Article

Structure and Properties of Ca and Zr Containing Heat Resistant Wire Aluminum Alloy Manufactured by Electromagnetic Casting

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Citation: Belov, N.; Akopyan, T.; Korotkova, N.; Murashkin, M.; Timofeev, V.; Fortuna, A. Structure and Properties of Ca and Zr Containing Heat Resistant Wire Aluminum Alloy Manufactured by Electromagnetic Casting. *Metals* **2021**, *11*, 236. <https://doi.org/10.3390/met11020236>

Academic Editor: Qudong Wang

Received: 20 December 2020

Accepted: 26 January 2021

Published: 1 February 2021

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Abstract: Experimental aluminum alloy containing 0.8% Ca, 0.5% Zr, 0.5% Fe and 0.25% Si (wt.%), in the form of a long-length rod 12 mm in diameter was manufactured using an electromagnetic casting (EMC) technique. The extremely high cooling rate during alloy solidification ($\approx 10^4$ K/s) caused the formation of a favorable microstructure in the ingot characterized by a small size of the dendritic cells, fine eutectic particles of Ca-containing phases and full dissolution of Zr in Al the solid solution. Due to the microstructure obtained the ingots possess high manufacturability during cold forming (both drawing and rolling). Analysis of the electrical conductivity (EC) and microhardness of the cold rolled strip and cold drawn wire revealed that their temperature dependences are very close. The best combination of hardness and EC in the cold rolled strip was reached after annealing at 450 °C. TEM study of structure evolution revealed that the annealing mode used leads to the formation of $L1_2$ type Al_3Zr phase precipitates with an average diameter of 10 nm and a high number density. Experimental wire alloy has the best combination of ultimate tensile strength (UTS), electrical conductivity (EC) (200 MPa and 54.8% IACS, respectively) and thermal stability (up to 450 °C) as compared with alloys based on the Al–Zr and Al–rare-earth metal (REM) systems. In addition, it is shown that the presence of calcium in the model alloy increases the electrical conductivity after cold forming operations (both drawing and rolling).

Keywords: aluminum–zirconium wire alloys; electromagnetic casting (EMC); drawing; electrical conductivity (EC); phase composition; nanoparticles

1. Introduction

For many years, electrical engineering applications have been recognized as one of the main uses of aluminum in terms of industry economics, which is constantly developing under the current widespread tendency for replacing copper conductors [1]. Most conductive Al alloys are related to 1xxx (Al–Fe–Si), 6xxx (Al–Mg–Si) and 8xxx (Al–Fe) families. For manufacturing electrical parts with appropriate parameters, continuous casting and rolling are currently used for shaping and deformation strengthening. However, the latter is highly reduced after heating to above ~ 250 °C due to recrystallization.

For the sake of both improving heat resistance and operating temperature, Al–Zr alloys have been developed for particular applications, like overhead cables for long-distance

power transmission [2–7]. Transition element Zr provides a far higher recrystallization temperature (up to 400 °C) due to the formation of the nanoscale metastable Al_3Zr phase with a L_{12} crystal lattice [8–13] while heating to above 350 °C and decay of solid solution (Al) [14–19]. However, if not controlling the foregoing parameters of melting and casting, the unfavorable Al_3Zr phase with a D_{023} structure may appear. According to the binary Al–Zr diagram [6], the liquidus temperature rises dramatically with Zr, hence, the temperature of the melt must be considered depending on the concentration. Additionally, for achieving metastable solubility, a relatively high cooling rate must be provided. The latter may be achieved by techniques like electromagnetic casting (EMC) that is superior to direct chill casting (DC). EMC allows producing long rod billets with far higher surface quality and an exceptionally fine microstructure due to support of the liquid pool by electromagnetic forces, continuous stirring, and increased cooling rates up to 10^4 K/s [20]. Based on the cooling rates, close to rapid solidification techniques [1,21], it may be argued that EMC is a very appropriate method for obtaining high-solute alloys, include those alloyed with transition elements. It was recently demonstrated [22] that Al alloy containing 0.6% Zr, 0.4% Fe and 0.4% Si (wt.%) may be successfully manufactured by EMC to long-length 12 mm circular cross-section rods with a microstructure containing Zr-rich solid solution. This structure provided excellent processability in cold drawing down to 3 mm, and the wire product showed a remarkable combination of strength (ultimate tensile strength (UTS) ~230 MPa) and electrical conductivity (55.6% IACS), both remaining stable after heating up to 400 °C.

