

Choice of Rational Alloying Concentration Intervals and Modifying of Al-Cu-Mg and Al-Zn-Mg-Cu Systems Aluminium Alloys

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For chemical composition optimization of Al-Cu-Mg and Al-Zn-Mg-Cu systems based multicomponent aluminium alloys, the principle of rational alloying, grounded on their thermal and micro X-ray spectral analyses results is substantiated.

The principle of rational alloying takes account of the following: ultimate conjoint solubility of alloying elements in aluminium alloy matrix at solution treatment temperature; a share of alloying elements participating in formation with impurity elements of practically insoluble phases, and also a share of the alloying elements forming among themselves excess phases which still are soluble, but cannot be dissolved at solution treatment temperature due to achieved saturation of α -solid solution.

At modifying of Al-Cu-Mg and Al-Zn-Mg-Cu system based multicomponent aluminium alloys via titan and titanium diboride additives it is necessary to aim at achieving the size of 200÷300 microns dendrite cast grains, receiving homogeneous size and branching degree of equiaxial grains, increasing of phase dispersibility in interaxial dendrite spaces, preventing to form defects in semi-finished products.

Keywords: *Al-Cu-Mg and Al-Zn-Cu-Mg alloys, thermal analysis, X-ray microanalysis, alloying*

1. Introduction

Optimization of chemical composition of multicomponent aluminium alloys used for production of semi-finished products with the required structure and properties is of highest importance [1-4]. One of the approaches to the problem is to minimize effective volume fraction and non-uniformity of excess phases orientation in semi-finished products [1]. This method fails to take into account phase composition and groundmasses, so content of alloying components and impurity elements in alloy composition cannot be optimized to the full extent. In this work for optimization of chemical composition of multicomponent aluminium alloys we suggest an approach based on the results of thermal analysis and X-ray spectrum microanalysis of quenched and aged alloys.

Al-5%Ti-1%B and Al-3%Ti-0,15%C alloying bars are coming into wide use for modifying of multicomponent aluminium alloys, though it is not decided yet what is the optimal consumption of these addition alloys for continuous modifying of wrought aluminium alloys during DC casting. This fact required us to perform extra research of aluminium alloys modifying with the mentioned addition alloys.

2. Experimental Procedure

The samples of industrial aluminium alloys of Al-Cu-Mg and Al-Zn-Mg-Cu systems were taken as the subjects of the research. The samples were taken from cast homogenized ingots of 300×1100 and 400×1320 mm in cross-section and heat treated thick plates.

We used the modern method of thermal analysis (TA) and numerical differentiation of heating and cooling curves to determine phase transformation temperatures (non-equilibrium solidus, equilibrium solidus and liquidus) of samples from aluminium based ingots and plates.

As there were smooth transitions in coordinate positions “temperature (t , °C) – time (τ , s)” on the chart, it was difficult to determine representative temperatures of alloys with minimum error. To determine these temperatures we numerically differentiated $t=f(\tau)$ curve and plotted a graph of rate-of-change of sample temperature ($\Delta t/\Delta\tau$, arbitrary unit) against its temperature (t , °C) (Fig. 1). In heating mode the rate prior to melting of a sample was 14°C/minute, and it was 45°C/minute prior to solidification.

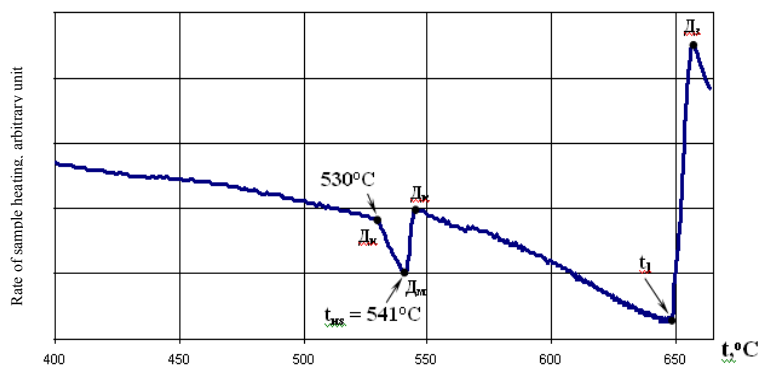


Fig.1 The curve of alloy heating rate ($\Delta E / \Delta\tau$) against its temperature

