

Heat capacity and thermodynamic functions of E-AlMgSi (Aldrey) aluminum conductor alloy doped with gallium

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Abstract

Aluminum is a metal having permanently broadening applications. Currently aluminum and its alloys successfully replace conventional metals and alloys in a number of application fields. The wide use of aluminum and its alloys is primarily stipulated by its advantageous properties e.g. low density, high corrosion resistance and electrical conductivity as well as the possibility of applying protective and decorative coatings. In combination with great abundance and relatively low cost which has been almost constant in recent years, this permanently broadens the application range of aluminum. The electrochemical industry is one of the promising application fields of aluminum. The E-AlMgSi type (Aldrey) conductor aluminum alloy 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. 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 gallium. The studies have been carried out in “cooling” mode.

It has been shown that with an increase in temperature the heat capacity and thermodynamic functions of E-AlMgSi (Aldrey) alloy doped with gallium increase while the Gibbs energy decreases. Gallium doping to 1 wt.% reduces the heat capacity, enthalpy and entropy of the initial alloy and increases the Gibbs energy.

Keywords

aluminum, E-AlMgSi (Aldrey) alloy, gallium, 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). Aluminum also has a low density, high atmospheric corrosion resistance and resistance to chemicals.

Another advantage of aluminum is its neutrality to insulators, e.g. oils, lacquers and thermoplastics, including at high temperatures. Aluminum differs from other

metals by a low magnetic permeability and the formation of a non-conductive easily removable powdered product (Al_2O_3) in the electric arc [1–3].

The use of aluminum and its alloys for the manufacturing of switching devices, power transmission line poles, cases of electric motors and switches etc. is regulated by special guidelines or general design rules.

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 [4–6].

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.

One method to increase the strength of aluminum alloys is doping. Doping elements should be chosen so as to provide an increase in alloy strength while retaining sufficiently high electrical conductivity. Most of impurities increase the strength of aluminum but reduce its electrical conductivity. One can choose impurities which improve the mechanical properties of aluminum while reducing its electrical conductivity but slightly, and introduce them aiming to increase the strength of aluminum.

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 [4–6].

Silicon doping gives the best results. However the strength of this alloy in a hardened state is insufficient. A successful combination of high mechanical strength and electrical conductivity can be achieved by producing ternary and more complex composition aluminum alloys with silicon, magnesium, iron and other elements. Special heat treatment of these alloys provides for the desired results. These alloys and collectively referred to as Aldrey [1–3].

One well-known Aldrey alloy is aluminum with the following impurities: 0.3–0.5% Mg, 0.4–0.7% Si and 0.2–0.3% Fe. The compulsory impurities which determine the advantageous properties of Aldrey are magnesium and silicon whose concentration ratio should meet the formula of the Mg_2Si compound forming in the alloy and acting as a hardening agent that delivers the good mechanical properties. However practical applications should be designed taking into account that the alloy always contains iron which is a still unavoidable yet often detrimental impurity in any technical grade of aluminum that forms a silicon containing compound ($\text{Al}_6\text{Fe}_2\text{Si}_3$). Therefore in order to provide for the formation of the Mg_2Si compound one should dope the alloy with a certain excess of silicon (0.4–0.5%) compared with its theoretically required amount [1–3].

The hardening action of the Mg_2Si compound is accounted for by the fact that its solubility in solid aluminum declines with a decrease in temperature. For example the maximum Mg_2Si solubility in aluminum at 595 °C is 1.85% while at 200 °C this figure is only 0.2%. Therefore if an Aldrey type alloy is heated to above 500 °C (at this

temperature all the Mg_2Si is in the solid solution) and rapidly cooled (quenched), a supersaturated Mg_2Si solution in aluminum is produced [1–3].

Long-term resting of the alloy leads to the precipitation of excess Mg_2Si from the solid solution in the form of a fine-grained component which increases the mechanical strength of the alloy (precipitation hardening). This resting of alloy is referred to as natural aging. The effect delivered by aging can be accelerated and amplified by slightly heating the alloy (to 150–200 °C), i.e., applying artificial aging. During aging the Mg_2Si impurity precipitates from the solid solution and increases the electrical conductivity of the alloy [1–3].

The heat treatment process route of Aldrey type alloy wire includes water quenching of rolled or pressed wire at 510–550 °C followed by drawing and artificial aging at 140–180 °C [1–3].

