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Research Article

Effect of bismuth additions on the thermophysical and thermodynamical properties of E-AlMgSi (Aldrey) aluminum semiconductor alloy

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Abstract

The economic feasibility of using aluminum as a conductive material is explained by the favorable ratio of its cost to the cost of copper. In addition, one should take into account that the cost of aluminum has remained virtually unchanged for many years.

When using conductive aluminum alloys for the manufacture of thin wire, winding wire, etc., certain difficulties may arise in connection with their insufficient strength and a small number of kinks before fracture. Aluminum alloys have been developed in recent years which even in a soft state have strength characteristics that allow them to be used as a conductive material.

The electrochemical industry is one of the promising application fields of aluminum. E-AlMgSi (Aldrey) conductor aluminum alloys represent this group of alloys. This work presents data on the temperature dependence of heat capacity, heat conductivity and thermodynamic functions of the E-AlMgSi (Aldrey) aluminum alloy doped with bismuth. The studies have been carried out in "cooling" mode. It has been shown that the heat capacity and thermodynamic functions of the E-AlMgSi (Aldrey) aluminum alloy doped with bismuth increase with temperature and the Gibbs energy decreases. Bismuth additions of up to 1 wt.% reduce the heat capacity, heat conductivity, enthalpy and entropy of the initial alloy and increase the Gibbs energy.

Keywords

E-AlMgSi (Aldrey) aluminum alloy, bismuth, heat capacity, heat conductivity, "cooling" mode, enthalpy, entropy, Gibbs energy.

1. Introduction

Aluminum and its alloys are widely used in electrical engineering as conductor and structural materials. As a conductive material, aluminum is characterized by high electrical and thermal conductivity (after copper, the maximum level among all technically used metals) [1].

Aluminum also has a low density, high atmospheric corrosion resistance and resistance to chemicals. However, aluminum alloys in specific states and under severe operation conditions may undergo dangerous corrosion types. Of special interest is aluminum corrosion in close-to-neutral solutions ($6 < pH < 8$). This corrosion occurs in natural environments: seawater, lacustrine and river water, potable water and atmospheric precipitation. Under these conditions and normal temperatures, the mobility of H^+ ions or H_2O molecules during hydrogen emission is negligibly low [2].

The economic feasibility of using aluminum as a conductive material is explained by the favorable ratio of its cost to the cost of copper. In addition, one should take into account that the cost of aluminum has remained virtually unchanged for many years [3, 4].

When using conductive aluminum alloys for the manufacture of thin wire, winding wire, etc., certain difficulties may arise in connection with their insufficient strength and a small number of kinks before fracture.

Aluminum alloys have been developed in recent years which even in a soft state have strength characteristics that allow them to be used as a conductive material [4].

One of conductor aluminum alloys is E-AlMgSi (Aldrey) pertaining to thermally hardened alloys. It has high strength and ductility. This alloy acquires high electrical conductivity upon appropriate heat treatment. Products made from it are used almost exclusively for overhead power lines [4–6].

Since overhead power lines made from aluminum and its alloys are used in open air, increasing the corrosion resistance of these alloys is an urgent task.

The aim of this work is to study the effect of bismuth additions on the thermophysical and thermodynamical properties of E-AlMgSi (Aldrey) aluminum conductor alloy, chemical composition (wt.%): 0.5 Mg, 0.5 Si, balance Al.

2. Experimental

The alloys were synthesized in a SShOL type resistance laboratory shaft furnace at 750–800 °C. A6 grade aluminum which was additionally doped with the calculated amount of silicon and magnesium was used as a charge in the preparation of the E-AlMgSi alloy. When doping aluminum with silicon, the metallic (0.1 wt.%) silicon present in primary aluminum was taken into account. Magnesium wrapped in aluminum foil was introduced into the molten aluminum using a bell. Bismuth was introduced into the melt in a form wrapped in aluminum foil. The alloys were chemically analyzed for silicon and magnesium contents at the Central Industrial Laboratory of the State Unitary Enterprise Tajikistan Aluminum Company. The alloy compositions were controlled by weighing the charge and the alloys. Synthesis was repeated if the alloy weight deviated from the target one by more than 1–2% rel.u. Then the alloys were cleaned from slag and cast into graphite molds in order to obtain samples for thermophysical study. The cylindrical samples had a diameter of 16 mm and a length of 30 mm.

