

Electrical Resistivity and Strength of Cold Rolled Sheets of Aluminium Alloys Containing up to 0.64 wt. % Zr

Nikolay A. Belov¹, Alexandr N. Alabin¹, Alexey Yu. Prokhorov²

¹National Research and Technological University "MIS&A", Leninskiy pr, 4, Moscow, 119049 Russia

²OAO "Kirskabel", ul. Lenina, 1, Kirs, Kirov reg., 612820 Russia

We have studied the effect of zirconium additions within the range from 0.22 to 0.64 wt. % on the structure (OM, SEM, TEM), electrical resistivity (ρ) and strength of cold-rolled aluminium sheets after various annealing regimes. Foundry flat ingots (thickness of 15 mm) prepared from pure aluminium (99.99%) were rolled in two variants: (1) without any intermediary annealing, (2) using an intermediary annealing (300 °C, 8 h+450 °C, 8 h). Sheets (0.7 mm) were annealed at 300 °C and held for 1 up to 500 h. In hardened condition the mechanical properties have been shown to be almost independent of the concentration of zirconium. A significant difference becomes apparent already after a 1-h annealing. In contrast with pure aluminium, all Al-Zr alloys retain unrecrystallized structure and strength. It was found that electrical resistivity of Al-Zr alloys is primarily determined by the concentration of zirconium in aluminium solid solution ($C_{Zr-(Al)}$), which strongly depends on temperature and duration of annealing. Particularly, the experimental values of ρ in hardened state are well described by a linear dependence of $\rho=27.3+14.4 \cdot C_{Zr-(Al)}$. According summarized results the optimal structure of Al-Zr alloys for electrical engineering applications is an aluminium matrix with a minimal value of $C_{Zr-(Al)}$ and a sufficiently large amount of Al_3Zr phase nanoparticles ($L1_2$) evenly distributed in the matrix.

Keywords: Al-Zr alloys, Al_3Zr nanoparticles, electrical resistivity, strength, annealing

1. Introduction

Aluminium, possessing a high electrical conductivity, is widely used in electrical products, where this quality is the basic one [1, 2]. As addition of other elements reduces electrical conductivity to this or that extent, technical-grade unalloyed aluminium or alloys of 6XXX series are used, as a rule.

Recently, there has been increased interest from power industry in thermally stable aluminium alloys, which should combine high electrical conductivity and sufficient strength preserved after heatings up to 300 °C [3–5]. The latter requirement rules out the use of unalloyed aluminium, as its recrystallization-onset temperature is low (less than 250 °C). To solve the problem, the most promising approach is to develop Al-Zr alloys. By the example of cold-rolled sheets, the works [6] showed that introduction of 0.4–0.6 % Zr into aluminium made it possible not only to retain strain hardening, but also to increase additionally the strength properties at the expense of secondary precipitates of the Al_3Zr ($L1_2$) phase at their size of about 10 nm. The effect of zirconium on the electrical resistivity at such high concentrations has not essentially been studied.

As after solidification all zirconium content should enter the aluminium solid solution (hereafter, (Al)), castings should be prepared in a process other than in the case of conventional alloys. Further on, due to annealing this element should totally precipitate from (Al) in the form of Al_3Zr nanoparticles, which enables both the required strengthening and thermal stability. On the other hand, a maximum decrease of the concentration of zirconium in (Al) (hereafter, $C_{Zr-(Al)}$) is also required from the point of view of achieving the lowest electrical resistivity. Assuming that it is exactly the high density of Zr-containing nanoparticles and the minimum level of $C_{Zr-(Al)}$ that determine the optimal structure, we formulated the main tasks of this work: 1) to study the effect of the concentration of zirconium on the electrical resistivity and strength of cold-rolled aluminium sheets

depending on the heat treatment and deformation processing regimes; 2) to analyze the relation between the structure and these properties.