The tensile strength of Aldrey is two times higher than that of aluminum. Given the same electrical conductivity this provides for a 1.5 times higher strength of Aldrey wire than that of copper wire, with a two times smaller specific weight. This advantage allows one to increase the pole spans of power transmission lines. The higher hardness of Aldrey reduces the risk of wire damage during installation in comparison with aluminum or steel-aluminum.

The aim of this work is to study the effect of gallium doping on the thermophysical properties and thermodynamic functions of E-AlMgSi (Aldrey) aluminum conductor alloy with the 0.5 wt.% Si and 0.5 wt.% Mg chemical composition.

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. The metallic gallium 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 cooling rate was determined by plotting cooling curves for the samples. The cooling curves were sample temperature dependences on time of cooling in air [7–15].

The process of heat transfer from a hotter body to a colder one tends to establish a thermodynamic equilibrium in a system consisting of an extremely large number of particles. Therefore this is a relaxation process which can be described by an exponential function of time. In the case in question the heated body transfers heat to the environment, i.e., a body having an infinitely large heat capacity. The ambient temperature can therefore be taken to be constant (T_0). Then the body temperature dependence on time τ can be written in the following form: $\Delta T = \Delta T_1 e^{-\tau/\tau_1}$ where ΔT is the difference between the temperatures of the heated body and the environment; ΔT_1 is the difference between the temperatures of the heated body and the environment at $\tau = 0$; τ_1 is the cooling constant which is equal to the time during which the difference between the temperatures of the heated body and the environment decreases by e times.

Schematic of the heat capacity measurement unit used in our experiment is shown in Fig. 1. The electric furnace 3 is movably mounted on the platform 6 along which it can move up and down on thread. The sample 4 and the standard 5 which are also movable are in the form of 30 mm long 16 mm diam. cylinders with channels drilled out in the butt ends in which thermocouples are inserted. The ends of the thermocouples are connected to a Digital Multimeter DI9208L multichannel digital thermometer (7). The electric furnace 3 is powered on from the laboratory transformer 1 after setting the required temperature with the thermocontroller 2. The initial temperature is read on the multichannel digital thermometer 7. The sample 4 and the standard 5 are put into the electric furnace 3 and heated to the required temperature, the latter being controlled with the multichannel digital thermometer 7 and the PC 8. The sample 4 and the standard 5 are simultaneously removed from the electric furnace 3, following which the temperature is recorded. The readings of the multichannel digital thermometer 7 are recorded with the PC 8 at 5, 10 and 20 sec intervals until the sample and the standard cool down.

The multichannel digital thermometer used for temperature measurements allowed PC recording of measure-

ment results in a tabular form. The temperature measurement accuracy was 0.1 °C, the temperature recording time interval being 1 sec. The relative temperature measurement error in the 40 to 400 °C was $\pm 1\%$. The heat capacity measurement error for this method was within 4–6% depending on temperature.

The measurement results were processed with MS Excel and data charts were built with Sigma Plot. The correlation coefficient was $R_{\text{corr}} > 0.999$ confirming the correct choice of approximating function.

3. Results and discussion

The experimental temperature vs time curves of the samples (Fig. 2) can be described with an equation of the following type.

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

where a , b , p and k are constants and τ is the cooling time.

Differentiating Eq. (1) with respect to τ we obtained the following sample cooling rate equation:

$$dT/d\tau = -abe^{-b\tau} - pke^{-k\tau}. \tag{2}$$

From Eq. (2) we calculated the cooling rates of the E-AlMgSi (Aldrey) alloy samples doped with gallium (Fig. 3). The values of the a , b , p , k , ab and pk coefficients in Eq. (2) for the test alloys are summarized in Table 1.

Table 1. a , b , p , k , ab and pk coefficients in Eq. (2) for E-AlMgSi (Aldrey) alloy with gallium.

Gallium content in E-AlMgSi (Aldrey) alloy, wt.%	a , K	$b \cdot 10^{-3}$, s ⁻¹	p , K	$k \cdot 10^{-4}$, s ⁻¹	$ab \cdot 10^{-1}$, K/s	$pk \cdot 10^{-3}$, K/s
0	165.61	4.46	314.72	2.27	7.38	7.14
0.05	172.18	4.55	314.99	2.20	7.83	6.92
0.1	159.14	4.71	314.85	2.02	7.49	6.35
0.5	153.82	4.64	313.99	1.81	7.13	5.67
1.0	159.234	4.73	315.17	2.10	7.54	6.62
Standard (Al Grade A5N)	494.26	5.01	319.92	2.57	0.25	8.23

