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MICROALLOYING OF CONTINUOUS CAST ALUMINUM STRIP AND STRUCTURAL MODIFICATION USING PLASTIC TREATMENT TO A 9 μm FOIL (PATENT NO. 39762, P-377/76)

Innovative procedure of microalloying continuous cast aluminum strip, thickness 10 mm, by Be, Zr and Mn using 3C Pechiney technology (no. 39762, P-377/76), and modifying the existing parameters for strip casting and crystallization was implemented under industrial conditions with two randomly selected batches 2×8 tones, without previous selection of standardized quality of aluminum, purity Al 99.5%, obtained by electrolysis. The application of microalloying and overall structural modification of the technology resulted in obtaining nanoscale, ultra-thin, compact oxide high-gloss film with uniform surface of continuous cast strip, instead of the usual thick and porous oxide film. The outcome of microalloying the obtained equiaxed fine-grained nano/micro structure was avoiding anisotropic and dendritic microstructure of the strip, and improving deformation and plastic properties of modified continuous cast strip subjected to the technology of plastic treatment by rolling until the desired foil thickness of 9 μm was obtained. The invention of microalloying and structural modification, including multiplying effect of several components, directly or indirectly, changed numerous structurally-sensitive properties. The obtained nano/micro structure of crystal grains with equiaxed structure resulted in the synergy of undesirable <111> and inevitable <100> and <110> textures. Numerous properties were significantly enhanced: elastic modulus was improved, and intensive presence of cracks in warm forming condition was prevented due to rapid increase of the number of grains to 10000 grains/cm^2 in as-cast state.

Keywords: microalloying; modified continuous cast aluminum strip; nano oxide film; corrosion stability; plasticity and superplasticity; equiaxed structure; strain hardening; surface tension; crystallization zone; dendrites, crystal twinning

Highlights and discoveries:

- As microalloying element, beryllium (Be) modifies the system Al (Be)-Al_2O_3 (Be)-environment (water-air).
- Beryllium (Be) reduces the remaining oxides in liquid aluminum, which results in their fragmentation to nanoscale particles.
- Beryllium (Be) produces very thin nano film with Al_2O_3, which is practically transparent.
- Thin beryllium (Be) film, which affects film crystallization and grain fragmentation by hardening and dislocations, accounts for the formation of large number of grains per cm^2 in as-cast state and approximately several hundred thousand grains per cm^2 during plastic treatment of the strips.
- As hardener, beryllium (Be) affects the value of hardening rate (n_1).
- Being a microalloying element, zirconium (Zr) forms nanoscale oxide films which are resistant to corrosion in water and water vapor.
- Zirconium (Zr) forms the system Al (Zr)-Al_2O_3 (Zr)-environment and creates the mixture of oxides of high corrosion resistance to water vapor.
- After testing microalloyed aluminum strip 40-50 ppm, thickness 0.1 mm, in aqueous solution of sodium chloride for 24 h under laboratory conditions, the strip kept its mirror-like gloss, with barely visible porosity points.

1. Introduction to Scientific-Technological Development of Overall Modification and Microalloying of Continuous Cast Strip Using 3C Technology and its Thermomechanical Treatment up to a 9 μm Foil

Aside from microstructure, which was achieved by continuous casting of the strip with l0000 grains per cm^2, further thermomechanical rolling treatment resulted in formation of new microstructure, using plastic treatment process which implied several hundred thousand micrograins, primarily nanograins.

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Large number of grains per m^2 and double rolling speed enabled transition from extreme plasticity to superplasticity. Thin nano oxide film, fine-grained as-cast structure, significant increase of hardness and residual degree of δ strain in % provided anticipated plasticity by cold rolling, drastic increase of σ_m and $\sigma_{0,2}$ hardening and new fine-grained equiaxed structure, accomplished by grain fragmentation and dislocations. Such structure, which would be confirmed by measuring σ_m, $\sigma_{0,2}$ and δ under the angles of 0°, 45° and 90°, with minimum difference in strength, accounted for the presence of anisotropy instead of isotropy. High percentage of additional yield point (δ) remained after each pass of rolled strip, with very high values of σ_m, $\sigma_{0,2}$ and δ at each pass. Strength of rolled microalloyed aluminum coils and foils with technical purity of 99.5% was much larger than the strength of numerous aluminum alloys which were stronger than technical aluminum ($AlMn_1$, $AlMg_2$ and $AlMg_3$). In terms of aluminum foil, the results obtained in this scientific project were exceptional, as microalloyed foil was three times stronger than any other foil of the same thickness, i.e. 9 μm, produced worldwide. The results would have been much more satisfactory if the scientists had selected standardized composition of aluminum by electrolysis, in line with global technical conditions for cold rolled coil (CRC).