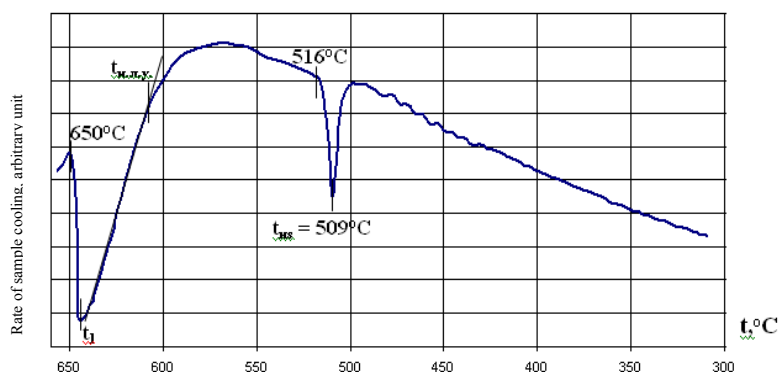


Fig.2 The curve of alloy cooling rate ($\Delta E / \Delta\tau$) against its temperature

By means of the graph the temperature values of non-equilibrium solidus (t_{HS}), equilibrium solidus (t_S) and liquidus (t_L) were found. Hot junction of a thermocouple was “frozen in” the sample to determine start temperature of linear shrinkage ($t_{H.L.Y}$). Then we steadily heated the latter and recorded the temperature when it was possible to remove the thermocouple from the sample, which was indicative of crystalline fracture. The recorded temperature value was taken as start temperature of linear shrinkage. Then the found value of $t_{H.L.Y}$ was compared to characteristics of the correspondent cooling curves (Fig.2). The error of the obtained temperature values was $\pm 1^\circ\text{C}$. We managed to reduce error of representative temperatures determination by means of the following: close contact of the sample with the thermocouple hot junction, digital voltmeter “ИЦ31” with

measuring accuracy of thermoelectromotive force ± 0.001 mV, computation of first-order derivative of temperature with respect to time, and computer processing of the obtained experimental data. If to maintain constant conditions of samples thermal analysis, values of phase transition temperatures are reproduced, regardless of the number of tests providing that samples are taken from the same area of an ingot or plate.

The scanning electron microscope “JSM-5900LV” with electron probe microanalyzer of $1\div 2$ μm locality was used for alloy structure investigation. The universal testing machine Instron 5585H equipped with automatic digital high resolution extensometer was used for testing of mechanical properties of ingots and semi-finished products.

3. Results and discussion

One of the challenges was to establish influence of chemical composition of 2024 and 2124 based on Al-Cu-Mg system on mechanical properties of plates $60\div 150$ mm thick produced by hot rolling of ingots $300\div 400$ mm.

Plates in this thickness range produced of 2024 and 2124 in different heat lots often had lower mechanical properties than required. Sometimes the properties of the produced plates met the

requirements of the normative documentation, though plates' mechanical properties had much variance (S).

We attempted to produce thick 2024 plates with the required mechanical properties and little variance by changing homogenization conditions of ingots, heating temperature of plates prior to quenching, and soaking time at quenching temperature; but we did not succeed. This situation served as a basis for determination of a role of 2024 and 2124 alloys chemical composition in structure and properties formation of thick plates.

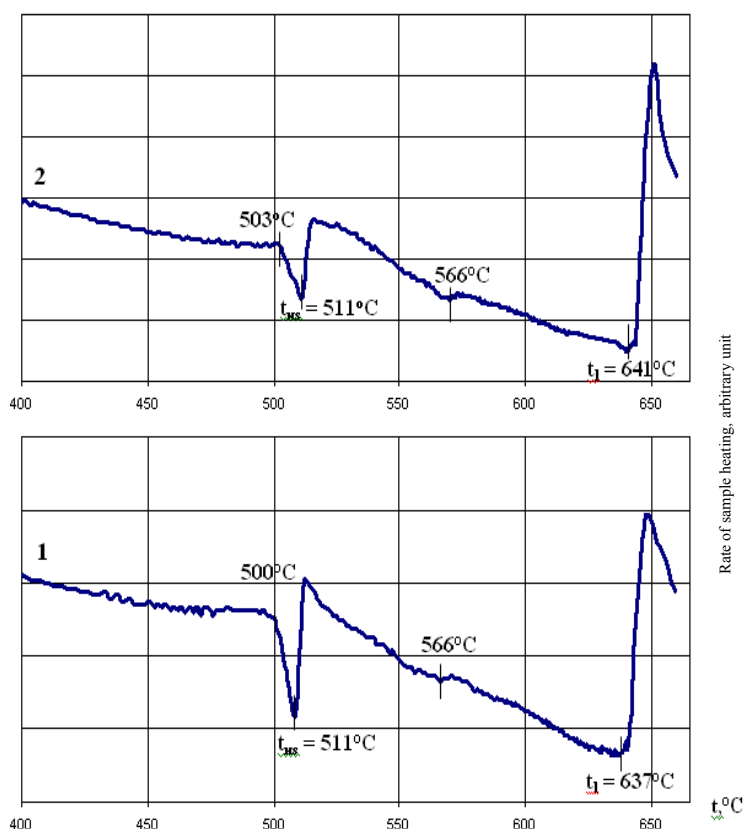


Fig.3 Heating patterns of industrial aluminium alloys at heating modes: 1 – 2024; 2 – 2124

