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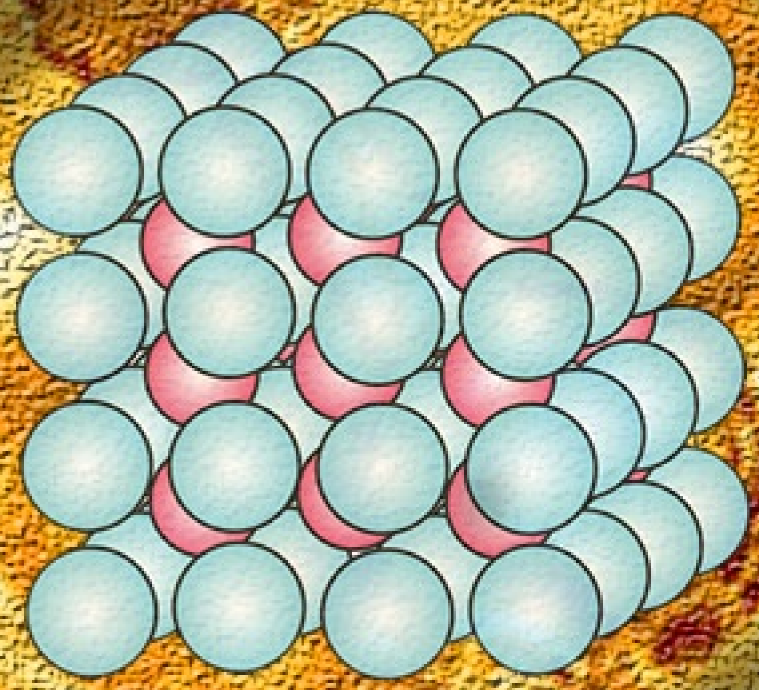

„NONEQUILIBRIUM PHASE TRANSFORMATIONS"

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C O N T E N T S

NONCONVENTIONAL METHODS OF HEAT TREATMENT OF ALUMINUM ALLOYS

НЕТРАДИЦИОННЫЕ СПОСОБЫ ТЕРМИЧЕСКОЙ ОБРАБОТКИ АЛЮМИНИЕВЫХ СПЛАВОВ

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Abstract: *This paper presents new methods of thermal processing of the aluminum alloys. It analyses the effects of boiling treatment of alloys Al–Cu and Al–Si in an oxidizing atmosphere on their microstructure, hydrogen content and the coefficient of linear thermal expansion (CLE). An increase of boiling time from 15 to 75 hours results in an initial increase in the hydrogen content in alloys later followed by a decline in the hydrogen content. These changes in the hydrogen content correlate with the dynamics of alloys' microstructure and their CLE. This study shows that atmosphere with a high oxygen content induces an acceleration of diffusion processes in aluminum alloys. If boiling time does not exceed 30 hours, the hydrogen content in a solid solution and etchability of grain boundaries of α-solid solution decrease and intermediate phases get partially dissolved. We demonstrate that boiling treatment of aluminum alloys in an oxidizing atmosphere leads to a decline of the CLE measured under the temperature 50-450°C which is especially strong when measured under the temperature 250-350°C.*

KEYWORDS*: ALUMINUM, ALLOYS, ATMOSPHERE, BOILING TREATMENT, HYDROGEN, MICROSTRUCTURE, COEFFICIENT OF LINEAR EXPANSION*

1. Introduction

Alloys with a low specific weight and a small coefficient of linear expansion (CLE) play a significant role in industry. Such alloys are especially important for aerotechnics and spacecraft engineering [1, 2]. In particular, aluminum alloys with a low coefficient of linear expansion (CLE) are required for the construction of special instruments, obtaining vacuum-tight junctions with different materials as well as for providing dimensional consistency of details. In most cases reduction of the coefficient of linear expansion is achieved by means of alloying. An important task for the current research is to explore and analyze other ways of reducing the coefficient of linear expansion of these materials.

In our previous studies we showed that if the content of alloying elements is kept constant technological factors such as fusion treatment, melt treatment and crystallization conditions can have considerable influence on microstructure, hydrogen content and coefficient of linear expansion of aluminum alloys [3, 4]. Furthermore, we showed that the composition of atmosphere significantly affects the structure formation and physic-mechanical properties of aluminum alloys [5-7]. Particularly, we demonstrated that heating treatment in atmosphere with higher hydrogen and nitrogen contents accelerates the process of phase transformations in aluminum alloys [7]. This happens because heating treatment stimulates hydrogen diffusion in aluminum alloys. In addition, there are a lot of other studies that also support the thesis that hydrogen plays an important role in the process of structure formation of aluminum alloys and has significant impact on their properties [8-12].