In addition to Fe and Si used, subsequent development can be considered in alloying by rare-earth metal (REM) [21,23] and calcium [24,25]. They are both recognized to be very efficient for improving the heat resistance of Al alloys. However, while rare earth metals (REM) are more established for Al alloys, unconventional calcium may bring far higher cost efficiency combined with favoring the physical and mechanical properties. Particularly, it was shown that the Al wire alloy containing Al-4% Ca-1% Fe-0.6% Si-0.2% Zr-0.1% Sc manufactured from DC cast 150 mm billet has an improved combination of properties compared with Al–REM alloys [24]. This is due to its structure combining an Al matrix strengthened by $\text{Al}_3(\text{Zr},\text{Sc})\text{-L}_{12}$ phase particles and uniformly distributed submicron particles of Ca-bearing phases. Simulation of DC casting and flat rolling for the Al-0.5% Ca-0.5% Fe-0.25% Si-0.2% Zr-0.1% Sc alloy also showed the possibility for achieving such a combination of basic characteristics [25]. In respect to the foregoing compositions, scandium alloying may bring excessive costs of products. Using EMC technology, it is possible to introduce up to 0.6% Zr, that can be as efficient as the combination of Zr and Sc. Hence, we find it expedient to consider the Al–Ca–Zr–Fe–Si system as the base one. According to our earlier results [5,22,24–26], the target structure can be achieved in the alloy containing ~1% Ca, 0.5% Zr, 0.5% Fe, 0.25% Si (wt.%). Based on above, the goal of the present work is to study the structure, mechanical properties and electrical conductivity of the aluminum wire alloy of the foregoing composition manufactured by direct cold drawing from an as-cast 12 mm circular cross-section EMC rod and subjected to various heat treatment routes.

2. Experimental Methods

Experimental aluminum alloy in the form of a long-length rod 12 mm in diameter and ~20 m in length was manufactured using electromagnetic casting (EMC) technique (equipment of the Research and Production Centre of Magnetic Hydrodynamics (Krasnoyarsk, Russia) [27]). The alloy was prepared from commercial aluminum (99.5 wt.%). Calcium, zirconium, iron and silicon were introduced into the aluminum melt at 880–900 °C in the form of master alloys. The casting was carried out at a temperature of ~830 °C which was higher than the alloy liquidus (810 °C). The fragment of long rod billet (Figure 1a) was used for experimental study. According to spectral analysis made using Oxford Instruments, the actual chemical composition of the experimental alloy (hereinafter referred to as ACZ) was close to the target one (Table 1). For a more detailed analysis of the quaternary Al–Ca–Fe–Si

system, additional studies of the microstructure of the ACZ alloy obtained during slow solidification (melt cooling rate is ~ 0.01 K/min) were carried out. From this, we can expect the formation of the phase composition close to the equilibrium one.

Figure 1. As-cast wire rod (12 mm) and cold rolled strip (a), and (b) cold drawn wire of ACZ alloy.

Table 1. Chemical compositions of experimental alloys.

Designation	Concentration, wt.% (at.%)				
	Ca	Fe	Si	Zr	Al
ACZ	0.81 ± 0.02 (0.55)	0.48 ± 0.03 (0.23)	0.24 ± 0.02 (0.23)	0.46 ± 0.05 (0.14)	balance
0 Ca ¹	–	0.68 ± 0.04 (0.40)	0.23 ± 0.03 (0.22)	–	balance
0.1 Ca ¹	0.13 ± 0.02 (0.09)	0.67 ± 0.03 (0.33)	0.22 ± 0.03 (0.21)	–	balance
0.2 Ca ¹	0.19 ± 0.02 (0.10)	0.65 ± 0.04 (0.33)	0.21 ± 0.03 (0.20)	–	balance
0.75 Ca ¹	0.73 ± 0.03 (0.42)	0.41 ± 0.04 (0.20)	0.15 ± 0.03 (0.14)	–	balance
1 Ca ¹	1.03 ± 0.04 (0.69)	0.41 ± 0.05 (0.20)	0.16 ± 0.04 (0.16)	–	balance