2. Experimental

2.1 Experimental methods

The main subjects of study were sheets of three Al–Zr alloys (designated as 22Zr, 34Zr and 64Zr) produced from ingots (15×30×180 mm). The ingots were prepared from high-purity aluminium (99.99%) by casting into a graphite mould (15×30×180 mm). Zirconium was introduced as an Al–Zr master alloy at ~900 °C according Al–Zr phase diagram (Fig.1). The chemical composition of specimens was analyzed at an ARL 3560B–1583 emission spectrometer. The actual concentrations are 0.22, 0.34, and 0.64 wt. % Zr (0.07, 0.10, and 0.19 at. % correspondingly). Foundry ingots were cold-rolled on a laboratory rolling mill to a final sheet thickness of 0.7 mm. Cast ingots were rolled in two variants: (1) without any intermediary annealing (designated as F), (2) using an intermediary annealing at a rolling thickness of 4.3 mm by the regime of 300 °C, 8 h+450 °C, 8 h (designated as T). 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. All variants of the process flow diagrams are given in Table1.

Table1. Regimes of cold rolling (CR) and annealing of Al–Zr alloys

Designation	Stages
F-0	CR ($\epsilon \sim 95\%$), no any heating
F-1	CR ($\epsilon \sim 95\%$)+300 °C, 1 h
F-10	CR ($\epsilon \sim 95\%$)+300 °C, 10 h
F-100	CR ($\epsilon \sim 95\%$)+300 °C, 100 h
F-500	CR ($\epsilon \sim 95\%$)+300 °C, 500 h
T-0	CR ($\epsilon \sim 71\%$)+300 °C, 8 h+450 °C, 8 h+ CR ($\epsilon \sim 83\%$)
T-1	CR ($\epsilon \sim 71\%$)+300 °C, 8 h+450 °C, 8 h+ CR ($\epsilon \sim 83\%$)+300 °C, 1 h
T-10	CR ($\epsilon \sim 71\%$)+300 °C, 8 h+450 °C, 8 h+ CR ($\epsilon \sim 83\%$)+300 °C, 10 h
T-100	CR ($\epsilon \sim 71\%$)+300 °C, 8 h+450 °C, 8 h+ CR ($\epsilon \sim 83\%$)+300 °C, 100 h
T-500	CR ($\epsilon \sim 71\%$)+300 °C, 8 h+450 °C, 8 h+ CR ($\epsilon \sim 83\%$)+300 °C, 500 h

The mechanical properties of sheets (ultimate tensile strength–UTS, yield strength–YS, and relative elongation–El) were determined by the results of uniaxial tension tests on a Zwick Z250 testing machine. The electrical resistivity (ρ) of sheet specimens of a given size was measured using a GWINSTEK GOM–2 digital programmable milliohmmeter. 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. An electron probe microanalysis (EPMA) was also done at the JSM–35CF microscope using a wave spectrometer. The TEM–structure (primarily, of nanoparticles of the Zr–containing phase) was studied on a JEM2100 transmission electron microscope at an accelerating voltage of 200 kV. As subjects of study, we used foils prepared as follows. First, we cut workpieces from sheets; then these workpieces were thinned by polishing to 0.2–0.25 mm. From plates obtained, we cut disks 3 mm in diameter, in which conical recesses were made on both sides by jet electropolishing with a 25 % solution of HNO₃ in water at a voltage of 75 V.

The final electrolytic thinning was done in an electrolyte of the following composition: 85 % C_2H_5OH and 15 % $HClO_4$ at a voltage of 12 V and electrolyte temperature of 0–4 °C.

To calculate the liquidus line in the Al–Zr system, the value of $C_{Zr-(Al)}$, and amount of Al_3Zr nanoparticles we used Thermo–Calc software (version TCW4, database TTAL5).

