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ALUMINIUM ALLOYS WITH ZIRCONIUM ADDITIONS, IN THE RANGE FROM 0.05 TO 0.32%, INTENDED FOR APPLICATIONS IN THE OVERHEAD ELECTRICAL POWER ENGINEERING

STOPY ALUMINIUM Z DODATKIEM CYRKONU W ZAKRESIE OD 0,05 DO 0,32% PRZEZNACZONE DO ZASTOSOWAŃ W ELEKTROENERGETYCE NAPOWIETRZNEJ

The main scientific challenge of the study was the selection of the zirconium amount, which will allow achieving high electric and strength properties of the alloy. The analysis of chemical compositions of the thermal resistive, conducting AlZr alloys allowed to estimate the most advantageous amount of zirconium, which was found to be within the range: from 0.05 to 0.32 wt % of Zr. The main aim of the study was the investigation of electric properties of alloys of the selected chemical compositions, being within the above given range. The endeavours were focused on determining the heat treatment influence (artificial ageing) on the resistivity of the AlZr alloys in the cast form. On these bases the ranges of obtainable electrical properties were estimated for the investigated alloys, which enabled the selection of optimal conditions of the heat treatment.

Keywords: aluminium alloys, heat treament, AlZr, resistivity, Nordheim rule

Głównym wyzwaniem naukowym pracy był dobór ilości cyrkonu, która pozwoli uzyskać wysokie własności elektryczne oraz wytrzymałościowe stopu. Analiza składów chemicznych odpornych cieplnie, przewodowych stopów AlZr pozwoliła określić najkorzystniejszą ilość dodatku cyrkonu, która mieści się w zakresie od 0,05 do 0,32 % wag. Zr. Zasadniczym celem pracy są badania własności elektrycznych stopów o wybranych składach chemicznych mieszczacych się w powyższym zakresie. W pracy skupiono się na określeniu wpływu obróbki cieplnej (starzenie sztuczne) na zmianę rezystywności stopów AlZr w postaci odlewanej. Na tej podstawie, dla badanych stopów, wyznaczono zakresy możliwych do uzyskania własności elektrycznych, co pozwoliło na dobór optymalnych warunków obróbki cieplnej.

1. Introduction

During the last years an intensive interest in additions of zirconium to aluminium is observed. Its aim is controlling grain sizes during recrystallisation processes [1] and a thermal resistance increase by increasing the recrystallisation temperature of aluminium or its alloys [2]. Application of aluminium alloys with zirconium addition as materials for transmitting electrical energy must warrant the determined level of strength properties and should be characterised by low electrical properties. Wires made of such alloys are applied in special high temperature conductors of the HTLS (High Temperature Low Sag) type. These conductors by applying heat resistant wires allow to increase the operation temperature from 80°C (in case of traditional steel-aluminium or AlMgSi conductors) to 150°C or even to 210°C, increasing by that the energy transmission effectiveness [3-6]. Interests and applications of HTLS conductors, due to various additional factors (procedural problems, social objections, place limitations) are currently very intense and concerns both a modernisation of old lines and building new electrical supply lines.

In case of the AlZr alloys obtaining the proper resistance properties is achieved in the technological process by introducing the determined value of cold-work strain (strengthening by strain). In turn, the resistivity value of the AlZr alloy depends both on the amount of zirconium added and on its location in the aluminium structure (solid solution or precipitates). On the bases of the literature data, in papers [7, 8] the list of contributions of zirconium and other alloying elements to the aluminium resistivity is given. According to individual authors the coefficient of zirconium influence is within the range from 0.4 to 45 nΩm for 1 wt% (Table 1). Willey, in his paper [10], divided the influence of zirconium into two categories. The first one, when zirconium is in the aluminium solid solution (17.4 nΩm for 1 wt%) and the second, when zirconium is in a form of precipitates (0.44 nΩm for 1 wt%) [5, 6].