¹ Zr-free alloys (0–1 wt.% Ca) were prepared in a resistance furnace (GRAFICARBO) in a form of flat ingots (10 mm × 40 mm × 180 mm in size) and considered in section “Discussion”.

The as-cast EMC rod was processed using drawing (the reduction ratio was 94%) to obtain the wire (3 mm diameter, see in Figure 1b). The obtained wire was subjected to annealing at 350–450 °C together with the 2 mm strip (Figure 1a) made additionally from the as-cast EMC rod by cold rolling (using a Chinetti LM160 laboratory-scale rolling mill machine). This strip was prepped for the analysis of the influence of deformation on the decomposition of (Al) during annealing. The stepwise annealing modes (Table 2) used for all experimental samples (EMC rod, wire and strip) were previously substantiated [22]. The Vickers hardness and electrical conductivity (EC) of the samples were measured at each annealing step. The measurement was carried out at room temperature.

Besides, the ternary and 4 quaternary alloys containing 0.5% Fe, 0.25% Si and up to 1% Ca were prepared to estimate the effect of calcium on the electrical conductivity. These alloys were poured at 750 °C into a flat graphite mold (of 10 mm × 40 mm × 180 mm in size). The cold rolled sheet products of 2 mm thickness were prepared from as-cast ingots.

The microstructure was studied using scanning electron microscopy (SEM, TESCAN VEGA 3, Tescan Orsay Holding, Brno, Czech Republic), electron microprobe analysis (EMPA, OXFORD Aztec, Oxford Instruments, Oxfordshire, UK), and transmission electron microscopy (TEM, JEM 2100, JEOL, Tokyo, Japan). Mechanical polishing was used together with electrolytic polishing, which was carried out at a voltage of 15 V at a temperature of −25 °C in an electrolyte containing 20% nitric acid and 80% methanol. The thin foils for

TEM were prepared by ion thinning with a PIPS (Precision Ion Polishing System, Gatan, Pleasanton, CA, USA) machine and studied at 160 kV.

Tensile tests for as-processed wire specimens were conducted by using a universal testing machine, model Zwick Z250 (Zwick Roell AG, Ulm, Germany). The Vickers hardness (HV) was measured using a MetkonDuroline MH-6 (METKON Instruments Inc., Bursa, Turkey) universal tester. A load of 1 kg and a holding time of 10 s were used to determine the Vickers hardness. The hardness was measured at least five times at each point.

The specific electrical conductivity (EC) of the EMC rod and the cold rolled strip was determined using the eddy current method with a VE-26NP eddy structures instrument (CJSC Research institute of introscopy SPEKTR, Moscow, Russia). The electrical resistivity of the cold drawn wire was measured for straightened samples of at least 1 m in length in the rectified part (in accordance with IEC 60468:1974 standard [28]).

Table 2. Annealing regimes for electromagnetic casting (EMC) rod, strip and wire.

Designation	Regime Treatment
R-EMC casting rod (diameter 12 mm)/S-cold rolled strip (thickness 2 mm)	
R/S	As-cast/as-cold rolled
R300/S300	Annealing at 300 °C, 3 h
R350/S350	R300/S300 + annealing at 350 °C, 3 h
R400/S400	R350/S350 + annealing at 400 °C, 3 h
R450/S450	R400/S400 + annealing at 450 °C, 3 h
R500/S500	R450/S450 + annealing at 500 °C, 3 h
R550/S550	R500/S500 + annealing at 550 °C, 3 h
R600/S600	R550/S550 + annealing at 600 °C, 3 h
W-Wire (diameter 3 mm) manufactured by cold drawing of as-cast EMC rod	
W	As-drawn
W350	W300 + annealing at 350 °C, 3 h
W400	W350 + annealing at 400 °C, 3 h
W450	W450 + annealing at 450 °C, 3 h