2.2 Results and Discussions

According Al–Zr phase diagram (Fig.1) the temperature of the melt before casting should be higher than the liquidus temperature (T_L). For a greater justification of this conclusion, we conducted an experimental determination of T_L of experimental alloys. As the thermal analysis (including DTA) is not sufficiently sensitive (due to the small thermal effect related to the formation of primary Al_3Zr crystals), we used a quenching method, the essence of which is described below.

Alumina crucibles with pieces of experimental alloys (about 10 g) cut from ingots were placed into a furnace heated to a given temperature (within the range of 700 to 900 °C) and held for 1.5 h. Primary crystals of the Al_3Zr phase were absent in the initial structure of ingots of all alloys. After a holding, the crucible (with the melt) was quenched in water, which made it possible to fix an equilibrium state at a respective temperature. As the Al_3Zr phase is heavier than the aluminium melt, sections were made in the vertical direction along the entire height of a specimen to have the possibility to study the structure near the bottom part (where Al_3Zr crystals were assumed to concentrate). By the SEM and EPMA methods, we studied the presence or absence of Al_3Zr primary crystals. The results of the quenching method are well consistent with the liquidus line calculated by Thermo–Calc (Fig.1). As an example, Fig.2 shows a cluster of Al_3Zr primary crystals in alloy 64Zr after quenching from 750 °C.

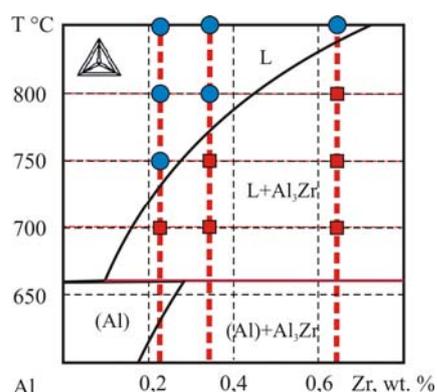


Fig.1. Positions of experimental alloys on Al–Zr phase diagram

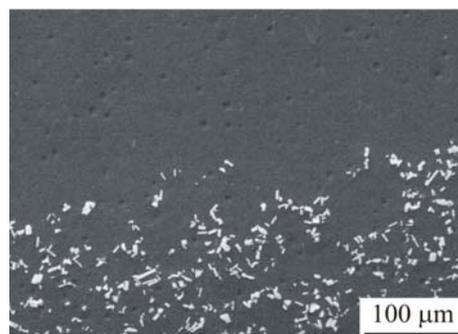


Fig.2. Microstructure of alloy 64Zr near the bottom part after holding at 750 °C and quenching

As the casting temperature (900 °C) was significantly higher than T_L , and the cooling rate was sufficient to prevent the formation of Al_3Zr primary crystals during solidification [5], the casting structure of all alloys was in fact single–phase. However, we observed a noticeable grain refinement with the zirconium concentration increasing. After rolling, alloys did not in fact differ in their structure, as it was fibrous in all of them. Strong changes were observed after annealing: in pure aluminium, a coarse recrystallized structure was observed already after 1 h, and in alloys with zirconium additions it remained fibrous even after a 500–h holding.

The results of a tension test show that in cold–worked state F-0 all alloys have approximately the same level of mechanical properties: UTS=140–160 MPa, YS=120–140 MPa and El=3–6 %. But already a 1–h annealing at 300 °C leads to a strong difference between them. While unalloyed aluminium sharply softens (UTS decreases down to 40 MPa and YS to 20 MPa), alloys with zirconium additions retain the initial level of the strength properties. The dependences of the yield strength versus Zr–content at all regimes (Table1) shown in Fig.3a,b graphically demonstrate the stabilizing effect of this element up to a 500–h holding. Herewith, cold–rolled sheets of alloy 64Zr produced by Scheme F demonstrate even some strengthening, which, evidently, can be associated

only with the formation of Al_3Zr nanoparticles.

