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The Effect of Zirconium and Scandium Additions on Electrical Resistance, Strength and Thermal Stability of Cold Rolled Aluminium Sheets

Alexander N. Alabin[1], Nikolay A. Belov[1], Alexey Yu. Prokhorov[2], Nataliya Yu. Tabachkova[1]
[1] National Research and Technological University "MIS&A", 4 Leninskiy pr., Moscow, 119049 Russia,
[2] OAO "Kirskabel", 1 ul. Lenina, Kirs, Kirovskaya oblast, 612820 Russia

We have studied the structure, electrical resistance, mechanical properties and thermal stability of cold rolled sheets of pure aluminium (99.99 %) and 3 alloys: Al–0.64%Zr, Al–0.3%Sc, and Al–0.24%Zr–0.1%Sc (wt. %). Foundry flat ingots (thickness of 15 mm) were rolled in two variants: (1) without any intermediary annealing (designated as F), (2) using an intermediary annealing (designated as T) . Sheets (final thickness of 0.7 mm) were annealed at 300 °C and held for 1 up to 500 h. To calculate the liquidus temperatures, the solubilities of Zr and Sc in aluminium solid solution-(Al) and volume fractions of $L1_2$ nanoparticles (Al_3Zr, Al_3Sc and $Al_3(Zr,Sc)$), we used *Thermo-Calc* software. It was found that all 3 alloys have the unrecrystallized structure after annealing (including 500 h holding). The size of subgrains is about 1 μm while the average size of $L1_2$ precipitates doesn't exceed 10-15 nm. The value of combination of various properties was estimated using the desirability function (D), which makes it possible to change characteristics with different dimensions into dimensionless values within the range of 0 to 1. The obtained results show that D strongly depends on the concentration of Zr and Sc in (Al) and on the process flow for fabrication of sheets. It was shown that the alloy Al–0.24%Zr–0.1%Sc (in T temper) has the best value of D comparing with binary alloys and pure aluminium.

Keywords: *Al-Zr-Sc alloys, $Al_3(Zr,Sc)$ nanoparticles, electrical resistance, strength*

1. Introduction

During last days in the different areas of electro-technical industry there is increased interest to the thermal stable aluminium alloys that should combine high electrical conductivity and sufficient strength which remains after heating up to 300 °C. The most prospective alloys for this application are low-alloyed alloys with zirconium addition [1-3]. In particular such alloys are used for manufacture of wire for high-voltage lines cables. The greatest effect from zirconium addition is reached under condition of complete bonding of this element in nano-particles of metastable phase Al_3Zr that has $L1_2$ structure [2-4]. The same particles are formed when scandium is introduced [5-8]. As soon as phases Al_3Zr and Al_3Sc are isomorphous, these two elements are often introduced together. In the last case the formula of $L1_2$ is usually noted as Al_3 (Zr,Sc).

In the paper [8] basing on ingots example it was shown that the most hardening effect in Al-Zr system is reached at ~0.6 % Zr, and in Al-Sc system an optimal concentration of scandium is about 0.3 %. Scandium is much more expensive than zirconium, but from the other side, introduction of the last element requests increased melting and casting temperatures. In alloys of Al-Sc system precipitation of $L1_2$ phase is forming quicker however they coarsen under heating over than 350 °C (i.e. their thermal shock is lower that alloys with zirconium addition have). The most successful combination of strength, adaptability, production cost and thermal shock is reached in ternary alloys, as was shown basing on example of Al-0.2%Zr-0.1%Sc composition [8]. Dependency of electrical characteristics from ratio between zirconium and scandium is not enough investigated.

Only heat treatment regime has influence on strengthening of ingots, but in wrought products the number of factors is considerably increasing and this requests special investigation. Therefore the main target of the current paper was to study the influence of parameters of strain-thermal treatment on strength, electrical resistance and thermal stability of cold-rolled sheets of three typical alloys of Al–Zr–Sc system.