3. Results

3.1. Characterization of as-Cast Structure

The extremely high cooling rate during ACZ alloy solidification caused the formation of a favorable microstructure (Figure 2a) characterized by small size of dendritic cells, fine eutectic particles of Ca-containing phases and full dissolution of Zr in Al solid solution. The measured average size of the dendritic cells is $\sim 4 \mu\text{m}$ (Figure 2b) which, according to other studies [22,29,30], corresponds to a cooling rate of $\sim 10^4 \text{ K/s}$. Calcium-bearing eutectic particles corresponding to the quaternary eutectic $(\text{Al}) + \text{Al}_4\text{Ca} + \text{Al}_{10}\text{CaFe}_2 + \text{Al}_2\text{CaSi}_2$ [26] are detected in the form of thin veins located along the boundaries of the aluminum dendritic cells. It should be noted that the as-cast structure does not contain needle-shaped inclusions, for example, iron-containing ones.

Remelting of EMC rod followed by pouring into a graphite mold (cooling velocity about 20 K/s) leads to coarsening of structure and the formation of some needle-like particles (Figure 2c). On the other hand, the structure of the alloy after slow solidification (in a furnace) differs considerably from that of the initial EMC rod. Along with the expected general coarsening of the structure, the phase composition of the alloy changes. In particular, needle-shaped Al_3Fe phase inclusions and segregation of primary Al_3Zr phase crystals (Figure 2d) that are absent in the EMC rod structure can be identified (Figure 2a,b) after slow solidification.

Figure 2. As-cast microstructure of alloy ACZ after various cooling velocities, SEM: (a,b) $\sim 10^4$ (12 mm EMC rod, R in Table 2), (c) ~ 20 K/s (10 mm $\times$ 40 mm $\times$ 200 mm ingot), (d) ~ 0.1 K/s (cooling in furnace).

3.2. Effect of Cold Deformation and Annealing on Structure, Hardness and Electrical Conductivity

Due to the fine structure of the eutectic, the as-cast EMC rod possesses high ductility, even during cold forming. During both rolling and drawing, apart from the formation of a fibrous grain structure, fragmentation of Ca-containing eutectic particles can also be observed. Their size is not greater than 1 micron and they are uniformly distributed in the aluminum matrix (Figure 3a,b). Annealing at up to 450 °C inclusively does not lead to a significant change in the size of Ca-containing eutectic particles. However, the structure remains non-recrystallized. Coarsening of particles is observed at higher temperatures (Figure 3c,d).

As expected, cold deformation leads to a hardening of the ACZ alloy—the hardness increases up to 65HV for strip and up to 70 HV for wire (states R and W, respectively, see Table 3). A surprising result is a significant increase in the electrical conductivity—up to ~ 25 MS/m (both for strip and wire). In an earlier study for a Ca-free Al-0.6% Zr-0.4% Fe-0.4% Si alloy obtained by a similar process, this effect was not observed [22].

According to EMC rod hardness data obtained during annealing (Figure 4a), hardening reaches the highest level at 450 °C annealing stage temperature (the R450 state). Further increase in the annealing temperature leads to a significant decrease in HV, which is mainly due to the coarsening of the Al_3Zr precipitates [5–11,16]. Deformation hardening was retained upon strip annealing to 450 °C. At this temperature, the hardness of the EMC rod is the same as for the cold rolled strip (Figure 4a). Further increase in the annealing temperature leads to a significant softening due to the formation of a recrystallized structure. At the maximum annealing temperature used, 600 °C, they had approximately the same

hardness (32–33 HV) due to the coarsening and transformation of the Al_3Zr precipitates to the equilibrium D0_{23} phase [6,15].