U.R. Evans proposed a mechanism of oxide spallation from the metal surface according to which oxygen on the metal surface induces acceleration of hydrogen inside of the metal [13, 14]. Hence, atmosphere with a high oxygen content should also affect the hydrogen diffusion inside of a metal in the course of heating treatment. Boiling treatment in water solutions could be considered as an example of such heating treatment. Hydrogen exhibits the highest degree of diffusive mobility in the temperature range of 80-100°C. Consequently, by means of boiling treatment of alloys in strong oxidizing atmospheres one could achieve acceleration of hydrogen diffusion inside of a metal. Water solutions of $KMnO_4$, $NaNO_3$, KOH could serve as examples of such oxidizing atmospheres that force hydrogen to move from intermetalloids to solid solution. This, in turn, leads to the change of the structure and properties of aluminum alloys, in particular, it affects their coefficient of linear expansion [15].

2. Materials and Experiment

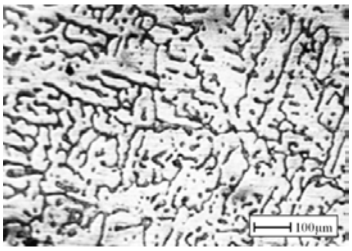
We analyzed how boiling treatment of alloys in water solutions of strong oxidizers affects microstructure and the coefficient of linear expansion of these alloys. For our analysis we used aluminum alloys Al – 5% Si, Al – 10% Si, Al – 5% Cu and Al – 10% Cu. Alloys were melted out of pure metals: aluminum A7, silicon Kp0, copper M1. Alloys were melted in the laboratory electric resistance furnace in alundum melting pot. First aluminum was melted, and then alloying elements were added. Alloys Al – 5% Cu and Al – 10% Cu were poured starting at the temperature 850-870°C into metal mold without hot-conditioning. Alloys Al – 5% Si, Al – 10% Si were poured at the temperature 730°C into cooling mold with further quenching into water being undertaken.

From the resulting ingots bars were cut out which then were used for further metallographic analysis and dilatometer investigation. These bars were treated using boiling water solutions KMnO4 и KOH. Three metal bars were exposed to each treatment regime. Alloys Al – 5% Cu and Al – 10% Cu were boiled in 0.05–0.1% water solution $KMnO_4$ during 5-45 hours, alloys Al – 5% Si, Al – 10% Si were boiled in 0.1% water solution KOH during 15-75 hours.

After boiling treatment we implemented dilatometer investigation, metallographic analysis and measured hydrogen content. Coefficient of thermal linear expansion was measured using the Chevenard photodilatometer. Metallographic analysis was implemented using optical light microscope OLYMPUS GX51. The content of atomic hydrogen was measured using vacuum hot extraction method implemented on the installation B-1 according to the State Standard GOST 21132.1-98 «Aluminum and aluminum alloys. Methods for determination of hydrogen in solid metal by vacuum hot extraction». The method is based on the extraction of hydrogen from the metal heated to the temperature lower than its melting temperature – in the range of 500-600°C – under vacuum and residual pressure of (6.65–9.31) • 10^{-5} Pa.

3. Results and discussion

We implemented comparative analysis of the properties of alloy Al – 5% Cu after boiling treatment during 15, 30 and 45 hours respectively. In the course of our empirical study we established that during the first 30 hours of boiling the hydrogen content in the alloy decreases from 3.3 to 1.9 cm^3 / 100 g Me, grain boundaries of α-solid solution get thinner and less exposed to etching (their etchability descreases) than they were under initial conditions, the continuity of grain boundaries is also affected (Fig. 1, a, b). Grain boundaries of α-solid solution exhibit different degrees of etchability, particularly, there are no breakdown products in the core of grains whereas considerable amount of these breakdown



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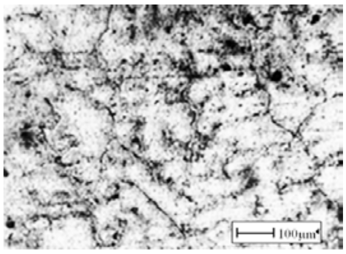