2. Results and Discussions

2.1 Experimental methods

The main subjects of study were sheets of three Al–Zr–Sc alloys produced from flat ingots (15×30×180 mm). The ingots were prepared from high-purity primary aluminium (99.99 %); zirconium and scandium were introduced as an Al–3.5%Zr and Al–2%Sc master alloys. The chemical composition of specimens (Table 1) was analyzed at an ARL 3560B-1583 emission spectrometer. Foundry ingots were cold-rolled on a laboratory rolling mill to a final sheet thickness of 0.7 mm in two variants: (F) without any intermediary annealing, (T) using an intermediary annealing at a rolling thickness of 4.3 mm by the regimes: 300 °C, 8 h for alloy 30 Sc and 300 °C, 8 h+450 °C, 8 h for Zr-containing alloys. Sheets were annealed at 300 °C and held for 1 up to 500 h. Intermediate and final annealing of sheets was done in a Nabeltherm electric muffle furnace at a temperature maintenance accuracy within the limits of ±2 °C.

Table 1. The chemical composition of experimental alloys and calculated values of the liquidus

Designation	chemical composition, wt .% (at.%)			T_L, °C[1]
	Zr	Sc	Zr+Sc	
64Zr	0.64 (0.19)	0 (0)	0.64 (0.19)	836
30Sc	0 (0)	0.30 (0.18)	0.30 (0.18)	660
24Zr10Sc	0.24 (0.07)	0.10 (0.06)	0.34 (0.13)	741

[1] the liquidus temperature (calculation with Thermo–Calc software)

The mechanical properties of sheets (ultimate tensile strength - UTS, yield strength – YS, and relative elongation El at room temperature) were determined by the results of uniaxial tension tests on a Zwick Z250 testing machine. The specific electrical resistance (ρ) of sheet specimens of a given size was measured using a GW INSTEK GOM-2 digital programmable milliohmmeter. The operating principle of the instrument is based on measuring a voltage drop by a digital voltmeter across a measured resistor at the flow of a calibrated value of current through it. The rated length of sheet specimens was 100 mm.

Metallographic studies were carried out using an Axiovert 200 MMAT light microscope and a JSM-35CF scanning electron microscope (LM and SEM, respectively). Sections cut from ingots and sheets (central parts) served as subjects of study. Sections were prepared using both mechanical (Struers Labopol-5) and electrolytic polishing, as these two methods complement each other to give a more complete idea of the microstructure. An electron probe microanalysis (EPMA) was also done at the JSM-35CF microscope using a wave spectrometer. The fine structure (primarily, of nanoparticles of the Zr-containing phase) was studied on a JEM2100 transmission electron microscope at an accelerating voltage of 200 kV (TEM).

To calculate the liquidus temperature, isothermal sections, the solubilities of zirconium and scandium in aluminium solid solution ($C_{Zr\text{-}(Al)}$), and volume fraction (Qv) of nanoparticles of $L1_2$ phase we used Thermo-Calc software (database TTAL5).

2.2 Experimental results

The phase diagram Al-Zr-Sc was analyzed by way of calculations in order to choose optimal casting temperature that should wittingly exceed liquidus temperature (T_L). Fig. 1a shows that typical temperature (720 °C) for majority of commercial aluminium alloys is too low for the experimental compositions 64Zr and 24Zr10Sc (primary crystals of Al_3Zr phase can't be dissolved in L). And for alloy 64Zr even 800 °C is not enough (Fig.1b), because corresponding value of T_L is 836 °C. Therefore this alloy was prepared and casted at ~900 °C, in order to guarantee receipt of single-phase structure. Alloys 30Sc and 24Zr10Sc were prepared under considerable lower temperatures (720 and 780 °C accordingly), as they have more lower values of T_L (Table1).