Figure 3. Microstructure of wire alloy ACZ in (a,c) 3 mm wire and (b,d) 2 mm strip: (a), as-drawn, (b) as-rolled, (c,d) annealed at 600 °C, SEM, (a) W, (b) S, (c) W600, (d) S600, designations see Table 2.

Table 3. Mechanical and electrical properties of ACZ wire alloy.

State	Mechanical Properties				Electrical Properties		
	YS, MPa	UTS, MPa	El, %	HV, MPa	ER, nΩm	EC, MS/m	EC, %IACS
W	246 ± 12	282 ± 7	4.1 ± 0.4	70 ± 3	40.26	24.8	42.9
W350	—	—	—	—	36.10	27.7	47.8
W400	197 ± 2	218 ± 1	8.9 ± 2.5	64 ± 3	34.24	29.2	50.4
W450	181 ± 6	202 ± 1	11.9 ± 1.3	60 ± 2	31.54	31.7	54.7

Decomposition of the aluminum solid solution with the formation of L_{12} (Al_3Zr) nanoparticles during annealing promotes the increase in electrical conductivity (EC), as shown in Figure 4b. At the same time, the difference between the EC values for the EMC rod and for the 2 mm strip remains approximately the same at all annealing temperatures up to 500 °C inclusively (2.5–3.0 MS/m). At this temperature, the maximum EC for a 2 mm strip is reached, but it corresponds to the softening stage (Figure 4a). Considering the maximum hardness and high electrical conductivity in the cold rolled strip after annealing at 450 °C, we used the same heat treatment for the prepared wire.

Figure 4. (a) Hardness (HV) and (b) electrical conductivity (EC) curves for EMC rod (R) and cold rolled strip (S) subjected to stepwise annealing in accordance with the processing route shown in Table 2 (see R (temperature)/S (temperature) designation).

TEM microstructure of the ACZ alloy was examined for cold rolled strip in the S350 °C (Figure 5a,b) and S450 °C (Figure 5c,d) states to confirm the main structure changes described. According to obtained data for the both states, the fine individual particles of the eutectic Ca-containing intermetallics (dark in appearance) with a less than 1 µm size can be detected at sub-grain boundaries confirming their high pinning ability. However, detailed analysis revealed very few subtle particles in the S350 °C state (Figure 5b) which can be attributed to the initial stage of L_{12} - Al_3Zr phase formation. This assumption meets well with the electrical conductivity data presented in Figure 4b. In contrast, for the S450 °C state an exceptionally high number density and uniform distribution of the L_{12} - Al_3Zr phase nanoparticles are detected (Figure 5d,e). The result obtained suggests almost complete decomposition of the aluminum solid solution which converges well with data on the maximum electrical conductivity (Figure 4b) and hardness of the EMC rod (Figure 4a).

(a)

(b)

Figure 5. Cont.

Figure 5. TEM structure of wire alloy ACZ (strip) and after annealing according to (a,b) S350 °C and (c–e) S450 °C regimes, (a–d) bright field, (e) dark field and diffraction patterns.

3.3. Properties of Wire

Mechanical and electrical properties of the wire ACZ alloy in as-drawn and annealed states are given in Table 3. In the initial state, the alloy has a good combination of strength (UTS ~ 280 MPa and YS ~ 250 MPa) and ductility (El ~ 4%), however, the electrical conductivity is small (~43% IACS). Annealing of the 3 mm wire according to the modes given in Table 2 allows one to increase the EC value significantly. In this case, the EC values are approximately the same as for the cold rolled strip (Figure 4b). This suggests that the decomposition of (Al) proceeds in a similar way. As can be seen from Table 3, the experimental alloy in the W450 state has the best combination of strength (UTS ~ 200 MPa and YS ~ 180 MPa), elongation (El ~ 12%) and electrical conductivity (54.7% IACS).

Fractography of wire samples after a tensile test revealed a fine-dimpled ductile structure of the fracture surface (Figure 6). Calcium-bearing particles found inside the dimples (Figure 6a,b, BSE mode) are much smaller than the average diameter of the dimples. It should also be noted that no oxides or nonmetallic inclusions were observed which meets well with a previous study [22] confirming melt refining tendency when using EMC technology.