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TABLE 1

Effect alloying element content for resistivity increment [7, 8]

Name of the author	Contribution of alloying elements to resistivity [nΩm per wt%]											
	Cr	Cu	Fe	Li	Mg	Mn	Ni	Si	Ti	V	Zn	Zr
Aluminium Taschenbuch 1974	41	3.3	32		5.1	36	1.8	6.8	31	43	1	20
Sacharow	36.5	4	4.1	43.6	5.1	26	3.8			45.6	1.5	15.8
Vassel	32.7	3.4			7	36		7.7	22	28	1.7	2
Van Horn	40	3.44	25.6	33.1	5.4	29.4	8.1	10.2	28.8	35.8	0.9	17.4
Kutner and Lang	42.2	3.06	8.5	36.8	5.6	30.7		5.16			1	45.4
CRC Handbook	44.2	3.2		36.6	5	32	0.5	6.7	31.4	41.6	0.9	13.5
Willey												
In solid	40	3.4	26	33	5	29	8	10	29	36	1	17.4
In precipitates												0.44
Harrington R. H.	38	5	1		6	25	1		18			5

The influence of additions of various alloying elements on the electrical conductivity of aluminium is presented in Fig. 1 [11]. The analysis of the presented characteristics indicates that Zr, in comparison to other elements, causes a significant decrease of the electrical conductivity of aluminium. Out of such heavy metals as Cr, Mn, Fe, Ti and V, zirconium influences the most unfavourably. It results from the analysis of the presented characteristics that the AlZr alloy of a conductivity at the level of 60% IACS should not contain more than 0.12 wt% of zirconium [5].

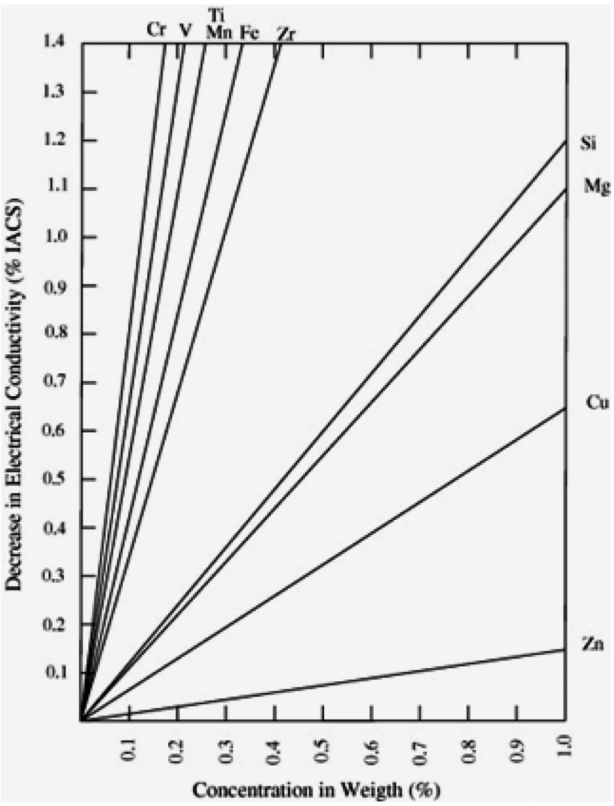

Fig. 1. Influence of a kind and amount of alloying additions on the electrical conductivity of aluminium [11]

Quantitative influence of alloying element addition on the alloy resistivity can be expressed by the Nordheim rule, which in case of alloys of variable solubility of alloying elements in the matrix, is in a form of equation 1 [5, 7-9]:

$$\Delta\rho_o = \Sigma c_j' \cdot A_j + \Sigma c_k'' \cdot A_k \qquad (1)$$

Coefficients c_j' and c_k" represent the given element content in the alloy, expressed in wt%, coefficients A_j and A_k determine the influence of individual elements on the resistivity of the basic metal, while index „j" means the alloying element presence – in the solid solution and index „k" – in precipitates.