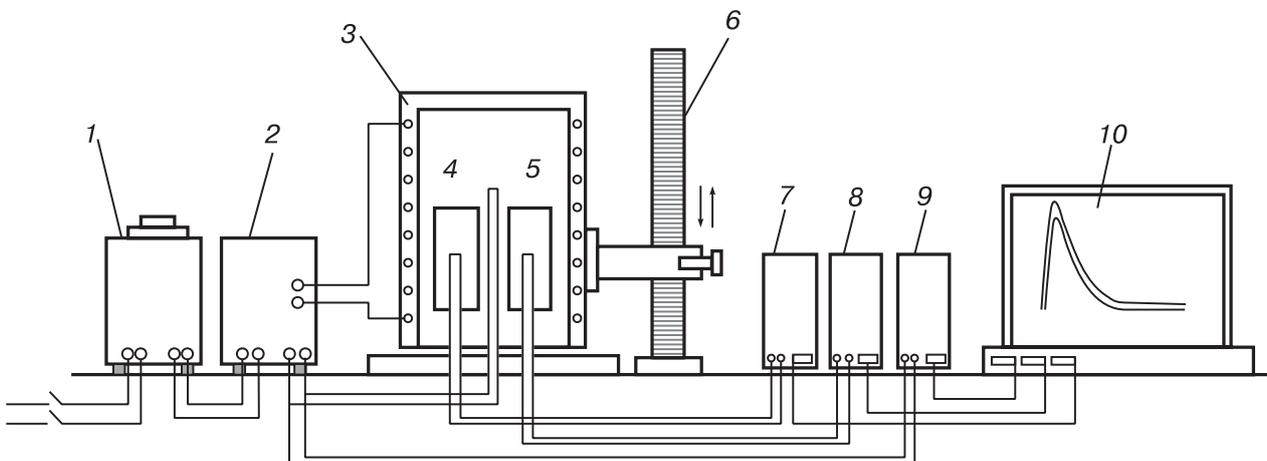


Figure 1. Solid body “cooling” mode heat capacity measurement unit: 1 automatic transformer, 2 thermocontroller, 3 electric furnace, 4 sample, 5 standard, 6 electric furnace platform, 7 multichannel digital thermometer and 8 recording device (PC).

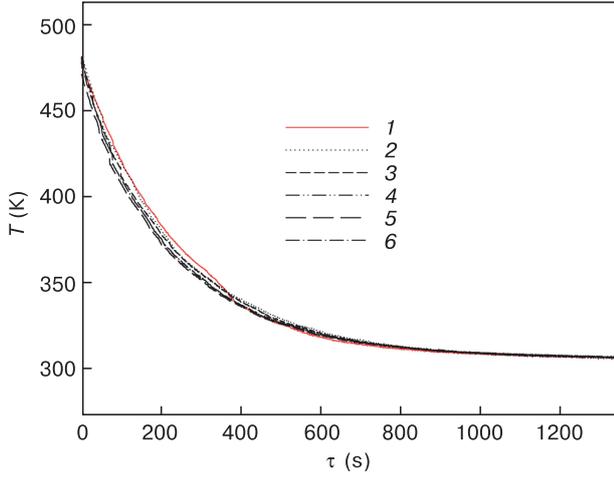


Figure 2. Temperature as a function of cooling time for (1) standard (aluminum Grade A5N) and (2–6) E-AlMgSi (Aldrey) alloy samples with different gallium contents, wt.%: (2) 0, (3) 0.05, (4) 0.1, (5) 0.5 and (6) 1.0.

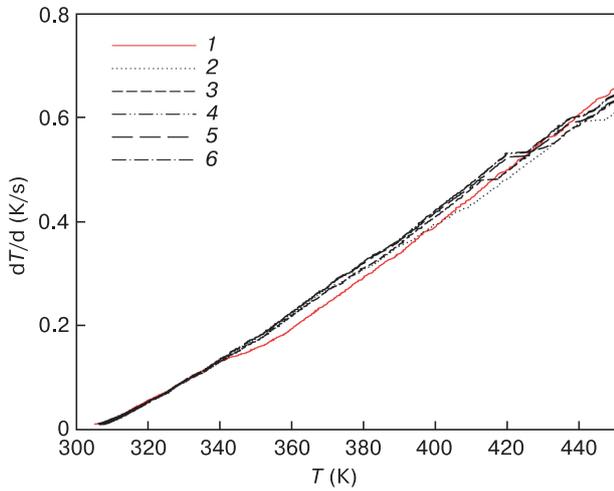


Figure 3. Temperature dependences of cooling rate for (1) standard (aluminum Grade A5N) and (2–6) E-AlMgSi (Aldrey) alloy samples with different gallium contents, wt.%: (2) 0, (3) 0.05, (4) 0.1, (5) 0.5 and (6) 1.0.