The heat capacity of the alloys was measured using the setup shown in Fig. 1. The electric furnace *3* is mounted on the support *6* and can move up and down (arrow shows movement direction). The specimen *4* and the reference *5* (also movable) are in the form of cylinders with a diameter of 16 mm and a length of 30 mm with drilled cavities at one side for thermocouple insertion. The thermocouple contacts are connected to a DI9208L Digital Multimeter (*7*, *8* and *9*). The electric furnace is powered via the laboratory transformer *1* by setting the required temperature with the thermocontroller *2*. The initial temperature is read on the DI9208L Digital Multimeters. The specimen and the reference are placed into the electric furnace and heated to the required temperature which is controlled from DI9208L Digital Multimeter readings on the compu-

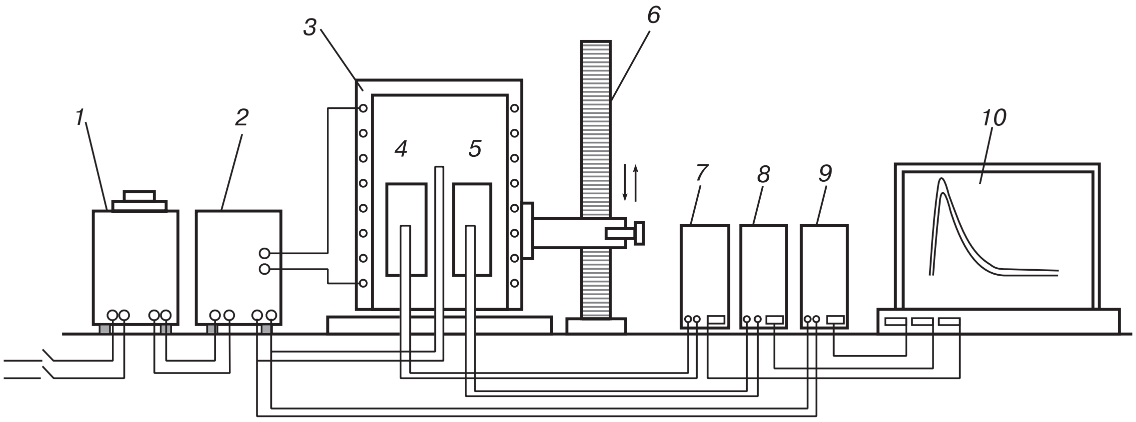

Figure 1. Experimental setup for determining the heat capacity of solids in "cooling" mode

ter *10*. The specimen and the reference are simultaneously removed from the furnace, and the temperature is measured from that moment on. DI9208L Digital Multimeter readings are recorded by the computer every 10 sec while the specimen and the reference are cooled down to room temperature (30 °C).

The temperature was measured with a multichannel digital thermometer allowing direct recording of the data on the computer in tabular form. The temperature measurement accuracy was 0.1 °C. The relative temperature measurement error in the 40 to 400 °C range was ± 1%. The heat capacity measurement error for this method is within 4–6% depending on temperature.

The measurement data were processed in MS Excel and plotted in Sigma Plot. The correlation coefficient was $R_{\text{corr.}} > 0.989$ which confirms the correct choice of the approximating function.

3. Results and discussion

To determine the cooling rate we plotted specimen cooling curves. The cooling curves are specimen temperature *vs* time functions for air cooling [7–15].

The experimental temperature vs time functions of the specimens (Fig. 2*a*) are described by the following equation:

$$T = ae^{-b\tau} + pe^{-k\tau}, \qquad (1)$$

where *a, b, p, k* are constants and t is cooling time.

Differentiating Eq. (1) by t we obtained the following equation for specimen cooling rate determination:

$$\frac{dT}{d\tau} = -abe^{-b\tau} + pke^{-k\tau}, \qquad (2)$$

Based on Eq. (2) we calculated the cooling rates for the specimens of E-AlMgSi alloy (Aldrey) doped with bismuth (Fig. 2*b*). The coefficients *a, b, p, k, ab, pk* in Eq. (2) for the test alloys are summarized in Table 1.