The performed analysis of the chemical compositions of the heat resistant AlZr alloys allowed to determine the most advantageous amount of zirconium addition, which is within the range: 0.05 – 0.32 wt% of Zr. The aim of the hereby study is investigating electrical properties of alloys of the selected chemical compositions falling into the above given range. The influence of the heat treatment (artificial ageing) of the AlZr alloy in a form of the Properzi ingot, characterised by properties and structure of the casting, for the alloy resistivity was tested. For the investigated alloys the ranges of the obtainable mechanical and electrical properties were determined, which allowed to select the optimal heat treatment conditions.

2. Material for research

The selected AlZr alloys were produced under industrial conditions in the NPA Skawina S.A. plant, in the continuous casting and rolling line: Continous-Properzi. The material in a form of a continuous casting was taken from the casting wheel of the Properzi system. Aluminium of PN-EN 1370 grade constituted the bases for producing alloy. Parameters of the casting process was developed in such a way as to obtain the aluminium supersaturation with zirconium. The detailed chemical composition of the tested AlZr alloys is presented in Table 2.

TABLE 2
The chemical composition of the tested AlZr alloys, wt%

Al	Zr	Fe	Si	Cu	Zn
99.70	0.05	0.146	0.058	0.001	0.008
99.65	0.09	0.156	0.063	0.001	0.005
99.60	0.15	0.133	0.063	0.004	0.008
99.45	0.22	0.185	0.067	0.002	0.004
99.40	0.29	0.163	0.070	0.002	0.001
99.42	0.32	0.122	0.067	0.003	0.001

Materials for testing were subjected to heat treatments in the temperature range from 20°C to 620°C (20, 100, 200, 300, 325, 350, 375, 400, 425, 450, 500, 550, 620°C), for 24, 120 and 192 hours. The heat treated materials were tested by means of the Sigmatest device of the Foerster Company, which operates on the bases of eddy currents. The calibration curve of the measuring device was based on four conductivity standards: 17.46; 22.24; 30.15 and 35.89 MS/m. On the grounds of the electrical conductivity measurements the resistivity values were determined for individual AlZr alloys.

3. Obtained results

The obtained measurement results for the investigated AlZr alloys are presented in a form of diagrams of the resistivity dependence on the heating temperature, on which lines of the resistivity changes for individual heating times were drawn. The detailed results are shown in Fig. 2 to 7. Successively: Fig. 2 – AlZr0.05, Fig. 3 – AlZr0.09, Fig. 4 – AlZr0.15, Fig. 5 – AlZr0.22, Fig. 6 - AlZr0.29 and Fig. 7 – AlZr0.32.

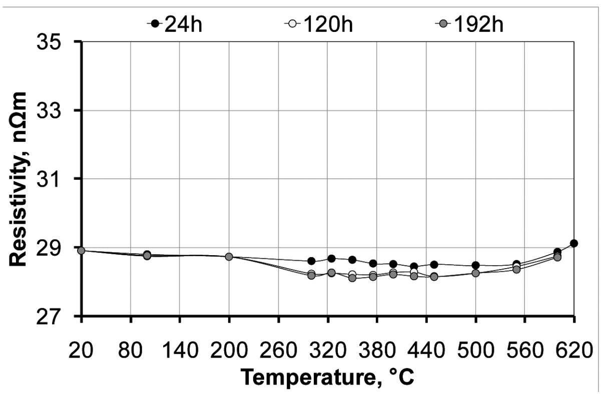

Fig. 2. The temperature dependence of resistivity for the AlZr0.05 alloy

The results of the AlZr0.05 alloy resistivity presented in Fig. 2 indicate a small change of this electrical property, which changed from app. 29 nΩm at a temp. 20°C to 28.4 nΩm at a temperature range from 20 to 500°C and finally obtained above 29 nΩm at a temp. 620°C. From the point of view, of obtaining optimal electrical properties by the AlZr0.05 alloy for the most advantageous heat treatment parameters a temperature of 350°C and heating time of 192 hours should be assumed. Similar changes are observed in Fig. 3 for the AlZr0.09 alloy, however resistivity changes were larger, since in this case more zirconium was dissolved in the aluminium solution. Optimal conditions of the AlZr0.09 alloy heat treatment are: heating time – 192 hours, temperature – 350°C.