New, overall modification significantly changed surface properties of liquid aluminum in 3C crystallizer by altering surface tension, which resulted in changing the zone size in crystallizer and cooling speed. These important parameters enabled modification of newly created phases and particles by transforming them from macro to micro and from micro to nano particles which moved and floated in liquid microalloyed aluminum, thus creating 10000 grains per cm^2. During plastic procession process, grain fragmentation was continued, while distribution of dislocations by grain boundaries resulted in formation of fine-grained structure of predominantly nano dimensions, which provided the synergy of strengths and elongations after each strip pass through the roller. Innovation author proposed applying short impact annealing which redistributed dislocations by edges of nano and micro grains, without initiating recrystallization process which would be very harmful at this stage. Numerous constituents of microphases and non-metallic oxide inclusions, under strong reducing effect of beryllium and zirconium, significantly minimized their dimensions and resulted in formation of stable suspension. Such distribution density, arrangement and dimensions of numerous nano and micro particles had minimum effect on plastic deformation process.

In terms of all the stated modifications, the author of the paper considered that providing ultra-thin nano oxide film (highly reflective, shiny surface visible to the naked eye) in all stages of plastic procession was of crucial importance. When in as-cast state, this film was so thin that macrostructure of continuous cast strip surface could be seen through the film, which was the first proof of top-quality microalloying process. Additionally, oxidation stability and properties of nano oxide films, as well as significant reduction of surface tension of liquid aluminum and its impact on the size of cooling zone made a significant contribution to the successful implementation of the stated technology.

1.1. Presentation of the issues with regards to unmodified continuous cast strip using 3C Pechiney technology

The quality of cold rolled aluminum strip and foil largely depends on the quality of continuous cast strip, which offers numerous possibilities of quality control in the field of thermomechanical plastic procession compared to cold rolled and soft annealed strip obtained by other processing procedures. Initial structure of continuous cast strip is specific for its extensive anisotropy of mechanical and other properties. Due to nonequilibrium crystallization conditions, the above structure, which depends on twinning process and is specific for its grain direction and diverse microstructure, is accompanied by micro and macro segregation of impurities, as it tends to achieve equilibrium- homogeneous state. As a result, internal structure of the strip is under enormous stress, especially due to twinning and secondary separation of impurities at twinning planes. Therefore, the final result may be either continuation of grain fragmentation process-twinning or creation of microcracks in grain areas in which twinning process is stopped by accumulated impurities and intermetallic phase.

On the other hand, upper and lower surface of continuous cast strip are different due to the presence of two hardening fronts. The effects of microalloying elements and modifiers are different at each front. As the collision of the hardening fronts cannot be avoided, the size and character of grains at upper and lower surface also differ. Since the location of front collision hardens last, majority of inclusions and impurities are intensively separated. Therefore, this zone is extremely sensitive and suitable for formation of micro and macro defects. Asymmetrical position of the zone in cross-section of 10 mm thick strip makes plastic procession of aluminum strip and foil extremely difficult.

Bearing in mind the above stated facts, it is quite clear that adequate quality of continuous cast aluminum strip for producing 9 μm foil cannot be achieved without microalloying and overall modification. Furthermore, corrosion stability is another scientifically relevant interdisciplinary aspect which is to be taken into consideration. Aluminum is well known for its exceptional corrosion stability. However, modern processing procedures use water as crystallization agent and consequently reduce corrosion stability of aluminum and its alloys. Obtaining aluminum of 99.5% technical purity with high corrosion resistance under humid conditions, i.e. avoiding corrosion during the procedure of continuous cast of aluminum strip using 3C Pechiney technology is a technical issue of great importance. Using water as cooling agent in 3C crystallization process results in surface corrosion of aluminum and formation of thick, dark grey porous oxide layer. Owing to high crystallization temperature, water vapor is dissolved to hydrogen and creates porous oxide layer of amorphous structure, while the presence of oxygen results in the occurrence of hydrogen spots on the surface.

Academician Milovan Purenovic, PhD, has resolved the above issue by scientific invention of microalloying and overall modification processes [6]. Microalloying of continuous cast strip enables the formation of a very thin nano/micro oxide film which is almost one million times thinner than thick porous oxide at unmodified continuous cast strip. In terms of thin film physics, it is clear that ultra-thin oxide film does not impede the process of plastic procession, which is not the case with thick oxides due to abnormal frictional resistance and strain hardness. This aspect of innovative microalloying procedure for controlled aluminum oxidation shall be explained in detail after the analysis of the results achieved on batches under industrial conditions in which 9 μm foils were produced from 16 tons of aluminum, without any scarps.