Figure 6. Fracture surfaces of experimental wire alloy (a) in initial (W) and (b) annealed (W450) states, SEM, **left**—backscattered electron image, **right**—secondary electron image, SEM.

4. Discussion

When comparing the basic characteristics of the new ACZ alloy and the previously studied Al-0.6% Zr-0.4% Fe-0.4% Si alloy [22] obtained under the same conditions, it can be seen that at close values of strength and electrical conductivity, the heat resistance of the Ca-containing alloy is significantly higher (450 vs. 400 °C) despite a smaller content of Zr (0.5 vs. 0.6 wt.%). Indeed, the hardness of the Ca-free alloy decreases down to 40 HV after annealing at 450 °C, which is significantly lower than that for the new alloy with calcium (Table 3). Obviously, the reason for the increase in the heat resistance is that the ACZ alloy contains calcium. Therefore, study of the effect of this element deserves special consideration. Considering that zirconium forms only the Al_3Zr phase (stable and metastable modifications), to understand the distribution of calcium, iron and silicon between phases, it is necessary to consider the Al–Ca–Fe–Si system. Earlier [26], the structure of this phase diagram in the range of Al–Ca alloys (concentration of Ca much higher than Fe and Si) was reviewed but other fields (with small Ca content) were not studied. Using the calculation in the Thermo-Calc software [31], as well as the results of previously published works [22,24–26,30,32] and additional experiments, we proposed structures of the Al–Ca–Fe–Si system in the aluminum corner including distribution of phases in the solid state (Figure 7a) and polythermal projection (Figure 7b). According to the proposed version, this system contains five four-phase regions: I—(Al) + Al_4Ca +

$\text{Al}_{10}\text{CaFe}_2 + \text{Al}_2\text{CaSi}_2$, II— $(\text{Al}) + \text{Al}_{10}\text{CaFe}_2 + \text{Al}_2\text{CaSi}_2 + \text{Al}_3\text{Fe}$, III— $(\text{Al}) + \text{Al}_2\text{CaSi}_2 + \text{Al}_3\text{Fe} + \text{Al}_8\text{Fe}_2\text{Si}$, IV— $(\text{Al}) + \text{Al}_2\text{CaSi}_2 + \text{Al}_8\text{Fe}_2\text{Si} + \text{Al}_5\text{FeSi}$, V— $(\text{Al}) + \text{Al}_2\text{CaSi}_2 + \text{Al}_5\text{FeSi} + (\text{Si})$. From the distribution shown in Figure 7a it follows that the Al_2CaSi_2 phase is present in all regions of this quaternary system. Considering the low solubility of Ca in (Al), this means that even at a small amount of calcium in Fe and Si containing alloys, the formation of this particular ternary compound is inevitable. Excess calcium should lead to the formation of the Al_4Ca and $\text{Al}_{10}\text{CaFe}_2$ phases. The influence of calcium on the equilibrium phase composition of the Al-0.5% Fe-0.25% Si alloy (i.e., with the same concentrations as in the ACZ alloy) is reflected in Table 4. The calculation results show that the phase composition of the base ternary alloy has a very high sensitivity to the calcium content. In this case, the ACZ alloy must certainly be in region I. However, for non-equilibrium solidification, the phase composition can differ greatly from the equilibrium one. This is largely due to the occurrence of incomplete peritectic reactions. As follows from the polythermal projection (Figure 7b), there are three invariant peritectic and three eutectic reactions in the aluminum corner of the Al–Ca–Fe–Si system. The compositions of the liquid phase and the temperatures of these reactions are given in Table 5.

Figure 7. Phase diagram of Al–Ca–Fe–Si system in aluminum corner: (a) distribution of phases in the solid state and (b) polythermal projection. Point 1 corresponds to the chemical composition of the ACZ alloy.

Table 4. Effect of Ca concentration on phase composition of alloy Al-0.5% Fe-0.25% Si (calculated at 200 °C).

