Features of thermal expansion of special-purpose aluminum alloys after treatment of melt and heat treatment

V K Afanasyev, M V Popova, M A Malyukh and A N Prudnikov
Siberian State Industrial University, 42 Kirova street, Novokuznetsk, 654007, Russia
E-mail: starostina_ma1976@mail.ru

Abstract. A combination of corrosion resistance, low specific gravity, and high dimensional stability over a wide temperature range is necessary for alloys for special purpose. The dimensional stability is determined, first of all, by the low temperature coefficient of linear expansion (TCLE). The paper presents the results of studies on the effect of melt treatment on TCLE of aluminum alloys for special purpose on the basis of the system Al-(11÷40)%Si. It is shown that melt treatment with an aqueous solution of CuSO₄ and modification of melt with a mixture of (CaCO₃∙MgCO₃) leads to the decrease in TCLE for all alloys under consideration in the low-temperature test interval tₑₜ₅ = 50÷150 °C. Treatment of the melt by CO(NH₂)₂ vapours leads to the decrease of TCLE of alloys Al-40%Si in the whole temperature range from 50 to 450 °C. For high silicon alloys it is established that the decrease in TCLE occurs in the interval tₑₜ₅ = 350÷450°C after additional heat treatment

1. Introduction
The special purpose of aluminum alloys is determined by the requirement for a specific set of mechanical, physical, physical and chemical and technological properties necessary for the operation of products in the specified conditions, for example, at low or elevated temperatures, in devices and units in the aerospace industry.

For special purpose alloys a combination of corrosion resistance, low specific gravity and high dimensional stability over a wide temperature range is necessary, since the lightening of structures and devices put into orbit facilitates significant fuel savings [1]. The latter requirement is ensured by the minimum temperature coefficient of linear expansion (hereinafter – TCLE) and minimization of structural transformations in time. We have established that the effect on the melt with the help of various physical, mechanical and chemical methods alters the ratio of hydrogen, nitrogen and oxygen in the melt, which during crystallization will control the formation of the solid metal properties [2]. Thermal and mechanical characteristics of aluminum and its alloys are the subject of many research papers. In the opinion of the authors [3], alloys of Al-Mg-Si (aluminum alloys of the 6xxx series) possess properties attractive for their use in the aviation industry. These properties include medium and high strength, good corrosion resistance, improved weldability, good strength, and reduced residual stresses in large plates and sheet products. The mechanical properties of these alloys, fatigue strength, damage resistance and corrosion resistance were investigated.

When developing new materials with improved physical properties, special attention is paid to the hypereutectic alloys of the Al-Si system. However, with conventional methods of casting their structure is characterized by the presence of a coarse eutectic and large crystals of the siliceous phase. For the purpose of grinding primary silicon and eutectic crystals and providing the necessary complex
of mechanical and technological properties, such alloys are subjected to modification, refining or progressive methods of heat treatment. A large number of methods for modifying silumin have been developed: the use of sodium-containing mixtures, the introduction of modifiers in the form of salts and ligatures, phosphorus-containing compounds, oxygen-containing reagents, additives and additives based on highly disperse components [4, 5]. It should be noted that the listed technologies, along with the advantages (convenience of modifiers introduction), have a significant drawback – the presence of harmful fluoride and chloride emissions into the atmosphere. Based on systematically conducted studies, the authors developed a method for treating a melt of hypereutectic silumin with a mixture of calcium and magnesium carbonates, which significantly improves their technological properties [6]. It is known that combined modifying agents, consisting of 2 or more elements, are superior in efficiency to each element separately. Calcium and magnesium are eutectic modifiers in hypereutectic silumins, and their introduction in the form of salts facilitates the crushing of primary silicon crystals.

In the development of special-purpose alloys, along with other requirements, they must have stable performance properties in the range of operating temperatures and pressures [7]. The use of castings is limited due to high natural gas saturation, which is undesirable in the conditions of vacuum. The most effective ways of changing the gas content are melt processing, selection of crystallization conditions and heat treatment [8]. It should be noted that the composition of the external medium has a significant influence on the formation of the structure and physicomechanical properties of aluminum alloys during heat treatment [9, 10]. In [10] we showed that heat treatment in media with an increased content of hydrogen and nitrogen accelerates the course of phase transformations in aluminum alloys, since it activates the diffusion of hydrogen in them. There is a large number of scientific publications confirming the active participation of hydrogen in the formation of the structure and properties of aluminum alloys [11-13]. In this regard, the purpose of this paper is to investigate the possibility of obtaining stable values of aluminum alloys TCLE Al-(11÷40)%Si in the working temperature range by treating the melt with compounds with an increased content of hydrogen, oxygen and nitrogen.