1.2. Know-how technology of continuous aluminum strip casting by overall modification and microalloying

The technology provides top-quality foil by processing continuous cast strip using 3C machine. The primary objective is to create synergy of the innovation patent, technical know-how and technology under industrial conditions. The paper presents the following sequence of essential technological procedures for continuous strip casting using comprehensive modification and microalloying:

- Selective sampling of liquid aluminum from cells for electrolysis and batch formation, Al 99.5 to 99.7%.
- Casting of selected metal into the melting furnace and formation of stable batch.
- Refining liquid metal by mixture of various standard salts and removing the slag successively, up to the stage in which metal contains only the traces of slag.
- Protective coating of refined metal by adding special salts. Slag is not to be removed until degassing procedure has been completed.
- After degassing process is completed and slag is removed by means of hexachloroethane (C_2Cl_6), liquid metal sample is taken and hydrogen content is measured.
- Metal is transferred from melting furnace to electric furnace which is set to 800 ± 20°C.
- The melted metal is poured into electrical furnace while 1/3 of the metal from the previous batch is still inside the furnace.
- Modification of structure and numerous structurally-sensitive properties of microalloying occur in the canal during metal transition from melting to electrical furnace.
- Prealloy Al-Mn (5%), quantity 2 kg/ton is added, after which the same quantity of prealloy Al-Ti-B with 5% Ti and 1% B is added. Finally, prealloy Al-Be (5%), quantity 1.2-1.5 kg/ton is added to the mix. Sufficient amount of zirconium could not be provided under industrial conditions, so zirconium was not added, but 200 ppm of Zr from prealloy Al-Zr (10%) was made under laboratory conditions and successfully added in experimental patent procedure.
- Temperature and casting speed conditions are determined, electrical furnace temperature is maintained at 750 ± 20°C, while the temperature in 3C machine vessel is 680 ± 5°C. Metal level is 8-10 cm.
- Maximum pressure at the 3C machine cylinder inlet is provided. Temperature difference at cylinder inlet and outlet is Δt = 3°C. The planned casting speed is 0.7-0.8 m/min and the anticipated cooling speed is up to 20°C/sec.
- The patent requirement is to produce high-gloss strip capable of extreme elongations (δ) during plastic procession in aluminum strip and foil mills.

1.3. Thermomechanical regime of plastic treatment of continuous cast, comprehensively modified and microalloyed strip until obtaining a foil

The following changes of thermomechanical regime were made at specific rolling operations, using the available industrial equipment of rolling mill, all with the aim of final processing of the strip and obtaining foil:

- Continuous cast strip, thickness d = 10 mm, was coiled to a specific diameter and width.
- Strip was rolled from 10 to 5(6) mm using optimum rolling speed of 150 m/min.
- Pechiney technology implied normal homogenization of rolled strip 5(6) mm at temperature of 570-580°C, during 15-20 hours in controlled ambience.
- After homogenization, rolling was continued by reducing 50% from the initial strip thickness until reaching 5-2.5-0.9-0.5 mm.
- Author's innovation implied introducing new intermediary (impact, short-term) annealing of the strip d = 0.9 mm, at 350°C during 2 hours in controlled ambience.
- Rolling of annealed strip d = 0.9 mm was continued up to 0,5 mm, after which the rolling speed was increased from 150 to maximum 300 m/min.
- Normal annealing of the strip d = 0.5 mm was carried out again using Pechiney technology in controlled ambience, during 12-25 hours, depending on the batch quantity- weight of the item in annealing furnace.
- After completing annealing process, samples were taken and subjected to thorough quality control in terms of producing foil.

1.4. Thermomechanical-plastic treatment of the strip suitable for producing foils

Examples described in subchapters 1.1, 1.2 and 1.3 referred to two cast batches of unspecified producer, labeled as 10901 and 10902. Aside from microalloying, the metal was processed and prepared in a usual manner. The entire quantity of continuous cast 3C strip, i.e. 16 tons, was subjected to continuous procedure of plastic rolling treatment. Chemical composition and presence of all microalloying elements (except for Zr, which was not doped) were analyzed. Significant change of quality was noted. After each pass of the strip through rolling stand, the strip surface became glossier, with brilliant, mirror-like shine. Additionally, specific shiny and glistening surface on 0, 5 mm strip was visible after annealing, which was an obvious proof of exceptional oxidation capacity. Surface oil was easily removed from smooth and reflexive surface without any stains, during the first pass of the foil, from 0.5-0.28-0.20 and after doubling and rolling of foil 0.090-0.04-0.020-0.009 mm, i.e. 9 μm. The initial thickness of continuous cast strip batch was 10.4 mm, and rolling of strip into a foil was conducted in line with the following schedule: 10,4-5,2-2,87-1,70-1,20-0,69-0,28-0,14-0,09-0,04-0,0020-0,009 mm. Rolling speed was much larger (300m/min) than the speed applied in everyday processing operations (150 m/min).