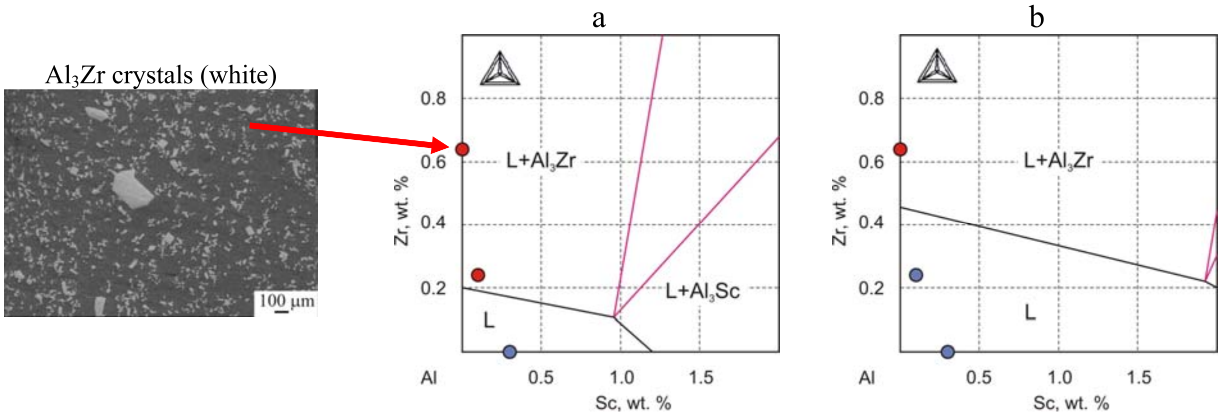

Fig. 1. Isothermal sections of the Al–Sc–Zr phase diagram: a) at 720 °C and b) at 800 °C.

Having approximately the same structure in as-casted state (single-phased) all three experimental alloys and pure aluminium didn't have difference in structure after rolling: all had fiber structure. Comparison of strength properties of sheets received according technological scheme (F) shows weak distinction between them. In particular, yield strength is at the level 150 MPa (Fig. 2a), i.e. a little bit higher that unalloyed aluminium has. It can be explained by the following: small additions of zirconium and scandium, which completely enter in (Al), lead to very insignificant solid-solution strengthening [5] and have weak influence on strain hardening. Second scheme (T) leaded to the more significant distinction in YS values (from 190 to 230 MPa), as shown at Fig. 2b. This result can be connected with some difference in Q_V values (Table 2) and different degree of decomposition of (Al) during process of intermediate annealing.

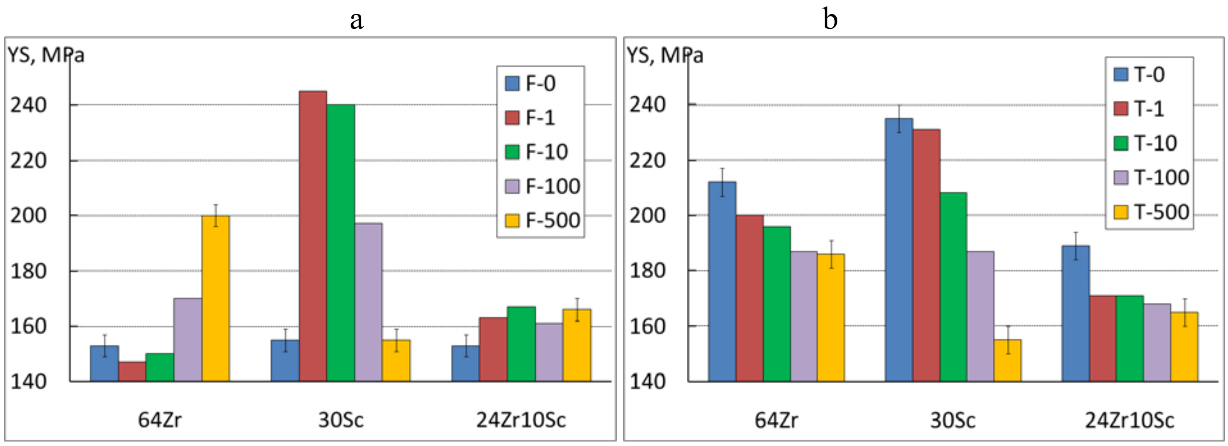

Fig. 2. Yield strength (YS) of cold–rolled aluminium sheets (64 Zr, 30Sc and 24Zr10Sc alloys) versus annealing time at 300 °C for 1 up to 500 h: a) scheme F, b) scheme T.