Concentration of Ca, wt. %	Phase Field	Designation in Figure 7a
0–<0.01	(Al) + Al ₈ Fe ₂ Si + Al ₅ FeSi	–
<0.01–0.10	(Al) + Al ₂ CaSi ₂ + Al ₈ Fe ₂ Si + Al ₅ FeSi	IV
~0.10	(Al) + Al ₂ CaSi ₂ + Al ₈ Fe ₂ Si	IV/III
0.10–0.18	(Al) + Al ₂ CaSi ₂ + Al ₃ Fe + Al ₈ Fe ₂ Si	III
~0.18	(Al) + Al ₂ CaSi ₂ + Al ₃ Fe	III/II
0.18–0.38	(Al) + Al ₁₀ CaFe ₂ + Al ₂ CaSi ₂ + Al ₃ Fe	II
~0.38	(Al) + Al ₁₀ CaFe ₂ + Al ₂ CaSi ₂	II/I
>0.38	(Al) + Al ₄ Ca + Al ₁₀ CaFe ₂ + Al ₂ CaSi ₂	I

Table 5. Calculated parameters of invariant reactions in the Al–Ca–Fe–Si system.

Reaction	T, °C	Point in Figure 7b	Concentration in Liquid, wt. %			
			Ca	Fe	Si	Al
L → (Al) + Al ₄ Ca + Al ₁₀ CaFe ₂ + Al ₂ CaSi ₂	611	E ₁	6.92	0.68	0.50	–
L → (Al) + Al ₅ FeSi + (Si) + Al ₂ CaSi ₂	576	E ₂	<0.01	0.84	12.48	86.68
L → (Al) + Al ₃ Fe + Al ₂ CaSi ₂ ¹	632	E ₃	1.52	1.61	2.24	94.63
L + Al ₃ Fe → (Al) + Al ₁₀ CaFe ₂ + Al ₂ CaSi ₂	~620	P ₁	~6	~1	~1	~92
L + Al ₃ Fe → (Al) + Al ₈ Fe ₂ Si + Al ₂ CaSi ₂	629	P ₂	0.60	1.90	3.69	93.91
L + Al ₈ Fe ₂ Si → (Al) + Al ₅ FeSi + Al ₂ CaSi ₂	612	P ₃	0.07	1.60	7.10	91.23

¹ In quasi-ternary section.

As follows from the polythermal projection (Figure 7b), in a quaternary alloy containing 0.8% Ca, 0.5% Fe and 0.25% Si (point 1 in Figure 7b), after primary crystallization of (Al), eutectic reactions $L \rightarrow (Al) + Al_3Fe$ and $L \rightarrow (Al) + Al_3Fe + Al_2CaSi_2$ (line E₃–P₁), and then peritectic $L + Al_3Fe \rightarrow (Al) + Al_{10}CaFe_2 + Al_2CaSi_2$ (point P₁) one should proceed. The incompleteness of the latter explains the presence of needle-like particles in the microstructure of the slowly solidified ACZ alloy (Figure 2d). With an increase in the cooling rate, the phase boundaries shift towards higher iron content (dashed line in Figure 7b), therefore the Al₃Fe phase is not formed and it is absent in the as-cast microstructure of the EMC rod (Figure 2a,b). The solidification of this quaternary alloy (and hence the ACZ alloy) should end via eutectic reactions with the formation of three Ca-containing phases (point P₁). To further confirm the proposed structure of the Al–Ca–Fe–Si system, several quaternary alloys were annealed at 600 °C. As can be seen from Figure 8a, in the alloy containing 0.8% Ca, 0.5% Fe and 0.25% Si, only globular particles are detected, which, according to the distribution maps for Ca (Figure 8b), Fe (Figure 8c) and Si (Figure 8d) elements, can be identified as Al₄Ca, Al₁₀CaFe₂ and Al₂CaSi₂.