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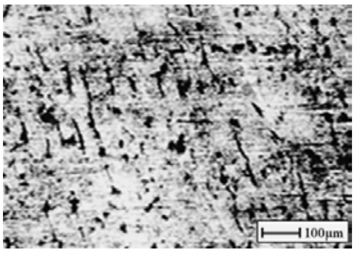


c

Fig. 1. Microstructure of alloy Al – 5% Cu: a – no treatment, [H] = 3.3 cm^3 / 100 g Me; b – after boiling treatment in 0.1% water solution of $KMnO_4$ during 30 hours [H]=1.9 cm^3 / 100 g Me; c – after boiling treatment in 0.1% water solution of $KMnO_4$ during 45 hours, [H]=4.5 cm^3 / 100 g Me

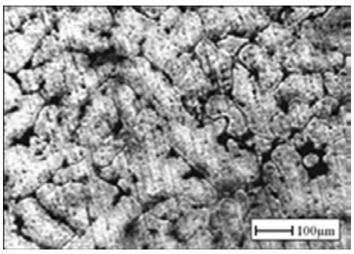
products was identified at the periphery of grains. This shows that the solid solution is characterized by a high hydrogen content in areas near grain boundaries due to breaking-up of the phase $CuAl_2$.

When boiling time is increased to 45 hours the hydrogen content again increases up to 4.5 cm^3 / 100 g Me (Fig. 1, c) and etchability of all structural components weakens. So, particles of the phase $CuAl_2$ almost cannot be etched and grain boundaries of α-solid solution partially cannot be revealed, too.

After boiling treatment in 0.1% water solution of $KMnO_4$ during 45 hours the hydrogen content in alloy Al–10% Cu increases from 4.3 to 12.2 cm^3 / 100 g Me. This happens because under the influence of oxidizing atmosphere hydrogen segregated at the interphase boundaries as well as hydrogen dissolved in the phase $CuAl_2$ migrate to the α-solid solution. At the same time etchability of the phase $CuAl_2$ and of α-solid solution increases (Fig. 2, a).

When boiling time is increased to 75 hours the hydrogen content in alloy Al–10% Cu again decreases to [H] = 3.5 cm^3 / 100 g Me. We believe that this happens due to further progressing diffusion processes and hydrogen moving out of an alloy into the atmosphere. This corresponds to the empirical finding that the overall etchability of metallographic spicement goes down, grain boundaries get much thinner and there are fewer particles of intermediate phase of $CuAl_2$ (Fig. 2, b).

In the course of comparative dilatometric analysis it was established that following boiling treatment in potassium permanganate solution the CLE of alloys Al–(5÷10) % Cu decreases to a larger extent than it does after boiling in water. Moreover, the more concentrated the $KMnO_4$ solution is, the more pronounced is the reduction of the CLE (Fig. 3).



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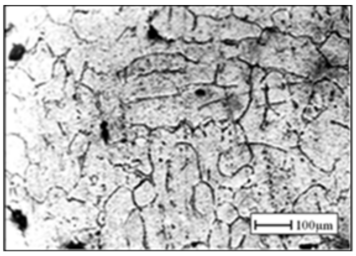
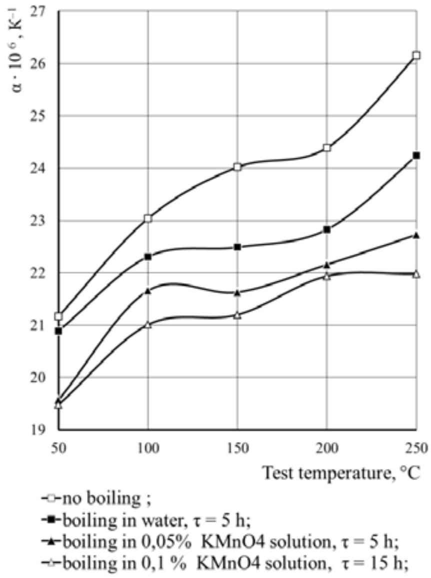


b

Fig.2. Microstructure of alloy Al–10% Cu: a – after boiling treatment in 0.1% water solution of $KMnO_4$ during 45 hours [H]=12.2 cm^3 / 100 g Me; b – after boiling treatment in 0.1% water solution of $KMnO_4$ during 75 hours, [H]=3.5 cm^3 / 100 g Me