Significant distinctions were observing already after 1-hour intermediate annealing at 300 °C. Values of YS of alloys 64Zr and 30Sc, manufactured according first scheme (F), are considerably differs. The strength of the first one stays at the initial level, but the second alloy reveals strong strengthening (approximately by 60 %). This explained by that scandium has more high diffusibility in (Al), therefore decomposition of (Al) happens much more faster. Note should be taken that the given temperature is an optimal for the precipitation hardening of alloys with scandium but too low for Al–Zr alloys [5]. When holding time is increased up to 500 h, the difference between these alloys is decreasing. For the first scheme it is connected with that alloy 64Zr is a little bit strengthening and alloy 30Sc, on the contrary, softening (Fig. 2a). For the both schemes ternary alloy demonstrates high stability: yield strength changes insignificantly in comparison with an initial level. As a whole, thermo-stability of all three alloys is much more than pure aluminium has, whose YS value after 1-hour annealing at 300 °C drops till 20 MPa.

Table 2. Calculated values of volume fraction of $L1_2$ phase and content of zirconium and scandium in aluminium solid solution

Alloy	Q_V[1], vol. %[2]		$C_{(Al)}$, wt. % (at. %)[2]			
	300 °C	450 °C	300 °C		450 °C	
			Zr	Sc	Zr	Sc
64Zr	0.74	0.54	0.037(0.011)	–	0.204 (0.060)	–
30Sc	0.75	0.65	–	0.004 (0.002)	–	0.046 (0.028)
24Zr10Sc	0.52	0.38	0.018 (0.005)	0.002 (0.001)	0.088 (0.026)	0.026 (0.016)

[1]maximal volume fraction of secondary precipitations of $L1_2$ at 300 and 450 °C, [2] content of Zr and Sc in (Al), calculation with Thermo–Calc software (stable phase Al_3Zr was excluded)

Deformation-thermal regime of treatment has significant influence on the specific electrical resistance (ρ), as shown at Fig. 3. As it was expected, maximum values of ρ of all three alloys are observed in F-0 state, so far as the maximum concentration of alloying elements in (Al) corresponds to exactly this state. Annealing leads to the monotonous decreasing of electrical resistance which is obviously connected with decomposition of (Al). Especially strong changes are observed in case of the first scheme (Fig. 3a). In particular, ρ value of 30Sc alloy during process of 500-hour annealing decreasing by $5.5 \cdot 10^{-9}$ Ωm··m. Intermediate annealing of the sheets (scheme T) significantly levels influence of holding (Fig. 3b). This is particularly noticeable for 24Zr10Sc alloy, where difference of ρ values in T-0 and T-500 states doesn't exceed $0.5 \cdot 10^{-9}$ Ωm··m.

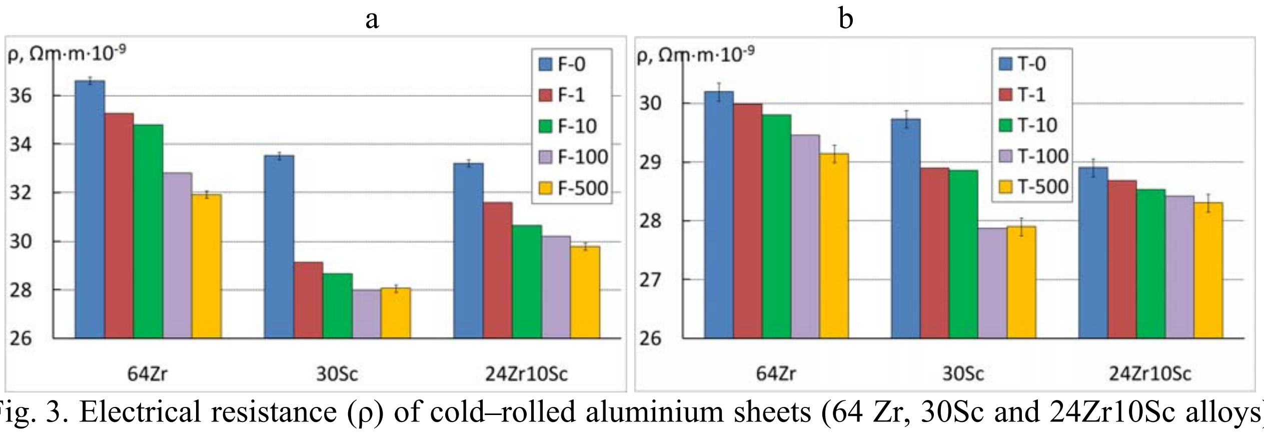

Fig. 3. Electrical resistance (ρ) of cold–rolled aluminium sheets (64 Zr, 30Sc and 24Zr10Sc alloys) versus annealing time at 300 °C for 1 up to 500 h: a) scheme F, b) scheme T.