1.5. Verification of comprehensive technology quality

Based on the analysis described in subchapters 1.1, 1.2, 1.3 and 1.4, two cast batches, i.e. 10901 and 10902 were subjected to microalloying, overall modification, acceptable daily procession and preparation of liquid metal. The entire quantity of continuous cast 3C strip, i.e. 16 tons, was subjected to continuous plastic rolling procedure. Chemical composition and presence of microalloying elements (except for Zr, which was not doped) were subjected to analysis. Substantial change of quality was noted after each pass of the strip through rolling stand. Namely, the strip surface became glossier, with brilliant, mirror-like shine. Specific, brilliant and glistening surface was especially notable on 0.5 mm strip, which undoubtedly proved exceptional oxidation capacity and minimum negative impact of nano oxide layer on plastic procession process. Oil from such smooth and reflexive surface could be removed easily and without leaving any stains. During the first pass of the foil, initial thicknesses 0.5, 0.28 and 0.20 mm, and after doubling and rolling of 0.09 mm foil, the state of the edges and number of rolling ruptures were checked. Due to extremely high strength and uniformity of the foil, the entire process was completed without any problems. Strain hardening of the foil and additional elongation pointed to the fact that foils 4-5 μm could have been obtained from 9 μm foil, which was the only drawback of industrial test of the new procedure of microalloying and modification (subjective failure in plant organization). The paper presented the results of industrial testing of the quality of innovative know-how technology. The author's proposal to increase the rolling speed from 150 to 300 m/min increased the quality and production capacity of rolling stands. The change of rolling speed resulted in the invention of high plasticity and superplasticity, which were analyzed from scientific point of view. Having in mind the complexity of production process, results of specific tests and practical observations during the procedure of casting and rolling of microalloyed strip, the following was noted:

- Extreme plasticity of the strip, accompanied by superplasticity, which was very rare for aluminum and its alloys.
- The strip could endure maximum front and back tension without undulation, until achieving the finest forms of foil.
- The strip could be rolled using maximum rolling speed, which initiated superplasticity.
- Wettability of the strip and rolling oil was so exceptional that the oil tended to slide from the strip surface, which was very useful during the production procedure.
- Foil duplication (2 × 20 μm) resulted in making exceptional contact, without sliding or undulation (almost no scrap).
- As expected after the initial testing, the strip did not darken or oxidize during the annealing process.
- The strip was very suitable for the so called "impact annealing" – intermediary annealing which relaxed the strip in a matter of minutes at temperature of 450-500°C.
- Monitoring the production process proved that the time of regular annealing, defined by Pechiney technology, could be reduced by 5-6 hours on condition that the annealing furnace had already been heated to working temperature.
- No in-process annealing was necessary during the procedure of cold rolling or rolling of the finest foils.
- Cutting the strip and foils to the desired dimensions was facilitated due to their extreme hardness.
- Continuous casting by 3C technology prevented failures and crystallizer clogging, as microalloying balanced crystallization and hardening of upper and lower zone, due to favorable contact angle and increase of surface tension of liquid microalloyed aluminum.
- Microalloying significantly reduced the possibility of forming deposits in the runner and electrical furnace because of the modification of oxide and other inclusions.
- Removing slag from the runner and vessel was not necessary or was reduced to a minimum.
- The initial results of mechanical testing proved that the finest foil was very strong and ductile.

1.6. Description of innovation solution for technical issue of microalloying, including examples of implementation, and scientific overview of the discoveries

Innovation title: **Procedure of producing technical aluminum with high corrosion resistance under humid conditions,** author Academician Milovan Purenovic, PhD. The technical issue is solved in the following manner: prior to casting the melted aluminum, prealloy Al-Be with 10% Be is added, after which either prealloy Al-Zr with 10% Zr or prealloy Al-Be-Zr-Mn with 10% Be and Zr: Mn ratio from 1:1 to 1:5 is added. Prealloy is melted and homogenized with technical aluminum batch at 750°C. The technical challenge is to obtain technical aluminum with high corrosion resistance under humid industrial conditions, especially in terms of continuous casting of aluminum strip, thickness 10 mm using Pechiney technology, having in mind that water is used for cooling and strip crystallization. In this case, water triggers surface oxidation and corrosion of aluminum which is to be used for obtaining aluminum foil. During the stage of continuous strip casting, water is essential for crystallizer operation. Water vapor, which is formed at 400-500°C, ruptures compact part of oxide film, forms thick porous oxide layer of amorphous structure, while water molecules decompose to O_2 and H_2. Before molecularization, hydrogen protons diffuse through oxide film to the metal, balancing the charge of aluminum cation which moves toward oxide layer-gas phase boundary. Protons are reduced to hydrogen atoms which interact with metal defects and synthetize hydrogen molecules. Because of extremely high gas pressure inside the defects and pores (up to 10^{14} bar in capillaries), metal is expanded, hydrogen spots are created on the surface of oxide layer and the appearance of gray porous oxide layer is significantly changed. Aluminum components with low overvoltage of hydrogen evolution, such as Fr, Ni, Ti, Ga, etc. have a significant positive effect on hydrogen evolution. As stated, aluminum which is subjected to significant changes during the casting stage creates products of reactions and ingredients which impede the process of plastic procession of strip and foil. Degree of corrosion on the surface of the oxide film is defined by optical means. The surface of corroded film is matted, while stabile oxide layer has mirror-like glossy surface.