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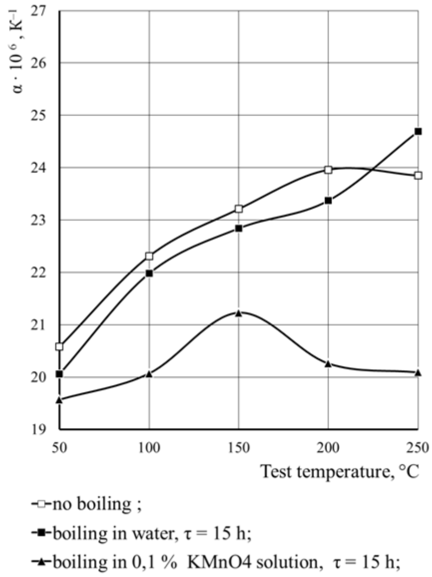
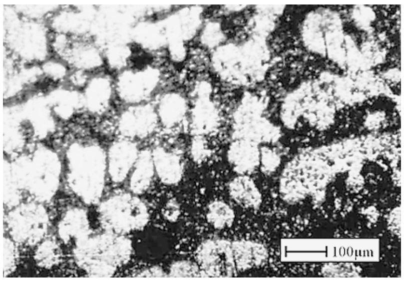


b

Fig. 3. Effects of atmosphere composition and boiling time on the coefficient of linear expansion of aluminum alloys with copper: a - Al–5% Cu; b - Al–10% Cu

The average inaccuracy of the computed coefficient of linear expansion is $\pm 0.1 \cdot 10^{-6}$ K^{-1}. As an illustration, the average CLE of alloy Al–5% Cu after five hours of boiling in water measured in the temperature range of 50–250°C is $23.0 \cdot 10^{-6}$ K^{-1}, after boiling in 0.05% $KMnO_4$ solution during five hours this alloy's CLE is $21.5 \cdot 10^{-6}$ K^{-1} and, finally, after boiling in 0.1% $KMnO_4$ solution during 15 hours the alloy's CLE is $21.1 \cdot 10^{-6}$ K^{-1}. Hence, in comparison to CLE of as-cast alloys boiling treatment in 0.1% $KMnO_4$ causes a decrease of the CLE of alloys Al–5% Cu measured in the range of test temperatures 50–250°C by 10-12%.

Generally, alloys Al-Si can only hardly be affected by atmosphere. However, a long boiling treatment with a hold of up to 75 hours in a 0.1% KOH water solution causes gradual breaking-up of eutectic silicon. This results in an increased measurable hydrogen content from 0.7 to 3.8 cm^3 / 100 g Me. Metallographic analysis also confirms this finding: the etchability of dendrites of α-solid solution increases and there are plenty of breakdown products on grain bodies (Fig. 4).



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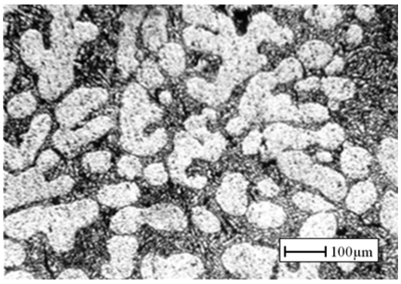


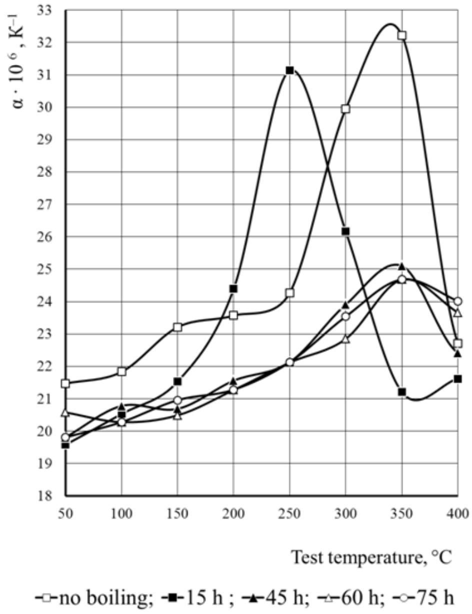
b

Fig. 4. Microstructure of alloy Al-10% Si: a – without treatment, [H]=0.7 cm^3 / 100 g Me; b – after boiling treatment in 0.1% water solution of KOH during 75 hours, [H]=3.8 cm^3 / 100 g Me

Empirical measurement of the coefficient of linear expansion of aluminum alloys with 5 and 10% of silicon provides evidence that boiling treatment in oxidizing environment leads to a reduction of the CLE over the whole range of test temperatures (Fig. 5). The maximum reduction of the CLE of alloy Al-5% Si is observed in the course of the first 30 hours of boiling whereas for alloy Al-10% Si the same result is achieved already after the first 15 hours of boiling. A further increase of boiling time leads only to a minor reduction in the coefficient of linear expansion. We believe that this phenomenon can be explained by the fact that hydrogen moves in and out of the solid solution.