Then, based on the calculated alloy cooling rates and using Eq. (3), we determined the specific heat capacity of the E-AlMgSi (Aldrey) alloy doped with gallium and the standard (Al Grade A5N):

$$C_{P_2}^0 = C_{P_1}^0 \frac{m_1}{m_2} \cdot \frac{\left(\frac{dT}{d\tau}\right)_1}{\left(\frac{dT}{d\tau}\right)_2}, \quad (3)$$

where $m_1 = \rho_1 V_1$ is the standard weight; $m_2 = \rho_2 V_2$ is the test sample weight; $\left(\frac{dT}{d\tau}\right)_1, \left(\frac{dT}{d\tau}\right)_2$ are the cooling rates of the alloy and standard samples at the specific test temperature.

Applying a polynomial regression we obtained the temperature dependence equation of the specific heat capacity of the E-AlMgSi (Aldrey) alloy doped with gallium:

$$C_{P_0}^0 = a + bT + cT^2 + dT^3 \quad (4)$$

Table 2. Values of the a , b , c and d coefficients in Eq. (4) for samples of E-AlMgSi (Aldrey) alloy doped with gallium and standard (Al Grade A5N).

Gallium content in E-AlMgSi (Aldrey) alloy, wt.%	a , J/(kg·K)	b , J/(kg·K ²)	c , J/(kg·K ³)	d , J/(kg·K ⁴)	R , %
0	-10394.96	84.30	0.21	1.71	0.9925
0.05	-10394.96	82.90	-0.20	1.66	0.9899
0.1	-13788.22	106.85	-0.26	2.11	0.9950
0.5	-19463.50	152.21	-0.38	3.15	0.9980
1.0	-10147.32	78.49	-0.19	1.51	0.9989
Standard (Al Grade A5N)	645.88	0.36	0	0	1.0

R is the correlation coefficient.

The values of the a , b , c and d coefficients in Eq. (4) are summarized in Table 2.

Results of heat capacity calculations for the alloys using Eq. (3) for different temperatures are summarized in Table 3. The heat capacity of the alloys increases with an increase in the gallium concentration in the E-AlMgSi (Aldrey) alloy and temperature. Using the specific heat capacity of the E-AlMgSi (Aldrey) alloy doped with gallium and the experimental data on the cooling rate we calculated the temperature dependence of the heat conductivity coefficient of the E-AlMgSi (Aldrey) alloy using the following equation:

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

where T and T_0 are the sample and environment temperatures, respectively; and S and m are the surface area and weight of the sample. The temperature dependences of the heat conductivity coefficient for the E-AlMgSi (Aldrey) alloy doped with gallium are shown in Fig. 4.

To calculate the temperature dependence of the enthalpy H , entropy S and Gibbs energy G we used integral specific heat capacities (Eq. 4):

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

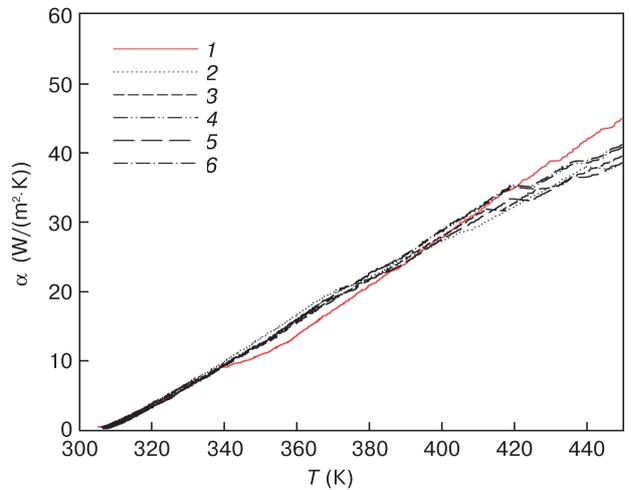


Figure 4. Temperature dependences of heat conductivity coefficient for (1) standard (aluminum Grade A5N) and (2–6) E-AlMgSi (Aldrey) alloy samples with different gallium contents, wt.%: (2) 0, (3) 0.05, (4) 0.1, (5) 0.5 and (6) 1.0.