Despite technical-technological issues and the present problem of interaction of aluminum with water, the author of the patent has introduced a special procedure of aluminum protection by microalloying the system Al-Al_2O_3-environment (H_2O or O_2). Using the system with two defined phase boundaries results in forming Al (M)-Al_2O_3 (M)-environment, where M refers to components which take part microalloying process [6]. Microalloying principle implies microalloying of solid metal first, then the newly created oxide film and phase boundary Al (M)-Al_2O_3 (M) and Al_2O_3 (M)-environment. Aluminum, phase boundary with oxide film and oxide film are modified in this complex micro-heterogeneous system. Once the structure of basic barrier oxide layer and overall oxide layer has been disrupted, corrosion and anode activity of defined system are increased. On the other hand, if microalloying synthetizes a stable system Al(M)-Al_2O_3(M)-environment containing very compact ultra-thin composite oxide film with microalloying improvers and thin oxide films, which are modifiers in the structure of Al_2O_3, this results in the formation of very **compact ultra-thin oxide layer of nano/micro dimensions**. Under the stated conditions, modification of continuous cast aluminum implies reducing oxide layer growth. Additionally, integration with microalloying improvers in solid phase results in numerous changes of structurally-sensitive properties. Microalloying initiates the change of grain size, grain fragmentation under the influence of deformation and dislocation during processing procedure, as well as the appearance of equiaxed texture which corresponds to plastic procession with high plasticity, including superplasticity of high strength and extreme elongation (σ_m, $\sigma_{0,2}$ and δ).

Primary microalloying elements for reducing oxidation are Be and Zr, while Mn inhibits the negative effects of Fe and Si, and Fe/Si ratio by making a complex intermetallic compound Al_6Mn (Fe, Si) with aluminum. The effect of adding Mn is of crucial importance, as it **bonds Fe and Si which are in continuous sequence of solid solution**. Adding Zr is significant for preventing the effects of water vapor as it is incorporated in mixed oxide film as ZrO_2. Its effects are even more crucial in the presence of boron (B) and titanium (Ti), which are added to technical aluminum as standard elements relevant for structure modification. Microalloying improvers presented in the patent are expressed in the following ppm values: 200 ppm Mn, 100 ppm Zr and 40 ppm Be. Beryllium has proved to have the best properties in terms of reducing oxidation process and increasing strength. Minimum concentration of beryllium (Be) which produces the effect of dominant oxidation is 30 ppm, i.e. **concentration of 10^{16}-10^{18} atoms/cm^3 of aluminum**. Aside from oxidation effect, Be is an exceptional hardener. In other words, this element has a multiplying effect on the system Al-Al_2O_3-environment. To summarize, **microalloying in line with invention proposal results in superposing of two reactions-peritectic and eutectic, thus obtaining equiaxed isotropic structure,** which affects the structure and thermomechanical regime of plastic procession of strip into foil in later stages.

2. Experimental Part

2.1. Material-aluminum of technical purity produced by electrolysis

The total of 16 tons of continuous cast-microalloyed strip was used for the research and tests (two batches: 10901 and 10902). The strip was of standard thickness ≠10 mm. Chemical composition corresponded to Al 99.5, as follows:

Batch	Fe	Si	Ti	B	Cu	Zn	V	Mn	Cr	Be
10901	0.25	0.08	0.016	0.01	0.0055	0.07	0.01	0.04	0.0045	0.01
10902	0.29	0.08	0.015	0.01	0.0025	0.08	0.0085	0.02	0.0045	0.01

Microalloying was carried out in the channel between melting furnace and electric furnace, on continuous casting machine, using Pechiney 3C technology, before casting at temperature of 800°C. Firstly, a specific quantity of prealloy Al-Mn (80% Mn) was added, then Al Ti 5 B 1, and finally prealloy Al-Be containing 5% Be was added to the mix. The casting procedure was initiated after the settlement of liquid metal. Thermomechanical process of continuous cast strip processing was described in detail in previous chapters.

2.2. Experimental measurement program

2.2.1. Tensile test

Mechanical tests were conducted based on appropriate test specimens made of cast and rolled strip. The samples were taken under the angles of 0°, 45° and 90° compared to casting and rolling direction. Three samples were tested for each pass, strip quality, and casing and rolling direction, respectively. Firstly, mechanical properties (σ_m, $\sigma_{0,2}$, σ_{HB}) were tested for solid state, and secondly, mechanical features were tested after soft annealing or specific regime of thermal procession.

Universal testing machine INSTRON 1195 was used for determining tensile strength, yield point and elongation. Specimen length was in compliance with the valid standards. Limit value $\sigma_{0,2}$ was defined by means of Instron electric extensometer which was planned for maximum elongation range of up to 50%. Since the tests were performed at minimum three test specimens, the obtained value represented the mean value of each measurement.