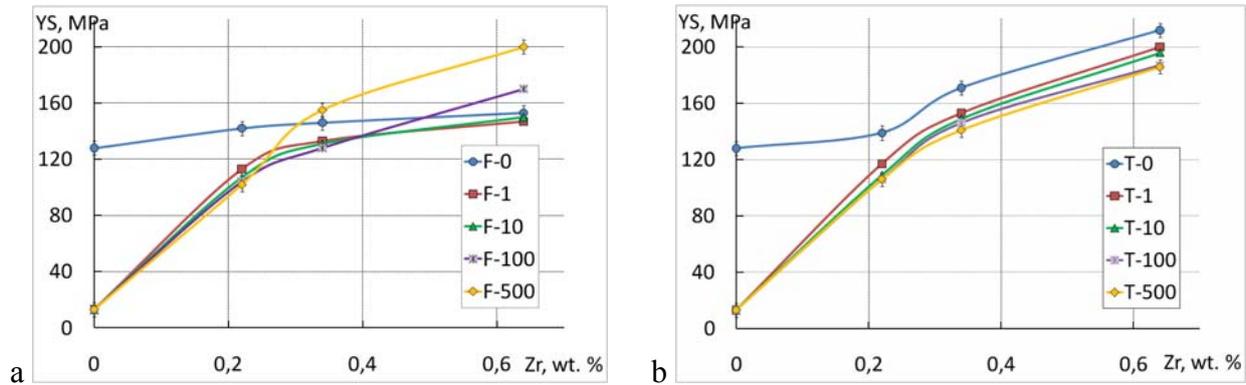


Fig.3. Yield strength of experimental alloys (sheets) versus Zr content:
a) F-scheme; b) T-scheme

To explain this effect, we studied the TEM structure of annealed sheets in representative states. In alloys with zirconium additions, a developed polygonized structure is formed; herewith, the subgrain size after a 500-h holding reaches $\sim 1 \mu\text{m}$ (Fig.4a). Inside and by the boundaries of subgrains, we revealed dislocations, which are fixed by particles of the Al_3Zr phase (Fig.4b). As the latter are persistent to coarsening at 300°C , such a structure makes it possible to retain the strength in annealed sheets on the level of no less than 90 % of the initial values (Fig.3). The average size of particles doesn't exceed 10 nm (Fig.4c).

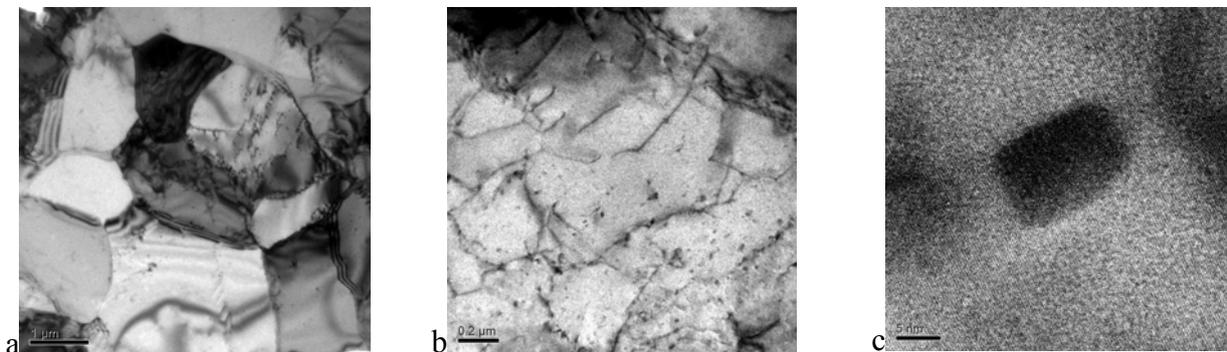


Fig.4. TEM-structure of alloy 64Zr after holding at 300°C during 500 hours (F-500 in Table1)

