	4,8-5,8	0,1	0,005	0,2	0,1	-
3	**Al-Mg**	91,9-94	0,5	0,5	0,1	0,3-0,8	4,8-5,8	0,1	0,005	0,2	0,2	-
4	**Al-Mg**	91,9-94	0,5	0,5	0,1	0,3-0,8	4,8-5,8	0,1	0,005	0,2	0,3	-

Table 2. Alloy in aluminum-copper system

№	Name	Percentage of elements in mass accounting, %										
		Al	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Ti**	**Be**	**Zn**	**Ge**	**Cr**
1	**Al-Cu**	91-94,7	0,5	0,5	3,8-4,9	0,3-0,9	1,2-1,8	0,1	-	0,3	-	-
2	**Al-Cu**	91-94,7	0,5	0,5	3,8-4,9	0,3-0,9	1,2-1,8	0,1	-	0,3	0,1	-
3	**Al-Cu**	91-94,7	0,5	0,5	3,8-4,9	0,3-0,9	1,2-1,8	0,1	-	0,3	0,2	-
4	**Al-Cu**	91-94,7	0,5	0,5	3,8-4,9	0,3-0,9	1,2-1,8	0,1	-	0,3	0,3	-

Table 3. Aluminum-manganese system alloy

№	Name	Percentage of elements in mass accounting, %										
		Al	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Ti**	**Be**	**Zn**	**Ge**	**Cr**
1	**Al-Mn**	96,3-99	0,6	0,7	0,05-0,2	1-1,5	-	-	-	0,1	-	-
2	**Al-Mn**	96,3-99	0,6	0,7	0,05-0,2	1-1,5	-	-	-	0,1	0,1	-
3	**Al-Mn**	96,3-99	0,6	0,7	0,05-0,2	1-1,5	-	-	-	0,1	0,2	-
4	**Al-Mn**	96,3-99	0,6	0,7	0,05-0,2	1-1,5	-	-	-	0,1	0,3	-

3. Results and Discussions

The samples prepared by cutting were grinded according to GOST 9012-59 [standard], and hardness was quantified using the Brinell scale was used to test for hardness [17-19]. The hardness was measured using an ITV-1-m brand hardness measurement devise (Fig. 3).

Figure 3: ITV-1-M hardness measurement tool

On the same surface, the samples' hardness was assessed three times. Figure 4 displays the results of the measurement.

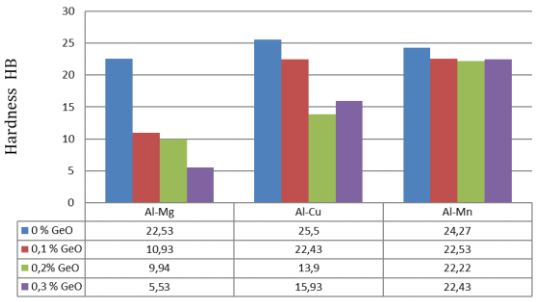

Figure 4: The hardness of the samples

As can be seen from figure 4, the hardness of aluminum alloys has decreased under the influence of germanium element. In particular, the hardness of aluminum-magnesium alloy was reduced to 76% when 0.3% germanium was added. The hardness of the aluminum-copper alloy has decreased by 48% under the influence of germanium.

Following to this, addition of germanium reduced the hardness of aluminum-manganese alloy by 7% - 8%.

Then, micro sections were prepared for metallographic analysis from the poured samples [20]. Then, an optical metallographic microscope E3230 was used to perform a microstructural study on the generated samples (Figure 5).

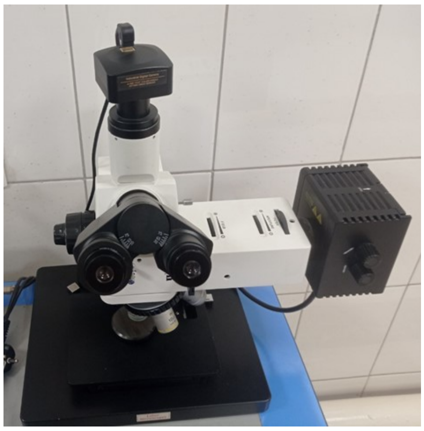

Figure 5: Optical metallographic microscope

The samples were examined in a 400-fold magnified state. Figure 6 shows the structure of samples of aluminum-magnesium alloy and germanium added in it.