In order to obtain specific results of the effects of hardening as consequence of microalloying and plastic procession, logarithmic dependence $\ln\sigma_m$-$\ln\varepsilon$ was recorded. Hollomon strain hardening equation was calculated as:

$$\sigma = K_1 \cdot \varepsilon \cdot n_1 \qquad (1)$$

where strain hardening index (n_1) could be obtained by function logarithm, i.e. slope of the function $\ln\sigma_m$-$\ln\varepsilon$:

$$n_1 = \frac{d\left(\ln \sigma_m\right)}{d\left(\ln \varepsilon\right)} \qquad (2)$$

Thus, each change in the slope of the function $\ln\sigma_m$-$\ln\varepsilon$ should indicate the change in hardening mechanism expressed by index (n_1). On the other hand, dependency $\ln\sigma_m$-$\ln\varepsilon$ should, in terms of quality, indicate the degree of anisotropy of mechanical property, i.e. isotropy degree, if isotropy was present.

2.2.2. Testing deep drawing capacity

Erichsen deep drawing test was used to reconfirm a specific degree of anisotropy or isotropy, and deep drawing capacity. As strip rolling was conducted in line with industrial passing plan, the obtained strip thicknesses were not entirely in compliance with ISO standards for testing deep drawing capacity. ISO standard was applied for soft annealed aluminum strip, thickness from 0.1 to 2 mm.

In this experiment, deep drawing was directly tested for cold rolled non-annealed sample, while the strip thickness was not in compliance with ISO standards. On the other hand, earing was tested for dimensions of annealed and non-annealed strips that were in compliance with ISO standards.

3. Result Overview

3.1. Results of testing mechanical properties at tensile testing machine

Figs 1, 2, 3, 4, 5 and 6 present the diagrams of dependency between tensile strength and elongation in logarithmic distribution $\ln\sigma_m$-$\ln\varepsilon$, for strips thicknesses 10, 5, 2.5 and 0.5 mm. All diagrams show straight lines with two different slopes and minor anisotropy of mechanical properties.

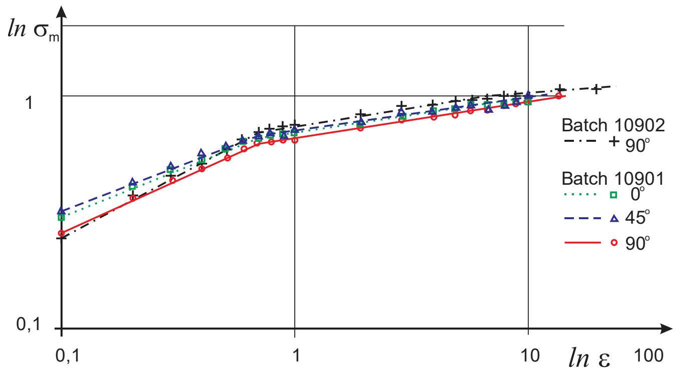


Fig. 1. Diagram of dependency between tensile strength and elongation in logarithmic distribution for 10 mm thick strips. Samples were taken under the angles of 0°, 45° and 90° compared to rolling direction

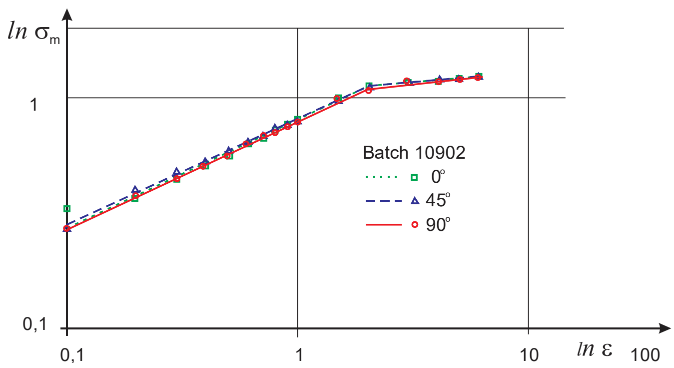


Fig. 2. Diagram of dependency between tensile strength and elongation in logarithmic distribution for 5 mm thick strips. Samples were taken under the angles of 0°, 45° and 90° compared to rolling direction