The heat patterns of 2024 and 2124 homogenized alloys are represented on Fig. 3. Main alloying elements included in 2024 and 2124 industrial alloys was (in mass percent) as follows: 4.60 and 4.40 Cu; 1.60 and 1.50 Mg; 0.63 and 0.47 Mn, correspondingly. Clearly defined endothermic spikes on the heating patterns came under notice at 511°C temperature. It indicated that full dissolution of non-equilibrium eutectic could not be achieved at chosen conditions of ingot homogenization. The part of the non-equilibrium eutectic located at grain boundaries of α -solid solution based on aluminium (α_{Al}) remained even after homogenization; and its following melting was characterized by endothermic spikes.

X-ray spectrum microanalysis of 2024 sample taken from homogenized ingot of 355×1370 mm in cross-section

corroborated presence of continuous layers at grain boundaries and dendritic mesh, the layers being of non-uniform non-equilibrium eutectic with complex chemical composition, which is not fully dissolved in aluminium groundmass at ingot homogenization. Non-equilibrium eutectic was represented by composition of crystals of α -solid solution based on aluminium (α_{Al}) and Al_2CuMg phase.

X-ray spectrum microanalysis of samples taken from 2024 plate quenched and aged at standard conditions for T351 was performed to determine maximum mutual solubility of magnesium and copper in aluminium groundmass of this alloy. It was founded out that Al_2CuMg phase that was not fully dissolved remained in the structure of the heat treated plate. The content of main alloying elements included into grains of α -solid solution was (in mass percent) as follows: (1.3 ÷ 1.42) Mg; (3.77 ÷ 3.88) Cu; (0.16 ÷ 0.59) Mn.

According to the normative documentation the content of copper, magnesium and manganese in 2024 and 2124 alloys may vary (in mass percent) as follows: 3.80 ÷ 4.90; 1.20 ÷ 1.80; 0.30 ÷ 0.90, correspondingly.

Thus, the obtained data provide strong evidence of 2024 alloy over-alloying with copper and magnesium.

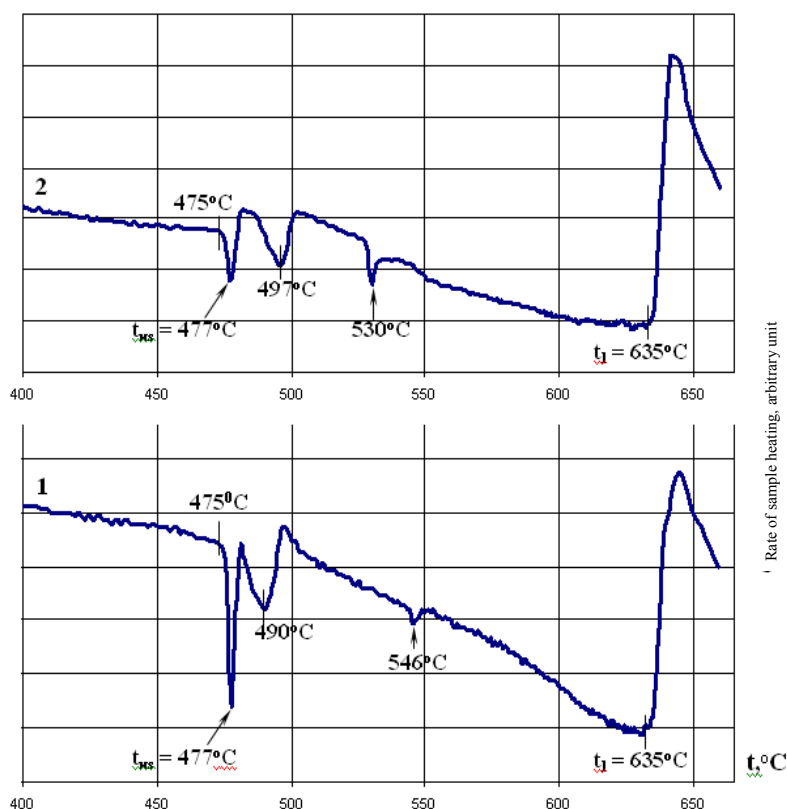


Fig.4 Heating patterns of 7050 industrial aluminium alloy at tempers: 1 – annealed; 2 – homogenized

On the grounds of the maximum mutual solubility of copper and magnesium in aluminium groundmass at temperature of 497°C the content of these elements equal to their maximum solubility is suggested to be taken as lower limit of alloying and the content by 0.1÷0.2 mass percent higher is suggested to be taken as upper limit.