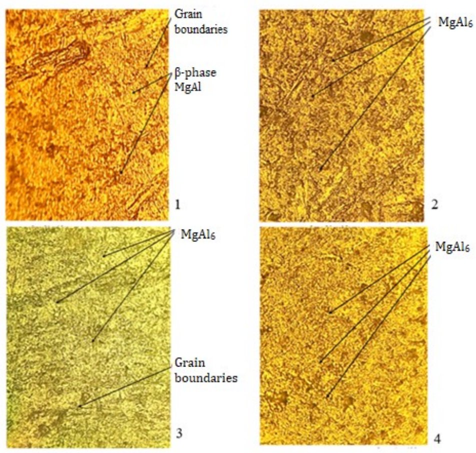

Figure 6: Sample microstructure X400. 1 - Al-Mg; 2 - Al-Mg+0,1% Ge; 3 - Al-Mg+0,2% Ge; 4 - Al-Mg+0,3% Ge

According to Fig. 6(1), the microstructure of the sample is a metal base with a relatively fine grain (No. 8-9 according to GOST 5639-82). With a magnesium content of more than 1.4%, a set of MgAl intermetallic compounds begins to appear, strengthening the base metal during cold working. The grain size of the β-phase is 2-3 microns.

The sample's microstructure is a base metal with a reasonably thin grain (No. 8 in accordance with GOST 5639-82), as shown in Fig. 6(2). With a magnesium content of more than 1.4%, MgAl intermetallic compounds begins to appear, strengthening the base metal during cold working. After adding 0.1% of a germanium content, it can be seen that spheroidization reaches a maximum and hardness is also low.

The date gave in Fig. 6(3) clairifies that the microstructure of the sample is a base metal with a fine grain (No. 9 according to GOST 5639-82). With a magnesium content of more than 1.4%, a chain of MgAl intermetallic compounds begins to appear, strengthening the base metal during cold working. When the germanium alloy contains 0.2%, there is a tendency to spheroidization of the MgAl intermetallic compound, the chain disappears, which affected the hardness of the sample.

Fig. 6(4) shows that the microstructure of the sample is a base metal with a relatively fine grain (No. 9-10 according to GOST 5639-82). With a magnesium content of more than 1.4%, a chain of MgAl intermetallic compounds begins to appear, strengthening the base metal during cold working. As indicated by the content of germanium in the alloy of 0.3%, there was a serious grinding of the metal grain, intermetallides have a fine dispersion, 2-3 microns and a rounded shape. The hardness of the sample is also low.

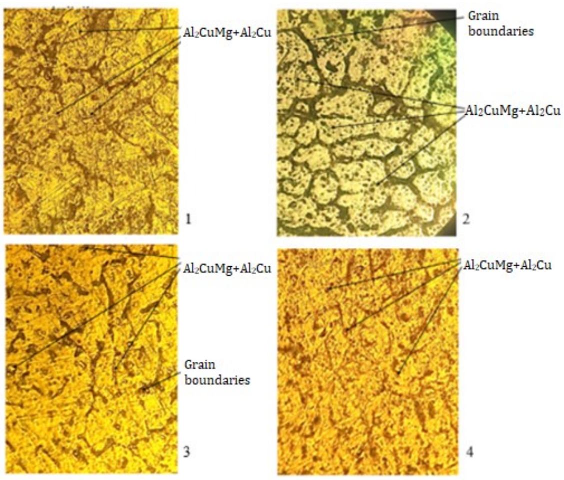

Figure 7: Sample microstructure X400. 1 - Al-Cu; 2 - Al-Cu+0,1% Ge; 3 - Al-Cu+0,2% Ge; 4 - Al-Cu+0,3% Ge

Figure 7 gives information about the structure of the aluminum-copper alloy and the samples in which germanium was introduced into it.