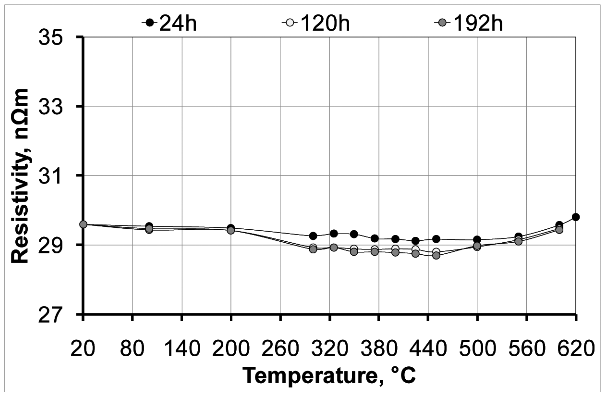

Fig. 3. The temperature dependence of resistivity for the AlZr0.09 alloy

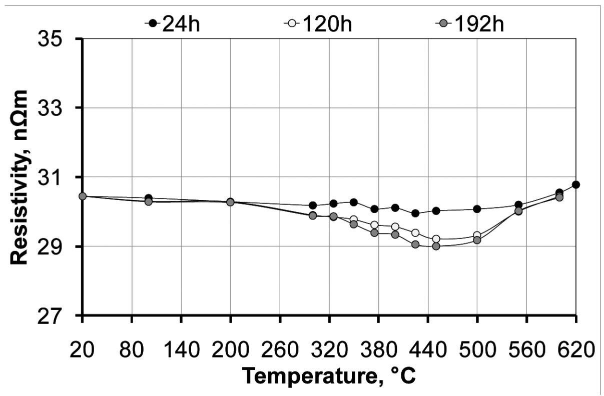

Fig. 4. The temperature dependence of resistivity for the AlZr0.15 alloy

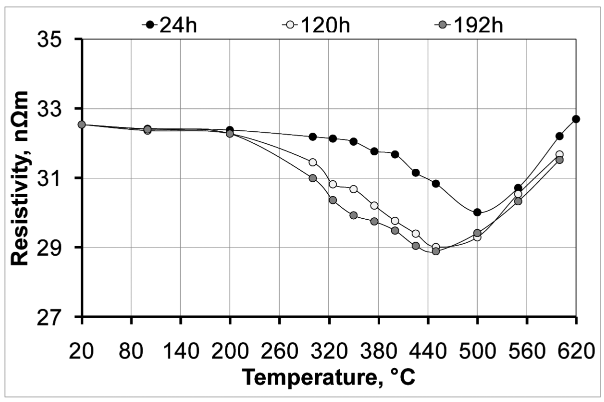

Fig. 5. The temperature dependence of resistivity for the AlZr0.22 alloy

In case of the AlZr0.15 alloy the resistivity curves shown in Fig. 4 have the characteristic letter U shape. The minimal electrical properties were obtained for this alloy at a temperature of 450°C after 192 hours of heating. The shape of the obtained diagram results from two main factors. In the first place, from striving – during the heating process – to precipitating the equivalent zirconium precipitates Al_3Zr, which are controlled by the thermally activated diffusion processes (zirconium ($7.28 \cdot 10^{-2}\,m^2/s$) has a high diffusion coefficient in aluminium ($1.88 \bullet 10^{-3}\,m^2/s$) [12]). In the second place, from obtaining thermodynamic equilibrium conditions at high temperatures, which due to a variable solubility (solvus curve) and the initial alloy supersaturation with zirconium, is not difficult to be achieved. The first factor concerns the left side of the letter U, while the second the right side of the letter U. The optimal heat treatment conditions, determined on the grounds of the performed tests, are in fact minima of the resistivity curves for the given heating time. For the alloys containing 0.22% and above (0.29% and 0.32%) of zirconium the shape of the diagram is very clearly marked. In the AlZr0.22 alloy, at temperatures from 20 to 450°C, thermally activated diffusion processes leading to a gradual decrease of the material resistivity, occur. It can be seen that the longer heating time the lower resistivity value. At temperatures from the range: 450 to 620°C, the AlZr0.22 alloy obtains conditions similar to equilibrium. The alloy solubility limit curve, causing that at high temperatures of the heat treatment only a small amount of zirconium is precipitating, is responsible for the character of resistivity changes, in this part of the diagram. It is related to relatively fast obtaining the alloy equilibrium conditions and its high resistivity. On the basis of the resistivity curves one can state that the most advantageous conditions of the heat treatment are: temperature of 450°C and heating time of 192 hours.