At Fig. 4a the light-field picture of polygonized substructure of ternary alloy is given. At the dark-field picture received in reflex 001 of phase $Al_3(Sc,Zr)$ it is seen that particles of precipitations of this phase have size of 10-15 nm and quite uniformly spread inside the sub-grain (Fig. 4b). There is no primary distribution of the particles of the second phase along sub-grains borders. At Fig. 4c picture of the particle of second phase received in high resolution is given. Mutual location of atom planes of the particle and matrix coincides, therefore lattices are coherent. Reflexes corresponding to the planes of Al and $Al_3(Sc,Zr)$ phase are present at Fourier image that form direct picture of matrix and precipitations lattice.

a b c

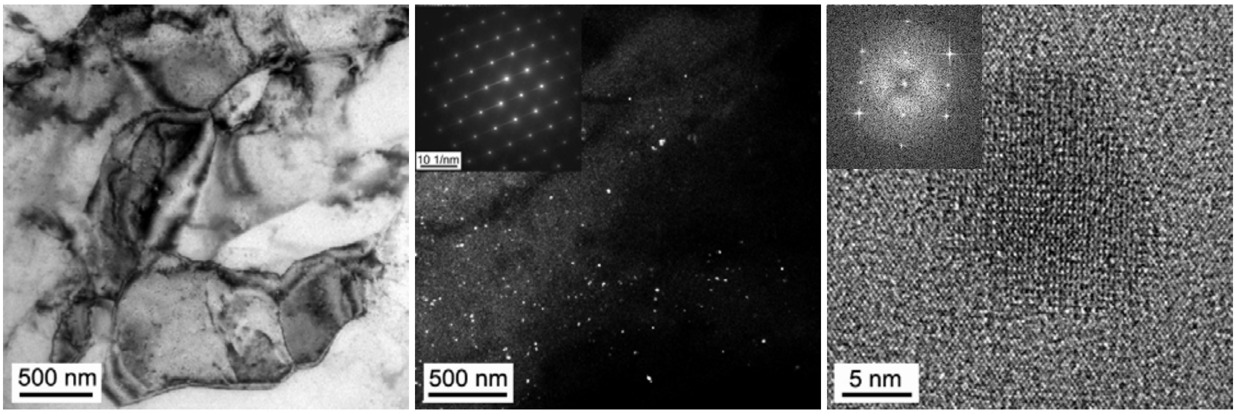

Fig. 4. TEM–structure of alloy 24Zr10Sc alloy after holding at 300 °C during 500 hours:
a) polygonized substructure; b),c) nanoparticles of phase $Al_3(Sc,Zr)$

2.3 Discussions

It is well known that in general case factors that lead to the alloy strengthening, increase ρ value, therefore the target of the maximum increasing of YS and saving of ρ level, is not simple [6-8]. However results achieved in current paper show more complicated ratio between ρ and YS (Fig. 5). In particular, alloys containing zirconium, manufactured according scheme F, demonstrate the contrary tendency: decreasing of ρ while YS is growing. This is connected with that the annealing of sheets at 300 °C lead to the formation of strengthening nano-particles of $L1_2$ phase and accompanying depletion of solid solution. The first factor is the reason of ρ decreasing and second – growing of YS. In 30Sc alloy decomposition happens so fast that increased electrical resistance observed only in work harded sheet manufactures according scheme F (upper point at Fig. 5b).