2. Materials and methods of research
Double alloys Al-(11÷40)%Si were chosen as the object of investigation. Charge aluminum was melted, silicon was introduced into it in an amount of 11, 20, 30, 40%, after its complete dissolution, the melt was treated with a mixture of calcium carbonate and magnesium carbonate, taken in the equal proportion in an amount of 1-7% of the mass of the melt. The treatment was carried out for 3-15 minutes at a temperature of 50-250 °C exceeding the melting point of aluminum (710-910 °C). To show the modification efficiency, the melt was simultaneously blown with vapours of aqueous solution of copper sulfate CuSO₄ in an amount of 0.1-0.2 wt% of the melt for 5-15 minutes at 800-1100 °C [14]. For comparison, the melt was blown with CO(NH₂)₂ carbamide vapours at 700...900 °C for 3...6 min [15]. Crystallization of alloys was carried out in the aluminum block mould at casting temperatures of 730...750 °C. From the obtained samples, samples were prepared for the dilatometric study. TCLE was determined using a differential optical photoregulatory dilatometer of Shevenar system, the error of determination was ±0.1·10⁻⁶ deg⁻¹.

To stabilize the properties of the investigated alloys Al-(11÷40)%Si, heat treatment was carried out, which consisted in heating for 10 hours at temperatures of 100, 150 and 200 °C followed by air cooling. The choice of treatment temperatures is due to the intervals of the most active diffusion redistribution of hydrogen in the metal, as well as its interaction with nitrogen, both intrinsic and introduced during melt processing [8].

3. Results and discussion
In the low-temperature range of the tests, a decrease in TCLE of alloys Al-20÷40%Si pretreated with an aqueous solution of copper sulphate in the smelting process was revealed, that can be seen in figure 1. Thus, the average TCLE of the ordinary Al-20% Si alloy in the range 50-150 °C has a value of \( \bar{\alpha}_{50-150} = 18·10^{-6} \text{ deg}^{-1} \), while the alloy obtained after treatment by copper sulfate has the values \( \bar{\alpha}_{50-150} = 16.6·10^{-6} \text{ deg}^{-1} \).
For the alloy Al-30%Si, there is a slight decrease in TCLE in the low-temperature interval. The greatest decrease in TCLE values is observed in alloy Al-40%Si. In this case, after the melt treatment, the average TCLE is $\bar{\alpha}_{50-150} = 11.3 \cdot 10^{-6}$ deg$^{-1}$, while the values of $\bar{\alpha}_{50-150}$ alloy of conventional preparation are $13.2 \cdot 10^{-6}$ deg$^{-1}$.

This decrease may be due to the increase in the copper content in the alloys composition and the occurrence of aging processes in the range 200-300 °C upon cooling from the crystallization temperatures.

In the high-temperature range of the test, the values of TCLE are increased due to the treatment of the melt, which is not determinative, since the devices are not operated at such temperatures. The chosen mode of blowing the melt is optimal, because with a shorter time of blowing, the TCLE decreases insignificantly, while with a longer period of time the amount of slag increases sharply, which reduces the yield of the usable metal.

It has also been established that blowing of the melt slightly increases the microhardness of the substrate, the amount of siliceous phase and gas saturation [14].

The data on the results of the effect of melt treatment by carbamide on linear expansion of alloys Al-11÷40%Si are shown in figure 2. It can be seen that the chosen preparation method significantly reduces the TCLE of alloys Al-11% Si in the entire temperature range of the test. The greatest decrease is observed in the low-temperature interval 50÷150 °C from the values $19.0 \cdot 10^{-6}$ deg$^{-1}$ to $15.7 \cdot 10^{-6}$ deg$^{-1}$. Processing of the melt of high-silicon silumins (20, 30, 40 % Si) leads to the appearance of an anomaly of linear expansion consisting in a sharp increase in TCLE at $t_{\text{vap}} = 300$ °C, which is characteristic of this group of alloys and hypothetically associated with the decomposition of the siliceous phase and the release of the interstitial elements in the basis metal. However, if we consider the low-temperature interval which is of interest to us, i.e. the operating temperature of the instrument equipment, then there is a uniform decrease in the TCLE for all processed alloys. It is known that silicon, which reduces TCLE aluminum to the greatest extent, with the introduction up to
12%, does not give the required values of thermal expansion, and the increase in its content beyond the eutectic composition leads to embrittlement of the alloy and, consequently, loss of producibility and serviceability. One of the reserves for fragility reduction is heat treatment.