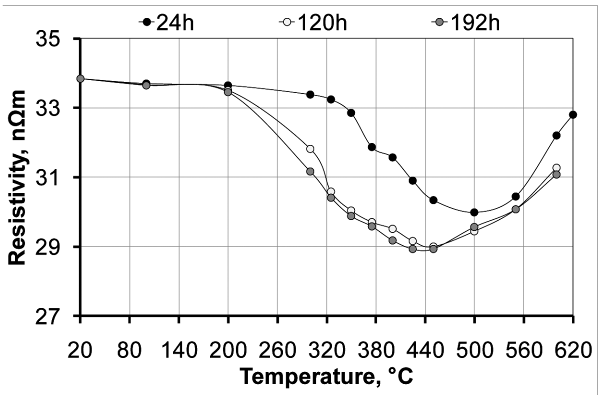

Fig. 6. The temperature dependence of resistivity for the AlZr0.29 alloy

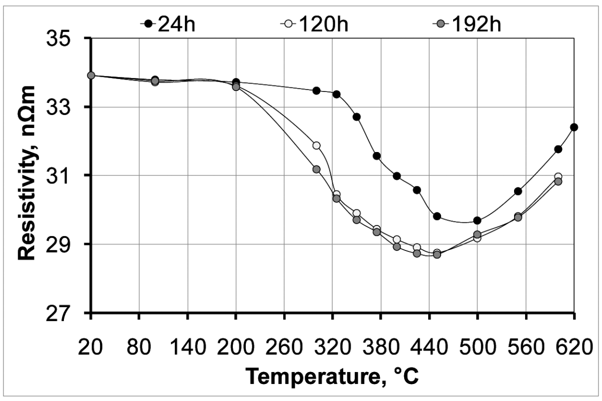

Fig. 7. The temperature dependence of resistivity for the AlZr0.32 alloy

The temperature dependence of the resistivity of the AlZr alloys containing 0.29 and 0.32% Zr is analogous. The most advantageous conditions of the heat treatment of both alloys – from the resistivity point of view – are obtained at a temperature of 450°C after 192 hours of heating.

Applying the Nordheim rule for the resistivity calculations of the tested AlZr alloys, it is possible to calculate the resistivity value which would correspond with the case when the total zirconium amount is either solved in the aluminium solid solution or is in precipitates (Al_3Zr). For the calculation needs, the initial resistivity value was assumed as being (for aluminium, PN-EN 1370 grade) 27.5 nΩm. This value is nearly the same as the experimentally determined value, for alloys supersaturated at the continuous casting and rolling line, which was 27.55 nΩm. Calculations of the zirconium influence on the tested alloy resistivity were performed on the bases of influence coefficients determined by Willey. Determined on this basis resistivity changes as a function of the Zr content plot a zone within which all experimentally obtained results will be situated. The diagram presenting the calculation resistivity results of the AlZr alloys is given in Fig. 8. The line with white markers concerns calculations – at assuming that the total zirconium amount is present in precipitates, while the line with black markers – at assuming that the total zirconium amount is in solid solution. The line with grey markers presents the experimental results.