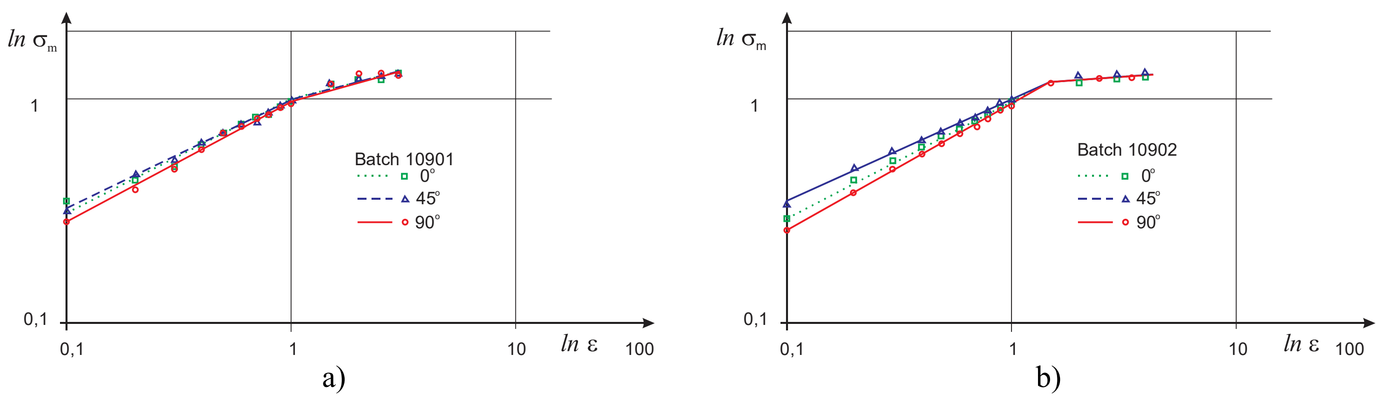
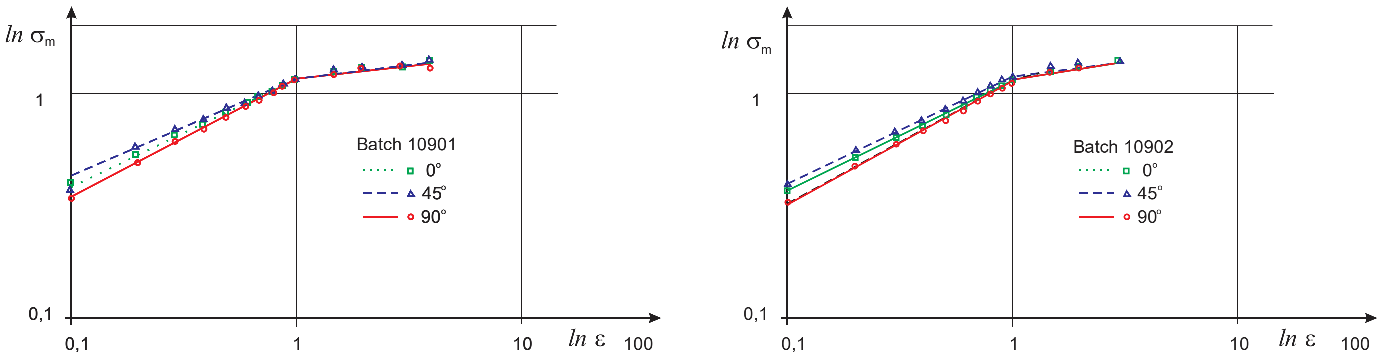
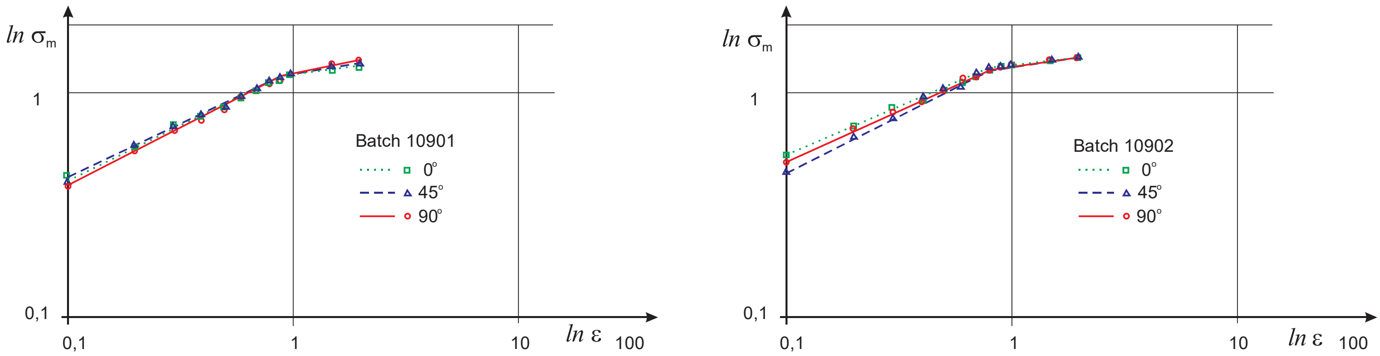


Fig. 3. Diagram of dependency between tensile strength and elongation in logarithmic distribution for 2.5 mm thick strips. Samples were taken under the angles of 0°, 45° and 90° compared to rolling direction. a – data for batch 10901, b – data for batch 10902