The decrease of CLE is particularly strong in the temperature range of 250-350°C when casted alloys feature anomalous linear expansion. This effect is more pronounced for the alloy with 10% Si. As an illustration, after boiling treatment during 15 hours the CLE of alloy Al-10% Si decreases from $\alpha=31.0 \cdot 10^{-6}$ K^{-1} to $\alpha=22.4 \cdot 10^{-6}$ K^{-1} in the temperature range 250-300°C – i.e. the CLE decreases by 28%. The maximum reduction of the CLE of alloy Al-5% Si in the temperature range of 300-350°C is achieved only after boiling during 60 hours - the CLE decreases from $\alpha=31.1 \cdot 10^{-6}$ K^{-1} to $\alpha=23.8 \cdot 10^{-6}$ K^{-1}, i.e. by 24%.

The reduction of the CLE can be explained in the following way. The role of hydrogen in the process of alloy's expansion is determined by the overall hydrogen content that is made by the hydrogen in a solid solution and by the hydrogen that gets dissolved during the precipitation of intermetalloid phases. Under low temperatures the CLE is equally determined by the hydrogen in a solid solution and the hydrogen in the phase. Under higher temperatures, however, the speed of diffusion process significantly increases and the hydrogen contained in a solid solution contributes more to the expansion than the hydrogen in the phase. When the share of the hydrogen in a solid solution is high the CLE takes on its maximum values whereas when it is low the CLE goes down. The reduction of CLE is caused by an overall decline of the hydrogen concentration in an alloy as well as by the partial dissolution of intermetalloid phases and an alloying element moving into the solid solution.



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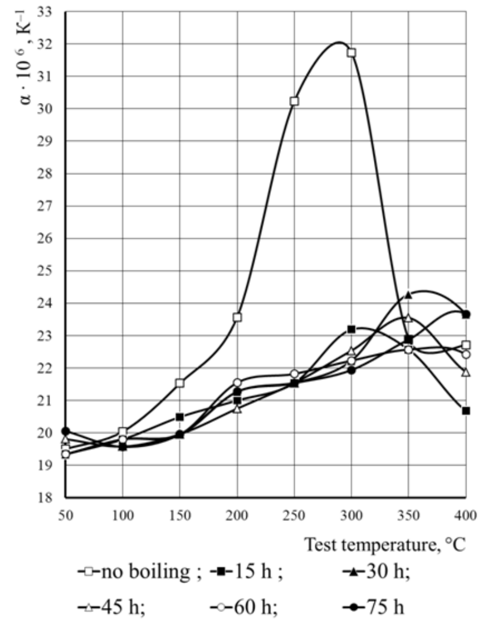

b

Fig 5. Effects of boiling time on the coefficient of linear expansion of aluminum alloys with silicon: a- Al-5% Si; b – Al-10% Si

4. Conclusions

In this paper we empirically demonstrated that in the course of boiling treatment atmosphere composition has a considerable impact on microstructure, hydrogen content and coefficient of linear expansion of alloys Al–(5-10)% Cu and Al–(5-10)% Si. Atmosphere with high hydrogen content is conducive to acceleration of diffusion processes inside of alloys, particularly, to the acceleration of atomic hydrogen diffusion. If boiling time does not exceed 30 hours hydrogen content in solid solution goes down, etchability of grain boundaries of α-solid solution decreases and intermediate phases get partially dissolved.

In the course of our study we established that boiling treatment in an oxidizing atmosphere causes a reduction of the CLE of alloys Al-(5-10%) Cu by 10-12% measured in the range of test temperatures of 50 - 250°C. For alloys Al–(5-10%) Si this effect is more pronounced, i.e. the CLE goes down in the range of test temperatures 50-400°C. In the temperature range 250-350°C the CLE reduction is particularly large – i.e. by 24-28%.

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