a b c

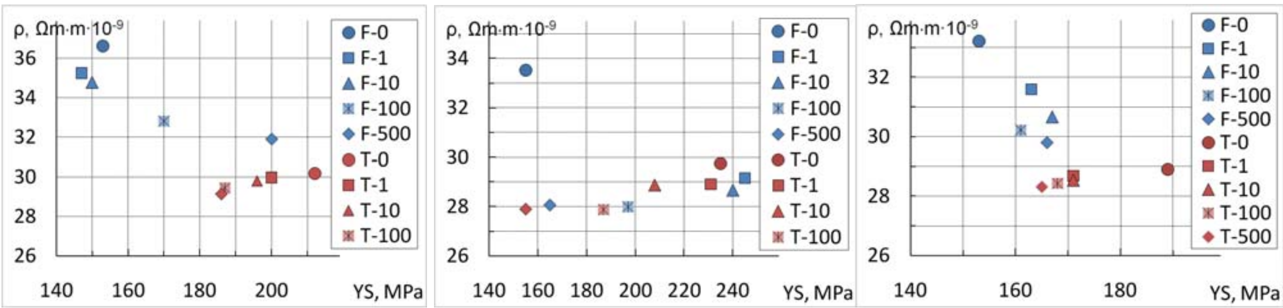

Fig. 5. Relationship between yield strength (YS) and electrical resistance (ρ) of cold–rolled aluminium sheets: a) 64Zr; b) 30Sc; c) 24Zr10Sc

The best combination of various properties was estimated using the desirability function (D), which makes it possible to change characteristics with different dimensions into dimensionless values within the range of 0 to 1 [9]. The sought-for value of D is determined as a geometric mean of the desirability of separate properties (d_i). We considered three basic properties: 1, the specific electrical resistance in the initial state (ρ^{20}); 2, the yield strength in the initial state (YS^{25}); 3, the yield strength after a 1-h annealing at 300 °C (YS^{300}). The following values were used as reference points: a satisfactory level (0.37): $\rho^{20} = 31 \cdot 10^{-9}$ Ωm·m, $\sigma_{0.2}{}^{20} = 140$ MPa, $\sigma_{0.2}{}^{300} = 120$ MPa; a good level (0.7): $\rho^{20} = 28 \cdot 10^{-9}$ Ωm·m, $\sigma_{0.2}{}^{20} = 250$ MPa, $\sigma_{0.2}{}^{300} = 230$ MPa.

Results adduced in Table 3, show that greatest values of D of all three alloys are reached when technological scheme T is realized. All of them in this state are much more exceed pure aluminium because thermal stability of the last one is very low (1-hour heating of sheets lead to the full recrystallization). The basic shortcoming of scheme F is obviously consists in increased value of ρ, that stipulates low value of corresponding desirability (d_1).

Table 3. Initial data for calculation of desirability function (D)

Alloy	state	ρ^{25}, Ωm··m 10^{-9}	YS^{25}, MPa	YS^{300}, MPa	D	d1	d2	d3
Al (99.99 %)	F	27.2	128	13	0.26	0.75	0.33	0.07
Al – 0.64 % Zr	F	36.6	147	150	0.07	0.00	0.39	0.47
	T	30.2	212	200	0.55	0.46	0.59	0.62
Al – 0.3 % Sc	F	33.5	155	245	0.31	0.10	0.42	0.73
	T	29.7	235	231	0.62	0.52	0.66	0.69
Al – 0.24 % Zr – 0.10 % Sc	F	33.2	153	163	0.30	0.12	0.41	0.51
	T	28.9	189	171	0.56	0.61	0.53	0.53
reference points		31	140	120	0.37	0.37	0.37	0.37
		28	250	230	0.7	0.7	0.7	0.7

3. Conclusion

1. Influence of parameters of deformation and thermal treatment on strength (YS), specific electrical resistance (ρ) and thermal stability of cold rolled sheets of three aluminium alloys with zirconium and scandium additions (0.64 % Zr, 0.3 % Sc, and 0.24 % Zr+0.10 % Sc) was investigated.
2. The additions of zicronium and scandium are significantly increase ρ value, which is possible to decrease by application of annealing. Parameters of annealing have to be chosen proceeding from ultimate concentration of Zr and Sc in (Al) and rate of decomposition of the last one.
3. All experimental alloys have high thermal stability to the heating at 300 °C, what stipulated by resistance of nano-particles of $L1_2$ phase (Al_3Zr, Al_3Sc and $Al_3(Zr,Sc)$) to the coarsening up to 500 hours.
4. By the use of desirability function it is shown that ternary alloy has the best combination of strength, electrical resistance and thermal stability.

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