The effect of heat treatment, which consisted in heating from 100 to 200 °C for 10 h and cooling in the air, is manifested in the decrease in TCLE of the investigated alloys (table 1). Thus, for alloys Al-11%Si, the decrease in TCLE is observed in the interval t = 300...450 °C after heating at any of the selected temperatures, but the heat treatment at 150 °C is most effective. However, it should be noted that re-heating with the same parameters does not lead to a further decrease in TCLE. Heating of high-silicon silumin reduces the anomaly of linear expansion, which manifests itself at t = 300 °C, the more effective the higher the heating temperature.

After heating at 200 °C, this anomaly is completely eliminated, which is probably due to the formation of interstitial elements for the intrinsic compounds with a small TCLE. An increase in the heating time at 200 °C to 20 h does not give any additional decrease in TCLE, which indicates the sufficiency of the chosen treatment time for the diffusion processes to be completed.

![Figure 2. Effect of melt processing by vapors CO(NH₂)₂ on linear expansion of Al-Si alloys.](image)

| Heating mode | 50  | 100 | 150 | 200 | 250 | 300 | 350 | 400 | 450 |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Al-11%Si     | 15.7| 14.9| 16.6| 17.8| 20.1| 24.3| 23.2| 18.0| 15.8|
| 100 °C       | 15.2| 17.7| 18.7| 19.4| 21.5| 25.6| 18.1| 15.4| 13.4|
| 150 °C       | 16.1| 16.9| 17.2| 18.3| 20.5| 20.4| 14.7| 12.4| 11.7|

*Table 1. Influence of heating (10 hours, air) on the linear expansion of high-silicon alloys Al – Si (melt treatment by vapours CO(NH₂)₂).*
melt processing for aluminum and Al-Si system alloys is indicated by the increase in the limiting degree
of plastic deformation prior to failure by 7-25% on average and a decrease in TCLE by 7-14% [6].

Treatment of the melt by the mixture (CaCO₃∙MgCO₃) is an additional factor in the reduction
of TCLE in the operating temperature range. After processing by the proposed method, the values of α
are 12 - 17% lower than for alloys of conventional preparation (figure 3). Increase of
physicomechanical properties of Al-Si alloys (CaCO₃ ∙ MgCO₃) subjected to treatment by the mixture
(CaCO₃∙MgCO₃) in the process of smelting is connected apparently with better assimilation of hydrogen
and oxygen introduced into the melt. Besides, particles of refractory oxides of Mg and Ca contained in
the mixture serve as additional numerous centers of crystallization. The effectiveness of this method
of melt processing for aluminum and Al-Si system alloys is indicated by the increase in the limiting degree
of plastic deformation prior to failure by 7-25% on average and a decrease in TCLE by 7-14% [6].

| Test temperature, °C | 200 | 150 | 100 | 60 |
|----------------------|-----|-----|-----|----|
| 200 °C               | 15.7| 17.1| 17.3| 17.8| 19.0| 20.0| 19.5| 16.7| 13.1|
| -                    | 14.6| 15.8| 16.2| 16.5| 18.7| 25.2| 19.1| 15.2|
| 100 °C               | 15.4| 16.2| 16.8| 17.5| 20.8| 26.1| 15.7| 13.1| 12.1|
| 150 °C               | 17.1| 17.4| 17.3| 17.9| 20.8| 23.9| 14.7| 14.1| 13.4|
| 200 °C               | 14.7| 16.2| 16.8| 17.2| 17.8| 18.0| 15.9| 15.0| 12.5|
| Al-20%Si             |     |     |     |     |     |     |     |     |     |
| -                    | 14.9| 14.9| 16.6| 17.8| 20.0| 24.3| 23.2| 18  | 15.8|
| 100 °C               | 15.1| 15.3| 15.3| 16.2| 19.4| 21.7| 14.9| 14.3| 12.4|
| 150 °C               | 15.2| 15.7| 16.0| 16.8| 21.0| 20.0| 15.2| 14.0| 13.2|
| 200 °C               | 15.0| 15.5| 15.7| 16.2| 16.0| 15.6| 13.1| 13.0| 11.2|
| Al-30%Si             |     |     |     |     |     |     |     |     |     |
| -                    | 12.4| 13.0| 13.1| 14.1| 17.1| 21.1| 15.9| 14.6|
| 100 °C               | 12.4| 13.7| 13.9| 14.9| 21.3| 17.4| 14.3| 13.6| 12.6|
| 150 °C               | 13.0| 12.9| 13.0| 14.1| 18.2| 17.0| 14.2| 14.0| 13.0|
| 200 °C               | 12.1| 12.8| 13.1| 13.6| 14.5| 14.9| 15.0| 15.0| 14.1|
| Al-40%Si             |     |     |     |     |     |     |     |     |     |
| -                    | 12.4| 13.0| 13.1| 14.1| 17.1| 21.1| 15.9| 14.6|
| 100 °C               | 12.4| 13.7| 13.9| 14.9| 21.3| 17.4| 14.3| 13.6| 12.6|
| 150 °C               | 13.0| 12.9| 13.0| 14.1| 18.2| 17.0| 14.2| 14.0| 13.0|
| 200 °C               | 12.1| 12.8| 13.1| 13.6| 14.5| 14.9| 15.0| 15.0| 14.1|