Then based on the calculated cooling rates for the alloys and the A5N grade Al reference specimens we calculated the specific heat capacity of E-AlMgSi alloy (Aldrey) doped with bismuth:

$$C^0_{P_2} = C^0_{P_1}\frac{m_1}{m_2}\frac{\left(\frac{dT}{d\tau}\right)_1}{\left(\frac{dT}{d\tau}\right)_2} \qquad (3)$$

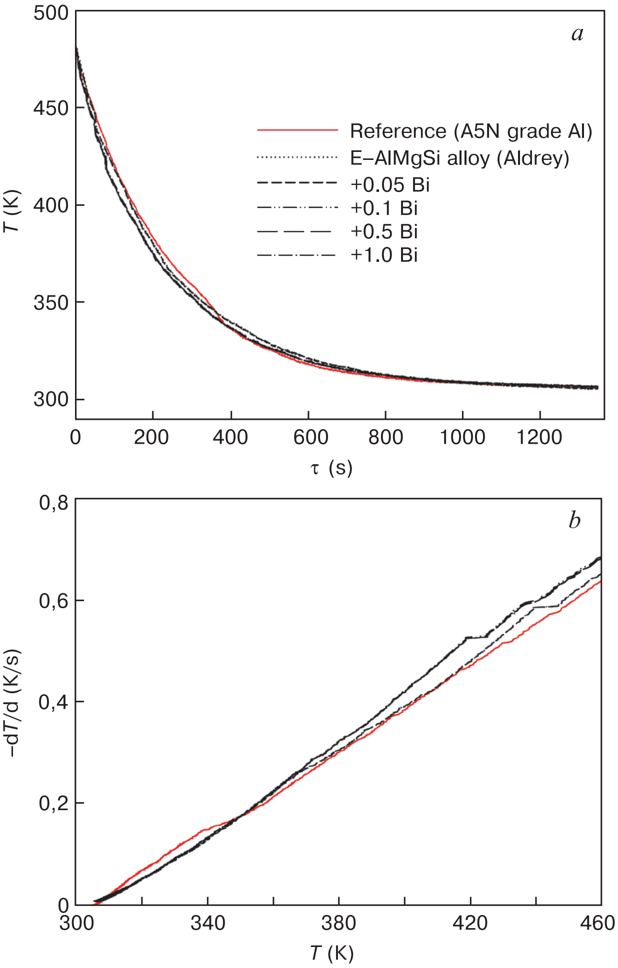

Figure 2. (*a*) temperature and (*b*) cooling rate for samples of E-AlMgSi alloy (Aldrey) doped with bismuth and reference (A5N grade Al) as functions of time

where $m_1 = \rho_1 V_1$ is the weight of the reference; $m_2 = \rho_2 V_2$ is the weight of the specimen and

$$\left(\frac{dT}{d\tau}\right)_1, \left(\frac{dT}{d\tau}\right)_2$$

are reference and alloy specimen cooling rates for a specific temperature.

Using polynomial regression we obtained an equation for the temperature dependence of the heat capacity of E-AlMgSi alloy (Aldrey) doped with bismuth:

$$C^0_{P_0} = a + bT + cT^2 + dT^3 \qquad (4)$$

The coefficients *a, b, c, d* in Eq. (4) are summarized in Table 2.

Table 1. Coefficients *a, b, p, k, ab, pk* in Eq. (2) for E-AlMgSi alloy (Aldrey) doped with bismuth

Bismuth content in E-AlMgSi alloy, wt.%	*a*, K	*b* × 10^{-3}, s^{-1}	*p*, K	*k* × 10^{-5}, s^{-1}	*ab* × 10^{-1}, K × s^{-1}	*pk* × 10^{-3}, K × s^{-1}
E-AlMgSi alloy	165.61	4.46	314.72	2.27	7.38	7.14
+0.05 Bi	164.02	4.46	314.82	2.31	7.32	7.26
+0.1 Bi	160.75	4.74	315.21	2.11	7.61	6.64
+0.5 Bi	158.44	4.72	314.99	2.06	7.48	6.48
+1.0 Bi	159.23	4.73	315.17	2.10	7.54	6.62
Reference (A5N grade Al)	494.26	5.01	319.92	2.57	0.25	8.23