According to the microstructure of the samples given in Fig. 7, the primary structural element of Al-Cu alloy, a base metal, is a solid solution of copper and magnesium in aluminum, along with the intermetallic phases Al_2CuMg and Al_2Cu. Melting foci close to intermetallide clusters and and intermittent eutectic secretions are not visually detected. All the grain sizes are according to GOST 5639-82. Fig. 7(1) shows that intermetallic grains are columnar, elongated 9-10x3 microns. The hardness of the alloy is high enough for non-hardened aluminum alloys. Moreover, it can be seen from Fig. 7(2) that the effect of 0.1% germanium grinds intermetallic grains as much as possible (5-6 microns). The hardness of the alloy is average. The effect of 0.2% germanium (Fig. 7(3)) grinds grains of intermetallides (3-4 microns). The hardness of the alloy is high enough for non-hardened aluminum alloys. And Fig. 7(4) shows that the influence of 0.3% germanium grinds intermetallic grains (2-3 microns). The hardness of the alloy is average.

Figure 8 gives the structure of the aluminum-manganese alloy and the samples in which germanium was introduced into it. The alloy structure results given in Fig. 8 consist of an a-solid solution of manganese in aluminum and secondary $MnAl_6$ phase secretions, and grain sizes are according to GOST 5639-82.

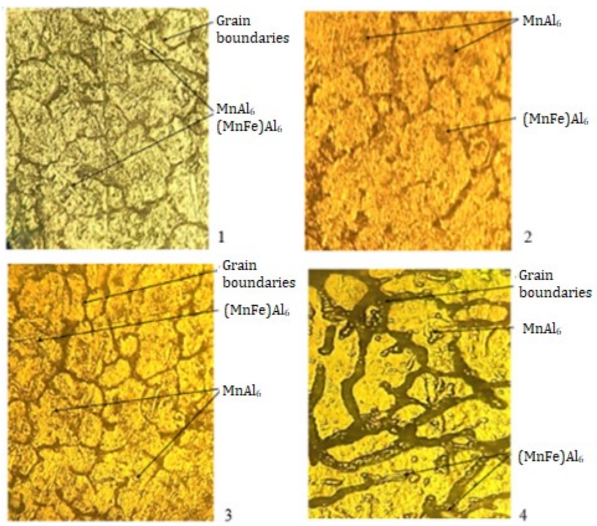

Figure 8: Sample microstructure X400: 1 - Al-Mn; 2 - Al-Mn+0,1% Ge; 3 - Al-Mn+0,2% Ge; 4 - Al-Mn+0,3% Ge

According to Fig. 8(1), in the presence of 0.7% iron, together with $MnAl_6$, a complex phase $(Mn Fe)Al_6$ is formed, which is practically insoluble in aluminum, therefore the AlMn alloy is not strengthened by heat treatment. Columnar crystals of the phase are visible, measuring 10x3 microns on average. The hardness of the sample is relatively high. Next structure showed in Fig. 8(2) shows that in the presence of iron, together with $MnAl_6$, a complex phase $(MnFe)Al_6$ (10-15 microns) is formed, which is practically insoluble in aluminum. The influence of germany is almost imperceptible. The hardness is relatively high in this structure. In the presence of 0.7% iron (Fig. 8(3)) together with $MnAl_6$, a complex phase $(MnFe)Al_6$ is formed, which is practically insoluble in aluminum, therefore the AlMn alloy is not strengthened by heat treatment. The influence of germanium is expressed in the grinding of intermetallides, they begin to acquire rounded shapes. The size of intermetallides is 6-7 microns. Finally, the structure showed in Fig. 8(4) gives information about that in the presence of 0.7% iron together with $MnAl_6$, a complex phase $(MnFe)Al_6$ is formed, which is practically insoluble in aluminum. The influence of germanium is expressed in the grinding of intermetallides, they acquire a spherical shape, measuring 8-9 microns. The hardness is relatively high.

4. Conclusions

Based on the experiments conducted in the research, it is possible to draw a general conclusion about the cast and analysed samples as follows.

Addition of germanium oxide reduced hardness of Aluminium-Magnesium and Aluminium-Copper sample alloys to 72%-76%, and 46%-48% respectively. However, addition of germanium slightly reduced the Aluminium-Manganese sample alloy's hardness by 7%-8%.

Results obtained from the metallographic analyses have shown that the germanium is absorbed during the melting of aluminium alloys, and provides a more granular microstructure of the alloy. The alloy granules are crushed to a size of 2-3 microns when 0.3 percent of germanium is introduced in relation to the charge. This indicates that the microstructure of aluminum alloys is enhanced by the addition of germanium.

Considering the influence of the germanium on the hardness of aluminium alloys, it is recommended add Germanium in the composition with other elements.

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