Table 3. Temperature dependence of specific heat capacity (kJ/(kg·K)) of E-AlMgSi (Aldrey) alloy doped with gallium and standard (Al Grade A5N).

Gallium content in E-AlMgSi (Aldrey) alloy, wt.%	C_p^0 , kJ/(kg · K)					
	300 K	325 K	350 K	375 K	400 K	450 K
0	751.00	855.36	907.62	923.83	920.00	916.37
0.05	678.55	794.12	858.13	886.15	893.72	909.80
0.1	574.54	731.23	820.21	861.25	874.13	894.55
0.5	531.77	712.59	802.69	831.60	828.86	846.53
1.0	531.62	658.39	733.81	772.05	787.26	805.20
Standard (Al Grade A5N)	854.62	877.90	901.55	925.45	949.48	997.46

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

$$[G^0(T) - G^0(T_0)] = [H^0(T) - H^0(T_0)] - T[S^0(T) - S^0(T_0)]; \quad (8)$$

where $T_0 = 298.15$ K.

Results of enthalpy, entropy and Gibbs energy calculations using Eqs. (6)–(8) with a 25 K step are summarized in Table 4.

Table 4. Temperature dependences of thermodynamic functions of E-AlMgSi (Aldrey) alloy doped with gallium and standard (Al Grade A5N).

Gallium content in E-AlMgSi (Aldrey) alloy, wt.%	Thermodynamic Functions					
	300 K	325 K	350 K	375 K	400 K	450 K
$[H^0(T) - H^0(T_0^*)]$, kJ/kg for alloys						
0	1.3799	21.5847	43.7138	66.6654	89.7383	135.4471
0.05	1.2451	19.7762	40.5196	62.3809	84.6546	129.5626
0.1	1.1125	18.4786	38.9238	60.9993	83.7508	129.9372
0.5	0.9674	16.7417	35.8409	56.3663	77.1572	118.5852
1.0	0.9726	15.9695	33.4642	52.3503	71.8750	111.5986
Standard (Al Grade A5N)	1.5795	23.2351	45.4777	68.3149	91.7514	140.4266
$[S^0(T) - S^0(T_0^*)]$, kJ/(kg·K) for alloys						
0	0.0046	0.0692	0.1348	0.1982	0.2577	0.3654
0.05	0.0042	0.0634	0.1248	0.1852	0.2427	0.3484
0.1	0.0037	0.0592	0.1198	0.1807	0.2394	0.3482
0.5	0.0033	0.0536	0.1102	0.1669	0.2205	0.3181
1.0	0.0033	0.0512	0.1030	0.1551	0.2055	0.2991
Standard (Al Grade A5N)	0.0053	0.0746	0.1405	0.2035	0.2640	0.3786
$[G^0(T) - G^0(T_0^*)]$, kJ/kg for alloys						
0	-0.0043	-0.9209	-3.4739	-7.6429	-13.3499	-28.9837
0.05	-0.0038	-0.8394	-3.1931	-7.0741	-12.4299	-27.2549
0.1	-0.0034	-0.7732	-3.0065	-6.7655	-12.0232	-26.7576
0.5	-0.0031	-0.6922	-2.7354	-6.2028	-11.0526	-24.5595
1.0	-0.0030	-0.6705	-2.5947	-5.8237	-10.3367	-22.9901
Standard (Al Grade A5N)	-0.0049	-1.0111	-3.7068	-8.0133	-13.8629	-29.9625