We suggested the range of concentration of main alloying elements exceeding maximum solubility by 0.1÷0.2 mass percent on the following grounds. Excess of copper results in formation of intermetallic compounds with other elements (for example, AlCuMnFeSi), that are practically insoluble at ingot homogenization. Besides, copper and magnesium form Al₂CuMg excess phase, which cannot be fully dissolved either during ingot homogenization or during plate heating for quenching. On the other hand, the range of concentration is

chosen on the basis of the existent alloy preparation process, when exact composition of it cannot be possibly obtained.

The suggested upper limit of alloying elements concentration makes it possible to provide guaranteed saturation of aluminium-based solid solution with magnesium and copper at plates heating prior to quenching and to minimize volume fraction of unwanted intermetallic compounds. This approach to choice of alloy chemical composition was called rational alloying concept.

The comparison of mechanical properties of plates produced of ingots with different chemical composition reveals that mechanical properties of plates with corrected chemical composition improves and variance in all directions decreases. The obtained data indicate the positive influence of corrected chemical composition of 2024 alloy on plate mechanical properties (Table 1).

Table 1 Mechanical properties of 2124 T851 plates 139.7 mm thick of standard and corrected chemical composition

Direction	Ultimate strength, MPa; (S)			Yield strength, MPa; (S)			Elongation, %; (S)		
	standard	corrected	required	standard	corrected	required	standard	corrected	required
longitudinal (L)	463; (3.76)	472; (3.55)	442	409; (6.79)	414; (5.25)	379	8,5; (0.34)	9,5; (0.34)	5
transverse (ST)	457; (4.75)	460; (2.94)	442	403; (6.16)	406; (3.77)	379	6,3; (0.56)	7; (0.09)	4
short transverse (ST)	421; (1.2)	426; (0.77)	421	388; (0.8)	390; (0.81)	366	1,8; (0.9)	2,5; (0.27)	1.5

Thus, correction of 2024 and 2124 alloys chemical composition enabled production of plates 60÷150 mm thick with stable and required mechanical properties, reduction of consumption of costly alloying elements, and significant decrease in scrap of the finished goods.

Plates 60÷150 mm thick manufactured of Al-Zn-Mg-Cu system alloys often demonstrated unacceptably low level and variance of mechanical properties. This acute problem was solved by using the concept of rational alloying of alloys, which is based on the results of their thermal analysis and X-ray spectrum microanalysis.

Thermal analysis of the samples taken from annealed and homogenized ingots (Fig.4) reveals clearly defined endothermal spikes on heat patterns, which indicates that non-equilibrium eutectic is not fully dissolved at standard conditions of ingots homogenization. Note that the endothermal spike of 7050 of Al-Zn-Mg-Cu-Zr system is dichotomous in contrast to Al-Cu-Mg system alloys. The first spike on the heat patterns at 477°C temperature is caused by melting of low-melting eutectic represented by composition of α_{Al} crystals and $Mg(Zn, Cu, Al)_2$ phase. As a result of the process, zinc diffuses into the grains of aluminium groundmass. $Mg(Zn, Cu, Al)_2$ phase develops into Al_2CuMg phase, which forms new eutectic together with α_{Al} crystals. The latter melts at the temperatures of the second endothermal spikes: 490°C and 497°C (the samples taken from the annealed and homogenized ingots, correspondingly). Excess of Al_2CuMg phase non-uniformly distributed in ingots and zinc dissolved in the phase (3÷4 mass %) lead to production of 7050 plates with low mechanical properties.

X-ray spectrum microanalysis of polished specimens from the central zone of quenched and aged 7050 T7451 plates 152.4 mm thick revealed disperse particles of Al_2CuMg phase that failed to dissolve at heating of plates prior to quenching at grain boundaries. The content of main alloying elements in 7050 T7451 alloy plate groundmass is as follows (in mass %): 7.30% Zn, 1.88%Mg and 2.19%Cu. Therefore, the specified values of concentration coincide with the maximum solubility of main alloying elements in aluminium groundmass upon heating of a plate for quenching up to 475°C and 30 minutes of soaking at this temperature. By reference to the concept of rational alloying we suggest the following lower limits of concentration of magnesium and copper in 7050 alloy (in mass %): 1.9%Mg and 2.2%Cu.