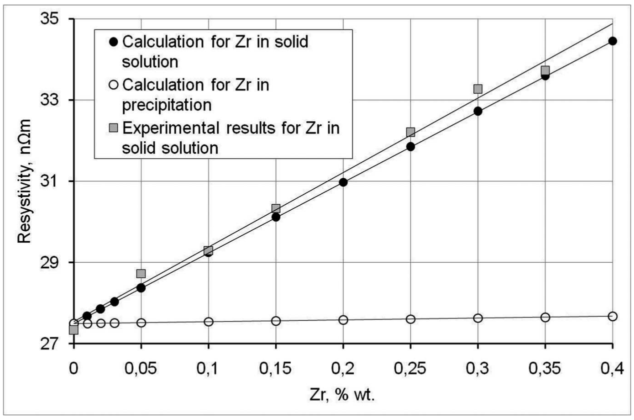

Fig. 8. Calculated and determined values of the resistivity for AlZr alloys

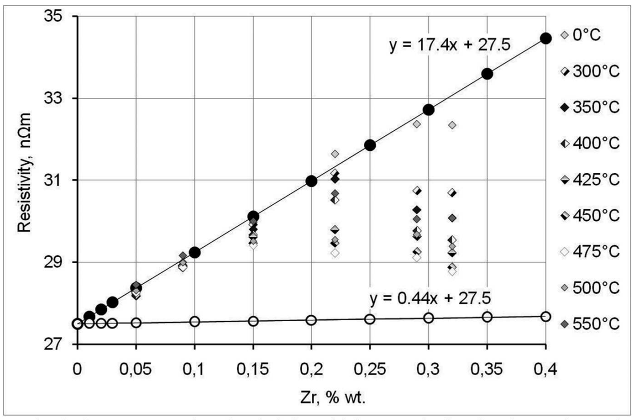

Fig. 9. Summary results of resistivity which was calculated and experimental

The dependence between the resistivity value and the amount of added zirconium is presented in Fig. 9. Points in the diagram represent the tested AlZr alloys resistivity values obtained as a result of artificial ageing. It can be seen, that the obtained values are relatively well localized within the zone determined on the calculations basis. In case of alloys containing 0.05, 0.09 and 0.15% of Zr, which are localised within the aluminium solid solution, small resistivity changes caused by the artificial ageing can be seen. The obtained measurement results are very near the calculation line corresponding with zirconium contained in the solid solution. In the remaining alloys (from 0.22 to 0.32% of Zr) the resistivity change is quite significant being approximately 4 nΩm. Along with the ageing temperature increase the diffusion process becomes faster and zirconium solubility in aluminium changes, which leads to faster obtaining conditions close to equilibrium. In a certain temperature range (to approximately 450°C) the given alloy resistivity strives in the direction of the calculated resistivity line corresponding with zirconium contained in precipitates. However, due to the solvus line path and a joint occurrence of zirconium in precipitates and in the solid solution (see Fig. 1) the lower line, representing Zr in precipitates is not reached, since – according to rule (1) – the alloy has a higher equivalent resistivity. Simultaneously this value – due to a slow Zr diffusion in aluminium – is very difficult to be obtained (very long thermal treatment time). It can be noticed that for the ageing time of 192 hours the lowest resistivity level of the tested alloys usually equals approximately 29 nΩm.

4. Conclusions

On the grounds of the performed investigation the following conclusions were formulated:

1. The zirconium influence on the electrical properties of the AlZr alloy increases with the its contents in the solid aluminium solution. To this end, the selection of the proper heat treatment conditions, taking into account the solubility limit curve, allows to decrease the initial resistivity value to a level of approximately 29 nΩm.
2. At temperatures from 20 to 450°C the diffusion process and zirconium precipitates decide on the alloy resistivity value, while at temperatures from 450 to 620°C the solubility limit curve of zirconium in aluminium decides.
3. The Nordheim rule and zirconium influence coefficients on aluminium resistivity, determined by Willey, allow to estimate the resistivity changes zone for the AlZr alloys. The obtained calculations relatively well correspond with the experimental values.

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