The results of determining the specific electrical resistivity (ρ) are reflected in the dependences shown in Fig.5. It follows from them that annealing has in fact no effect on the value of ρ of pure aluminium, but in alloys with zirconium additions we observed a decrease. The effect is especially pronounced in alloy 64Zr produced by Scheme F. Intermediate annealing of sheets (Scheme T) significantly levels off the effect of holding. Assuming that the major factor determining the electrical resistivity of experimental alloys is the content of zirconium in aluminium solid solution ($C_{\text{Zr-(Al)}}$), we assayed the relation of ρ and $C_{\text{Zr-(Al)}}$. Note that in state F-0 the value of $C_{\text{Zr-(Al)}}$ should coincide with the concentration of zirconium in the alloy, because sheets were produced from cast ingots at room temperature. As seen in Fig.5, the experimental values of ρ are well described by a linear dependence (1).

$$\rho = 27.3 + 14.4 \cdot C_{\text{Zr-(Al)}} \quad (1)$$

Herewith, the free term of this equation is close to the experimentally measured value of ρ for pure aluminium, and the linear coefficient reflecting the effect of the concentration of zirconium in (Al) is consistent with the literature data [3]. In many other states, zirconium is distributed between (Al) and Al_3Zr nanoparticles, so the effect of this addition on the electrical resistivity is more complex. In

particular, in states T-0 and T-500 (see Table 1) after a sharp rise of the value of ρ at the introduction of 0.22% Zr we observed a weak rise of ρ at a further increase of the concentration of zirconium.

To assay the dependence of ρ on $C_{Zr-(Al)}$ using the Thermo-Calc program, we calculated the values of the equilibrium solubility of Zr in (Al) for the annealing temperatures used (300 and 450 °C) (Table 2). Herewith, we considered both the stable (D0₂₃) and metastable (L1₂) variants, as the phase composition for all annealing regimes conforms exactly to the second variant [6–8]. From the literature data, it is known that a significantly greater value of $C_{Zr-(Al)}$ corresponds to the metastable equilibrium of (Al) with the phase L1₂ as compared with the stable equilibrium [9]. Herewith, the difference increases with temperature going up, which is indicated by the values given in Table 2. Assuming that the remaining zirconium (i.e., the difference between its content in the alloy and in (Al)) occurs in precipitates of the Al₃Zr phase ($C_{Zr-Al3Zr}$), we calculated the dependences of ρ on $C_{Zr-Al3Zr}$. As is seen in Fig. 5, in both characteristic states (T-0 and T-500), for which we can assume the achievement of a metastable equilibrium, the dependences are almost linear. From these dependences, it follows that zirconium in the form of Al₃Zr nanoparticles increases the electrical resistivity by an order of magnitude weaker as compared with solid-solution alloying. Herewith, higher values of the free term conform to the state T-0 (450 °C) as compared with T-100 (300 °C), which, evidently, is related to a greater concentration of zirconium in (Al) (Table 2). As an example, Table 2 presents experimental and calculated values for alloy 64Zr. Note that the values of $C_{Zr-(Al)}$ for the metastable variant are more consistent with the experimental data. Herewith, we did not take into account the intradendrite liquation of zirconium, which is formed in crystallization and leads to an inhomogeneous distribution of secondary precipitates. Probably, a slight discrepancy between the experimental and calculated values of ρ is largely related to exactly this factor.

Table 2. Calculated and experimental values of electrical resistivity (ρ) of alloy 64Zr for states T-0 and T-500 (see Table 1)

State	Al ₃ Zr Lattice	Q _v (vol. %)	C _{Zr-(Al)} (wt.%)	ρ (Ohm·m·10 ⁻⁹)		
				Calc.	Exp.	Diff.
T-0	D0 ₂₃	–	0.038	28.97	30,2	-1.23
	L1 ₂	0.475	0.204	31.05		0.85
T-500	D0 ₂₃	–	0.003	28.25	29,1	-0.85
	L1 ₂	0.677	0.037	28.69		-0.41

On the whole, the experimental results demonstrate that the optimal structure of Al–Zr alloys for electrical applications is an aluminium matrix with a minimum content of zirconium at a sufficient amount of Al₃Zr nanoparticles evenly distributed in the matrix.