To confirm the effect of cold deformation on the electrical conductivity of the ACZ alloy mentioned above, additional studies on the effect of calcium on EC of both as-cast ingots and cold rolled sheets containing 0.5% Fe and 0.25% Si at varying calcium concentrations (Table 1) were carried out (Figure 9). As can be seen from Figure 9, the difference between the ingot and cold rolled sheet is small at small Ca content but at 0.75–1% Ca it reaches ~2 MS/m, i.e., similar to the ACZ alloy (Figure 4b). Taking into account the low solubility of Ca in (Al) and the invariability of the phase composition during deformation, this effect can probably be caused by the influence of the dislocation structure, vacancies and other defects of the crystal structure. This requires special study. A slight increase in EC should be noted with the addition of 0.1% Ca to the ternary alloy. This can be explained by a decrease in the concentration of Si in (Al) due to the formation of Al₂CaSi₂ compound.

Figure 8. Microstructure of alloy Al-1% Ca-0.5% Fe-0.25% Si (ingot 10 mm $\times$ 40 mm $\times$ 200 mm) after annealing at 600 $^{\circ}\text{C}$: (a) SEM, (b–d) electron microprobe analysis (EMPA) mapping (b—Ca, c—Si, d—Fe).

Figure 9. Electrical conductivity of Al–Ca–Fe–Si alloys containing 0.5% Fe and 0.25% Si vs. calcium content curves: R—EMC rod, S—cold rolled strip.

5. Summary

1. Experimental aluminum alloy containing 0.8% Ca, 0.5% Zr, 0.5% Fe and 0.25% Si (wt.%) in the form of a long-length rod 12 mm in diameter and ≈ 20 m in length was manufactured using an electromagnetic casting (EMC) technique. The extremely high cooling rate during alloy solidification ($\approx 10^4$ K/s) caused the formation of a favorable microstructure containing fine eutectic particles and full dissolution of Zr in Al solid solution. Due to the microstructure formed, the ingots possess high manufacturability for both cold drawing of a wire 3 mm in diameter and cold rolling of a strip in 2 mm in thickness.
2. EMC rod hardness reaches the highest value at 450 °C annealing temperature which is associated with the formation of the $L1_2$ type Al_3Zr phase precipitates with an average diameter of 10–20 nm and a high number density. Decomposition of aluminum solid solution during annealing also promotes the increase in the electrical conductivity (EC). Further increase in the annealing temperature leads to significant softening due to the coarsening of the Al_3Zr precipitation structure. Deformation hardening in the cold rolled strip can be maintained at up to 450 °C annealing, which is associated with the high pinning ability of zirconium and calcium containing phases: Al_4Ca , $Al_{10}CaFe_2$ and Al_2CaSi_2 . Further increase in the annealing temperature leads to softening due to the recrystallization. The best combination of hardness and EC in the cold rolled strip was reached after annealing at 450 °C.
3. The general structure of Al–Ca–Fe–Si system in the Al corner (including distribution of phases in the solid state and polythermal projection) was proposed.
4. The experimental wire alloy had the best combination of strength (UTS = 200 MPa, YS = 180 MPa), electrical conductivity (54.8% IACS) and thermal stability (up to 450 °C) as compared with alloys on the basis of Al–Zr and Al–REM systems.
5. It was shown that the presence of calcium in the model alloy increases the electrical conductivity after cold forming operations (both drawing and rolling).

Author Contributions: Conceptualization, N.B.; investigation, N.K. and M.M.; methodology, V.T. and T.A.; supervision, N.B.; writing—original draft, N.B.; investigation, A.F., writing—review and editing, M.M., T.A., and N.K. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the financial support of the Ministry of Science and Higher Education of the Russian Federation in the framework of Increase Competitiveness Program of MISiS (No. P02-2017-2-10) (TEM, tensile tests, discussion) and the Russian Science Foundation (project No. 20-79-00239) (SEM, hardness and electrical conductivity tests, calculations).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available from the corresponding author on reasonable request.

Acknowledgments: The results were obtained by using the equipment of RPC Magnetic hydrodynamics LLC, Krasnoyarsk, Russia; Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, Ufa, Russia; and Department of metal forming, National University of Science and Technology MISiS, Moscow, Russia.

Conflicts of Interest: The authors declare no conflict of interest.

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