Table 2. Coefficients *a, b, c, d* in Eq. (4) for samples of E-AlMgSi alloy (Aldrey) doped with bismuth and the reference (A5N grade Al)

Bismuth content in E-AlMgSi alloy, wt.%	*a*, J/(kg × K)	*b*, J/(kg × K^2)	*c*, J/(kg × K^3)	*d* × 10^{-4}, J/(kg × K^4)	Correlation coefficient *R*, %
E-AlMgSi alloy	-10394.96	84.30	0.21	1.71	0.9925
+0.05 Bi	-8928.68	72.90	-0.18	1.48	0.9899
+0.1 Bi	-11529.79	89.00	-0.21	1.71	0.9950
+0.5 Bi	-11560.07	89.54	-0.216	1.75	0.9980
+1.0 Bi	-10548.49	81.60	-0.20	1.57	0.9989
Reference (A5N grade Al)	645.88	0.36	0	0	1.0

Table 3. Temperature dependence of specific heat capacity (kJ/(kg×K)) of E-AlMgSi alloy (Aldrey) doped with bismuth and reference (A5N grade Al)

Bismuth content in E-AlMgSi alloy, wt.%	Heat capacity, kJ/(kg·K)						
	300 K	325 K	350 K	375 K	400 K	450 K	500 K
E-AlMgSi alloy	751.00	855.36	907.62	923.83	920.00	916.37	1025.00
+0.05 Bi	737.65	832.24	882.20	901.42	903.76	913.31	1021.87
+0.1 Bi	590.20	735.49	822.57	867.46	886.20	909.32	1020.20
+0.5 Bi	560.05	701.29	785.45	828.91	848.10	879.25	1010.15
+1.0 Bi	557.44	690.13	769.55	810.40	827.42	848.78	951.40
Reference (A5N grade Al)	854.62	877.90	901.55	925.45	949.48	997.46	1044.57

The data on the heat capacity of the alloys calculated using Eq. (3) with 25 K intervals are summarized in Table 3. The heat capacity of the alloys decreases with an increase in the bismuth concentration in E-AlMgSi alloy (Aldrey) and increases with an increase in temperature. Based on the heat capacity of E-AlMgSi alloy (Aldrey) doped with bismuth and the experimental data on the cooling rate we calculated the temperature dependence of the heat conductivity of E-AlMgSi alloy (Aldrey) using the following equation:

$$a = \frac{C_p^0 m \frac{dT}{d\tau}}{(T - T_0)S} \qquad (5)$$

where T, T_0 are the specimen and environment temperatures, respectively, and S, m are the specimen surface area and weight, respectively. The temperature dependence of the heat conductivity coefficient of E-AlMgSi alloy (Aldrey) doped with bismuth is shown in Fig. 3.

To calculate the enthalpy, entropy and Gibbs energy as functions of temperature using Eqs. (6)–(8), we integrated the specific heat capacity calculated using Eq. (4):

$$\left[H^0(T) - H^0(T_0)\right] = a(T - T_0) + \frac{b}{2}\left(T^2 - T_0^2\right) + \\ + \frac{c}{3}\left(T - T_0^3\right) + \frac{d}{4}\left(T^4 - T_0^4\right) \qquad (6)$$

$$\left[S^0(T) - S^0(T_0)\right] = a \ln\frac{T}{T_0} + b(T - T_0) + \\ + \frac{c}{2}\left(T^2 - T_0^2\right) + \frac{d}{3}\left(T^3 - T_0^3\right) \qquad (7)$$

$$\left[G^0(T) - G^0(T_0)\right] = \\ = \left[H^0(T) - H^0(T_0)\right] - T\left[S^0(T) - S^0(T_0)\right] \qquad (8)$$

where T_0 = 298.15.