As for zinc, it almost fully dissolves in aluminium groundmass during heating of plates for quenching. That is why it is appropriate to choose its content in alloy somewhere in the middle of the concentration range specified in normative documents.

On the basis of the obtained results we suggest the well-balanced chemical composition of main alloying elements of 7050 alloy; which content shall vary (in mass percent) as follows: (1.95 ÷ 2.15) Mg; (2.20 ÷ 2.35) Cu; (6.20 ÷ 6.40) Zn. Less alloying of 7050 alloy with magnesium and copper eliminated instability and increased relative elongation values for thick plates in T7451 temper in short transverse direction and strength properties in transverse and longitudinal directions.

In modern production of ingots of wrought aluminium alloys by DC casting alloys are modified using combined method (addition alloy as Al-3%Ti pigs + Al-5%Ti-1%B bars). Titanium content in alloy is maintained within 0.04÷0.06 mass % due to addition of Al-3%Ti; consumption of Al-5%Ti-1%B bars is 1 kg per 1 tonne of alloy. The results of structure investigation indicate significant refinement of cast grain size (up to 100÷150 μm). However thickening of eutectic layers at grain boundaries and increase in size of intermetallic phases of crystallization origin are observed in ingot microstructure.

The analysis of the standard combined method of modifying alloy Al-8.1%Zn-2.2%Mg-1.6%Cu-0.12%Zr revealed that significant refinement of cast grain in ingots of this alloy does not result in the expected increase of ductility at hot working temperatures (390÷410°C). Modifying of this alloy with Al-5%Ti-1%B bar provided 1 kg consumption per 1 tonne of the melt results in

considerable reduction of fracture toughness of plates T12 temper. The same results were obtained for 7050 and 7075 alloys.

Besides, exfoliation-type defects are found in macrostructure of complex-shaped forgings manufactured of 7050 T74 alloy. The particles of phases specific for 7050 alloy are found on the surface of the exfoliations: Al_2CuMg , $\text{Al}_7\text{Cu}_2\text{Fe}$ и Mg_2Si . Meanwhile, the surface of the discovered bright exfoliation has not only the phases specific for this alloy, but also the particles with high content (up to 20%) of titanium, that were not discovered by X-ray spectrum microanalysis both of natural fracture and specially prepared polished specimens. The obtained data contributed to clarification of the mechanism of bright exfoliation formation and we made an inference that over modifying of aluminium alloys with titanium (at 1 kg of Al-5%Ti-1%B per 1 tonne of melt) has negative effect due to its high hydride-forming ability.

Full-scale experiments indicated that reduction of Al-3%Ti and Al-5%Ti-1%B consumption provides production of 2014T6 and 7050T74 forgings without exfoliation. On the basis of the numerous experiments we expressed the concept of the rational alloying of multicomponent aluminium alloys as follows. The amount of the introduced modifier shall provide uniform macrostructure of ingots with branched equiaxed grains $200\div 250$ μm dia and, as consequence, dispersion of phases in-between branches areas. For this purpose modifier content in alloy shall be minimal and its distribution in microvolume of alloy shall be uniform to the extent possible. Through this approach to modifying we managed to prevent exfoliation forming in forgings and plates, improve fracture toughness and fatigue life of semi-finished products.

4. Summary

The concept of rational alloying based on the results of thermal and X-ray spectrum analyses is justified for optimization of chemical composition of multicomponent aluminium alloys of Al-Cu-Mg and Al-Zn-Mg-Cu systems. The concept of rational alloying takes into account the following: maximum mutual solubility of alloying elements in aluminium groundmass at temperature of plate heating for quenching; the portion of alloying elements that contribute to formation of almost insoluble phases together with impurity elements and the portion of alloying elements that form excess phases which are soluble but cannot be dissolved at heating for quenching because of saturation of α -solid solution.

When multicomponent aluminium alloys based on Al-Cu-Mg and Al-Zn-Mg-Cu systems are modified with addition of titanium and titanium diboride, it is necessary to try to achieve refinement of dendrite cast grains up to $200\div 250$ μm , equiaxed grains uniform in size and branching, increase in phase dispersion in-between branch areas of dendrites, elimination of such defects as bright exfoliation in semi-finished products.

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