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 [10]. 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 resistivity in the initial state (ρ^{20}); 2, the yield strength in the initial state (YS^{20}); 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): $\rho^{20} = 31 \cdot 10^{-9}$ Ohm·m, $\sigma_{0.2}^{20} = 140$ MPa, $\sigma_{0.2}^{300} = 120$ MPa; a good level (0.7): $\rho^{20} = 28 \cdot 10^{-9}$ Ohm·m, $\sigma_{0.2}^{20} = 250$ MPa, $\sigma_{0.2}^{300} = 230$ MPa. The calculated results show that the value of D strongly depends on the concentration of zirconium and on the process flow for fabrication of sheets. This is shown more demonstrably by Fig. 6, from which it is seen that exactly Scheme T makes it possible to get the best set of basic properties by addition of zirconium. The main drawback of Scheme F is, evidently, a rather high value of ρ (Fig. 5). The respective desirability strongly decreases with the increase of the concentration of zirconium. Thus, to get the best combination of the main properties of aluminium conducting alloys, zirconium additions should be much more than those

conforming to branded alloys (0.1–0.2 %). Exactly this is the necessary condition for reaching an optimal structure.

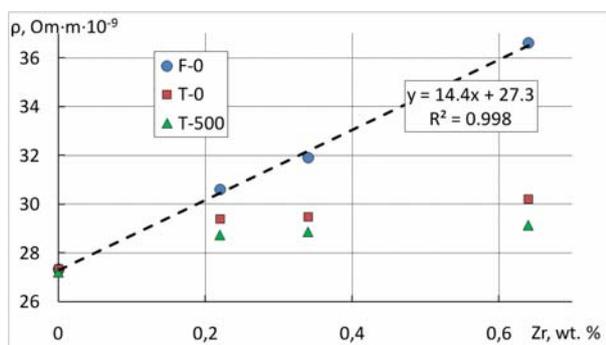


Fig.5. Electrical resistivity versus Zr content

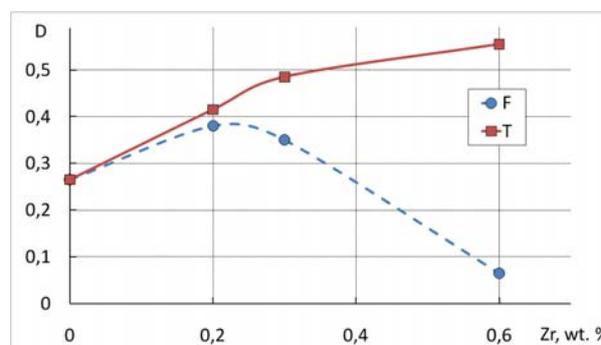


Fig.6. Desirability function (D) versus Zr content

3. Conclusions

1. We have studied the effect of zirconium additions within the range from 0.22 to 0.64 wt. % on the structure, electrical resistivity and strength of pure aluminium cold-rolled sheets after various annealing regimes up to 500 hours.
2. In hardened condition (without annealing), the mechanical properties (strength and ductility) have been shown to be almost independent of the concentration of zirconium. A significant difference becomes apparent already after a 1-h annealing at 300 °C. In contrast with unalloyed aluminium, all Al-Zr alloys retain strain hardening.
3. Electrical resistivity of Al-Zr alloys is primarily determined by the concentration of zirconium in aluminium solid solution, which strongly depends on temperature and duration of annealing.
4. The optimal structure of Al-Zr alloys for electrical engineering applications is an aluminium matrix with a minimum content of zirconium and a sufficiently large amount of Al₃Zr phase nanoparticles evenly distributed in the matrix.

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