**Figure 3.** Effect of melt processing by the mixture (CaCO₃∙MgCO₃) on the linear expansion
of Al-Si alloys.
4. Conclusions
1. Comparing the obtained data on the influence of the considered methods of pretreatment of the melt, we can conclude that blowing with vapours of aqueous solution of copper sulfate for 5-15 minutes at a temperature 800-1100 °C leads to a decrease in TCLE of alloys Al-20÷40%Si in the low-temperature interval of testing. Thus, for the alloy Al-20%Si TCLE decreases from the values $\alpha_{50-150} = 18 \cdot 10^{-6}$ deg$^{-1}$ to $16.6 \cdot 10^{-6}$ deg$^{-1}$ and for the alloy Al-40% Si from the values $\alpha_{50-150} = 13.2 \cdot 10^{-6}$ deg$^{-1}$ to $11.3 \cdot 10^{-6}$ deg$^{-1}$.

2. Processing of the melt with carbamide vapours leads to the decrease in TCLE of aluminum alloys Al-Si with the pre-eutectic composition throughout the temperature range. The greatest decrease is observed in the interval 50÷150 °C with the values $19.0 \cdot 10^{-6}$ deg$^{-1}$ to $15.7 \cdot 10^{-6}$ deg$^{-1}$. Thermal treatment at 100÷200 °C promotes further reduction of TCLE: for low-silica alloys treatment at 150 °C is considered to be the most effective, for highsilicon – at 200 °C.

3. Processing of the melt by the mixture of calcium and magnesium carbonates is not only an environmentally friendly technological option of modifying alloys Al-20 ÷ 40% Si but also is an additional factor for reducing TCLE in the operating temperature range. After processing by the proposed method the values of $\alpha$ are by 12 - 17% lower than for alloys of usual preparation. Thus, in the interval 50÷150 °C the average TCLE of the alloy Al-20% Si decreases from $18 \cdot 10^{-6}$ deg$^{-1}$ to $16.9 \cdot 10^{-6}$ deg$^{-1}$, for the alloy Al-30% Si from $16 \cdot 10^{-6}$ deg$^{-1}$ to $12.6 \cdot 10^{-6}$ deg$^{-1}$. The additional advantage of using the mixture of carbonates is not only in complex modification but also in the reduction of superheating temperature of the melt from 1100-1200 °C to 900 °C and in the reduction of the melting time from 5- 6 to 1-1.5 hours.

References
[1] Afanas'ev V K and Popova M V 2012 Metallurgy of Machine Building 6 8–13
[2] Afanas'ev V K and Popova M V 2001 Steel in Translation 31(2) 50–53
[3] Ehrstrom J and Warner T 2000 Metallurgical Design of Alloys for Aerospace Structures ICAA 7 vol 1 5–16
[4] Popova M V and Kibko H B 2014 Processing of Metals 2(63) 107–16
[5] Zu Fangqiu and Li Xiaoyun July 2014 China Foundry 11(4) 287–95
[6] Popova M V, Gertsen V V, Doronchenko A V and Afanas’ev V K 1999 Patent of the Russian Federation No 98104521 appl. 05.03.1998, publ. 10.09.99
[7] Afanas’ev V K, Pопova M V and Samon V A 2014 Metallurgy of Machine Building 5 21–28
[8] Afanas’ev V K, Malyukh M A, Popova M V, Dolgova S V and Lavrova N B 2017 Metallurgy of Machine Building 1 33–40
[9] Starink M J, Sinclair I and Gregson P J 2000 Aluminium Alloys: Their Physical and Mechanical Properties vol 331-337 pp 97–110
[10] Afanas’ev V K, Popova M V, Gertsen V V, Dolgova S V and Leys V A 1983 Processing of Metals 4(61) 28–34
[11] Hess P D and Tumbull G K 1974 Paper from Hydrogen in Metals (American Society for Metals) pp 277–87
[12] Afanas’ev V K, Popova M V, Starostina M A (Malyukh M A) and Krivicheva N V 2011 Metallurgy of Machine Building 3 30–3
[13] Borisov G P 2005 Metallurgy of Machine Building 5 11–20
[14] Ushakova V V, Popova M V and Luzyanina Z A 1995 Izv. Vuzov. Ferrous Metallurgy 4 69
[15] Afanas’ev V K, Dolgova S V et al 2014 Proc. on Actual Problems in Machine Building (Novosibirsk: NSTU) pp 381–87