* $T_0 = 298.15$ K

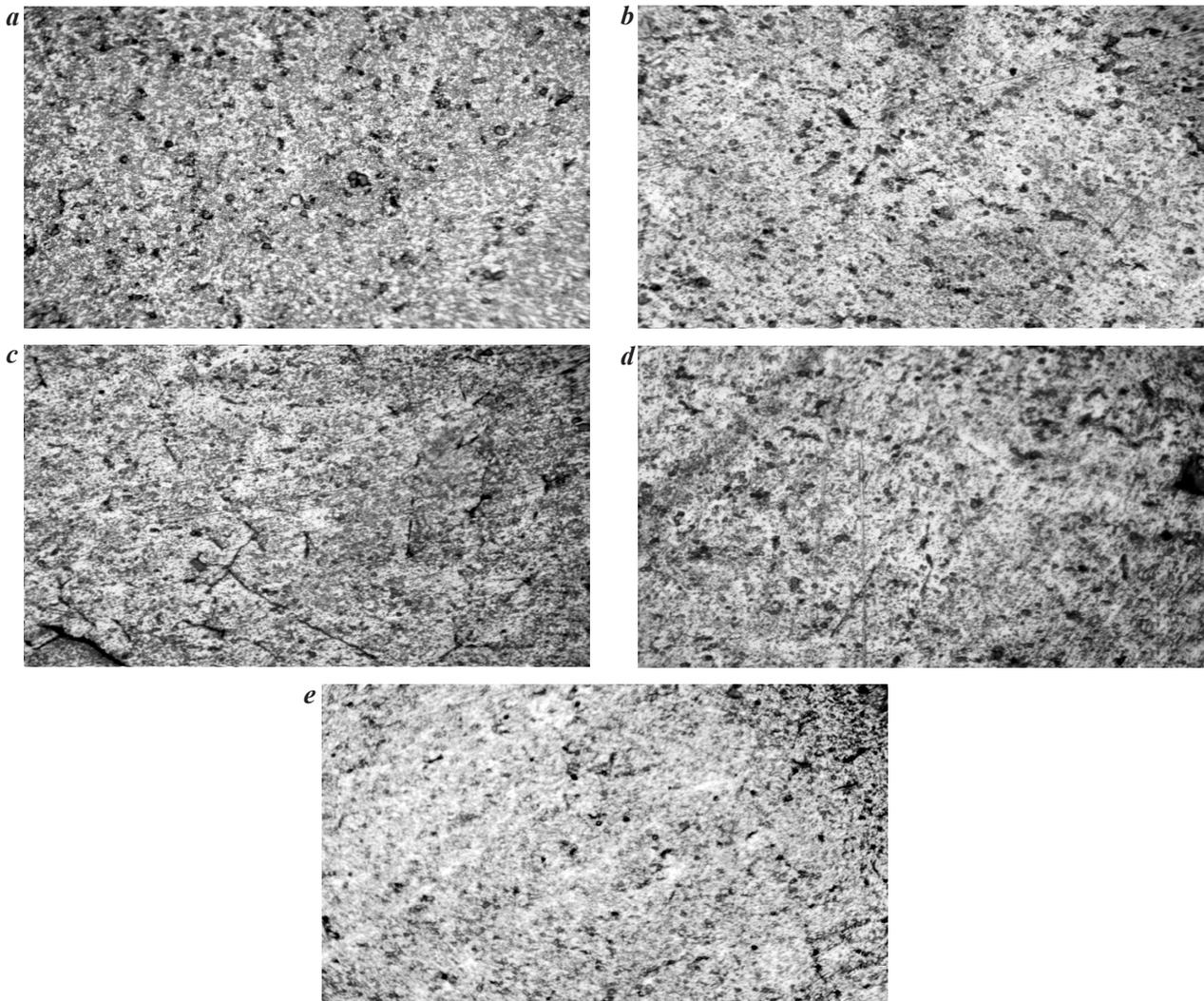


Figure 5. Microstructure ($\times 650$) of E-AlMgSi (Aldrey) alloy (a) pure and (b–e) doped with gallium, wt.%. (a) 0, (b) 0.05, (c) 0.1, (d) 0.5 and (e) 1.0.

The increase in the enthalpy, entropy and Gibbs energy of the E- AlMgSi (Aldrey) alloy upon gallium doping can be accounted for by an increase in the heterogeneity of the structure of the alloys [16–18]. As can be seen from Fig. 5d, e, the microstructure of the E- AlMgSi (Aldrey) alloy containing 0.5 and 1.0 wt.% gallium does not exhibit primary Mg_2Si precipitates. In the initial alloy (Fig. 5a) and low-gallium alloys (Fig. 5b, c) the Mg_2Si phase precipitates crystallize in a needle-shaped form in the aluminum solid solution matrix.

4. Conclusion

The heat capacity of the AlMgSi (Aldrey) alloy doped with gallium was determined in “cooling” mode based

on the known heat capacity of a A5N aluminum standard. Using the obtained polynomial dependences we showed that with an increase in temperature the heat capacity, enthalpy and entropy of the alloys increase and the Gibbs energy decreases. Gallium doping within the experimental concentration range (0.05–1.0 wt.%) reduce the heat capacity, enthalpy and entropy of the initial AlMgSi (Aldrey) alloy but increase the Gibbs energy. The increase in the heat capacity, heat conductivity, enthalpy and entropy of the alloys with gallium content is accounted for by the modifying action of gallium on the structure of the α -Al solid solution and hence an increase in the heterogeneity of the structure of the multi-component alloys.

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