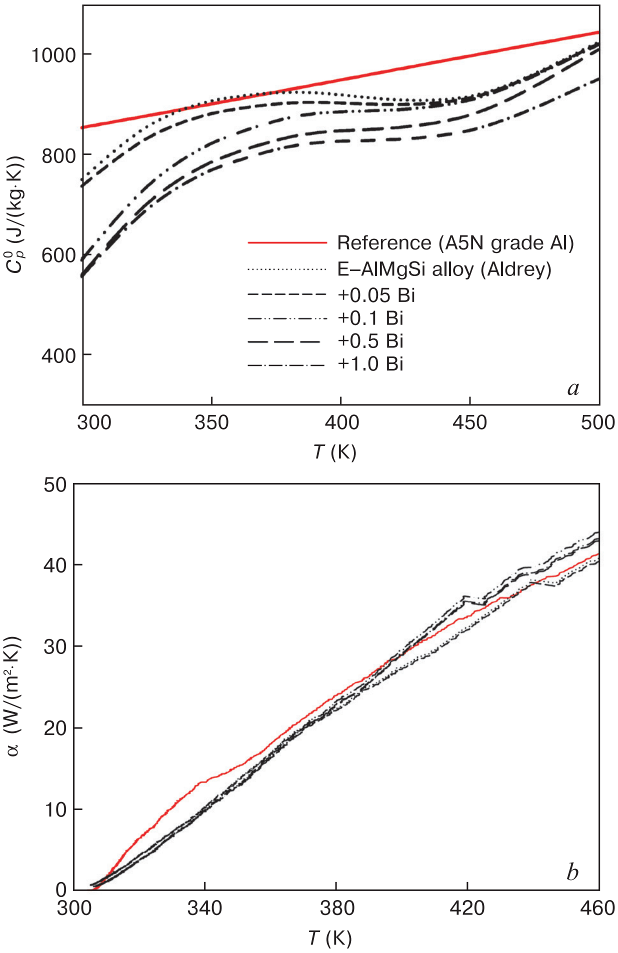

Figure 3. Temperature dependence of (*a*) heat capacity and (*b*) heat conductivity coefficient of E-AlMgSi alloy (Aldrey) doped with bismuth and reference (A5N grade Al)

The calculation data for the enthalpy, entropy and Gibbs energy as functions of temperature obtained using Eqs. (6)–(8) with 25 K intervals are summarized in Table 4.

Table 4. Temperature dependence of the thermodynamical functions of E-AlMgSi alloy (Aldrey) doped with bismuth and reference (A5N grade Al)

Bismuth content in E-AlMgSi alloy, wt.%	**Thermodynamical functions**						
	300 K	**325 K**	**350 K**	**375 K**	**400 K**	**450 K**	**500 K**
$[H^0(T) - H^0(T_0^*)]$, kJ/kg for alloys							
E-AlMgSi alloy	1.3799	21.5847	43.7138	66.6654	89.7383	135.4471	183.2466
+0.05 Bi	1.3562	21.0873	42.5965	64.9414	87.5269	132.7727	180.5087
+0.1 Bi	1.0794	17.7886	37.3691	58.5658	80.5244	125.3141	172.9194
+0.5 Bi	1.0240	16.9277	35.6147	55.8629	76.8600	119.9037	166.4520
+1.0 Bi	1.0199	16.7410	35.0828	54.8974	75.4046	117.2165	161.6372
Reference (A5N grade Al)	1.5795	23.2351	45.4777	68.3149	91.7514	140.4266	191.4833
$[S^0(T) - S^0(T_0^*)]$, kJ/kg ·K for alloys							
E-AlMgSi alloy	0.0046	0.0692	0.1348	0.1982	0.2577	0.3654	0.4660
+0.05 Bi	0.0045	0.0676	0.1313	0.1930	0.2513	0.3579	0.4584
+0.1 Bi	0.0036	0.0570	0.1150	0.1735	0.2302	0.3357	0.4359
+0.5 Bi	0.0034	0.0543	0.1096	0.1655	0.2197	0.3210	0.4190
+1.0 Bi	0.0034	0.0537	0.1080	0.1627	0.2156	0.3141	0.4076
Reference (A5N grade Al)	0.0053	0.0746	0.1405	0.2035	0.2640	0.3786	0.4862
$[G^0(T) - G^0(T_0^*)]$, kJ/kg for alloys							
E-AlMgSi alloy	-0.0043	-0.9209	-3.4739	-7.6429	-13.3499	-28.9837	-49.7672
+0.05 Bi	-0.0042	-0.9014	-3.3917	-7.4534	-13.0161	-28.2969	-48.7033
+0.1 Bi	-0.0033	-0.7460	-2.8923	-6.5011	-11.5525	-25.7408	-45.0265
+0.5 Bi	-0.0031	-0.7084	-2.7516	-6.1912	-11.0094	-24.5605	-43.0455
+1.0 Bi	-0.0031	-0.7030	-2.7201	-6.1057	-10.8391	-24.1202	-42.1591
Reference (A5N grade Al)	-0.0049	-1.0111	-3.7068	-8.0133	-13.8629	-29.9625	-51.6098

* T_0 = 298.15 K.

Aldrey alloy consists of aluminum with the following impurities: 0.3–0.5% Mg, 0.4–0.7% Si and 0.2–0.3% Fe. Compulsory impurities which determine the properties of Aldrey are magnesium and silicon the content ratio of which should meet that for the Mg_2Si compound which forms in the alloy and acts as a strengthening agent ensuring the high mechanical strength of the alloy. However one should take into account that in practice the melt always contains iron which is a still unavoidable but often detrimental impurity in any technical grade aluminum, forming the silicon containing compound $Al_6Fe_2Si_3$. Therefore to completely ensure the formation of the Mg_2Si compound one should compose the melt with a certain excess of silicon (0,4–0,5%) above the theoretical level [1–3].

The strengthening action of the Mg_2Si compound stems from the fact that its solubility is solid aluminum decreases with a decrease in temperature. For example the maximum solubility of Mg_2Si in aluminum is 1.85% at 595 °C and only 0.2% at 200 °C. Therefore rapid cooling (quenching) of an Aldrey type alloy heated to above 500 °C at which all Mg_2Si is in the solid solution produces a supersaturated Mg_2Si solid solution in aluminum [1–3].

Long-term tempering causes precipitation of excess Mg_2Si from the solid solution in the form of a fine-grained structural component which increases the mechanical strength of the alloy (precipitation hardening). This tempering of the alloy is referred to as natural ageing. Ageing can be accelerated by slightly heating the alloy (to 150–200 °C), i.e., artificial ageing. In the course of ageing Mg_2Si impurity precipitates from the solid solution causing an increase in the electrical conductivity of the alloy [1–3].

Bismuth doping of E-AlMgSi alloy modifies the primary precipitates of binary and ternary phases in the alloy, providing a generally positive contribution to its performance.

Thus we determined the heat capacity of bismuth doped E-AlMgSi alloy (Aldrey) in “cooling” mode based on the known heat capacity of a reference A5N grade aluminum specimen. Using the experimentally obtained polynomial dependences we showed that with an increase in temperature the heat capacity, enthalpy and entropy of the alloys increase while the Gibbs energy decreases. Bismuth additions in the experimentally studied concentration range 0.05–1.0 wt.% reduce the heat capacity, heat conductivity coefficient, enthalpy and entropy of the initial E-AlMgSi alloy (Aldrey) and increase the Gibbs energy. The increase in the heat capacity, heat conductivity coefficient, enthalpy and entropy with an increase in the bismuth concentration in the alloy is caused by the modification of the α-Al solid solution structure, i.e., a higher heterogeneity of the structure of the multicomponent alloys [16–18].

4. Conclusion

Experimental data on the temperature dependence of the heat capacity, heat conductivity coefficient and thermodynamical functions of E-AlMgSi aluminum alloy (Aldrey) doped with bismuth were presented for “cooling” mode measurements.

We show that with an increase in temperature the heat capacity and the thermodynamical functions of E-AlMgSi alloy (Aldrey) with bismuth increase and the Gibbs energy decreases. Bismuth additions of up to 1 wt.% reduce the heat capacity, heat conductivity, enthalpy and entropy of the initial alloy but increase the Gibbs energy.

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