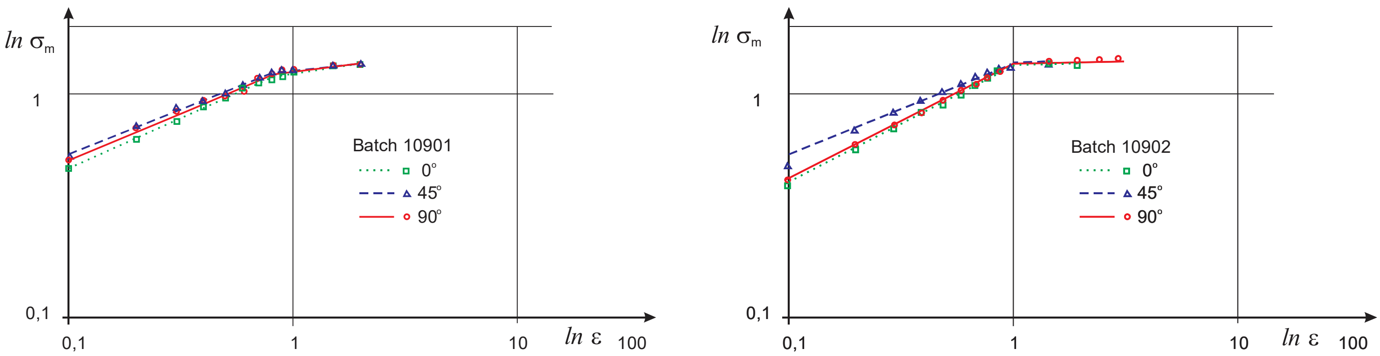
a) b)

Fig. 4. Diagram of dependency between tensile strength and elongation in logarithmic distribution for 1.4 mm thick strips. Samples were taken under the angles of 0°, 45° and 90° compared to rolling direction. a – data for batch 10901, b – data for batch 10902



a) b)

Fig. 5. Diagram of dependency between tensile strength and elongation in logarithmic distribution for 0.9 mm thick strips. Samples were taken under the angles of 0°, 45° and 90° compared to rolling direction. a – data for batch 10901, b – data for batch 10902



a) b)

Fig. 6. Diagram of dependency between tensile strength and elongation in logarithmic distribution for 0.5 mm thick strips. Samples were taken under the angles of 0°, 45° and 90° compared to rolling direction. a – data for batch 10901, b – data for batch 10902

TABLE 1 and Fig. 7 show the results of tensile strength tests, 0,2% yield point, elongation and hardness for strips of different thicknesses, after each pass, under the angles of 0°, 45° and 90°, compared to casting and rolling direction. The results refer to cold rolled state, starting from continuous cast strip to foil.

3.2. Effects of thermal treatment on mechanical properties

Mechanical properties of thin strips and foils, thickness 160 and 90 μm were tested at annealing temperature of 450°C. Test results are shown in TABLE 2 below.

TABLE 1

Mechanical properties of thin strip and foil

Thickness [mm]	Tensile strength, σ_m [N/mm^2]			Yield point $\sigma_{0.2}$ [N/mm^2]			Elongation δ [%]			HB hardness		
Angle	0°	45°	90°	0°	45°	90°	0°	45°	90°	0°	45°	90°
10.41	84.1	80.7	80.5	41.2	41.2	40.4	40.8	43.9	30.3	25.9	25.9	25.9
5.45	127	135	—	120	129	—	6.3	6.2	—	42.4	42.4	—
2.85	152	153	164	143	144	157	4.1	3.3	5.0	52.5	52.5	52.5
1.72	162	169	179	155	162	170	3.5	3.9	3.4	53	53	53
1.22	169	171	183	163	165	176	5.0	3.1	4.2	52.5	52.5	52.5
0.69	179	176	191	177	167	180	5.5	3.8	3.5	50.9	50.9	50.9
Annealed												
0.69	84.6	—	—	—	—	—	45.0	—	—	—	—	—
0.28	130	—	142	—	—	—	3.5	—	2.6	—	—	—
0.14	149	—	177	—	—	—	3.3	—	2.5	—	—	—
0.09	172	—	—	—	—	—	2.5	—	2.5	—	—	—
0.04	169	—	177	—	—	—	2.0	—	2.4	—	—	—
0.02	177	173	187	—	—	—	1.5	1.3	1.9	—	—	—

TABLE 2

Effect of annealing time on foil mechanical properties

Annealing time [h]		3		2		1	
Thickness [mm]	Rolling angle-direction	Tensile strength σ_m [N/mm^2]	Elongation δ [%]	Tensile strength σ_m [N/mm^2]	Elongation δ [%]	Tensile strength σ_m [N/mm^2]	Elongation δ [%]
0.16	0°	73	10	—	—	75	12.1
	45°	70	10.5	—	—	99.3	30.2
	90°	90	11.5	—	—	—	—
0.09	0°	158	13.7	163	25.5	163	23.5
	45°	140	16.8	146	30	143	20.7
	90°	13.3	16.8	148	16.3	133	20.5

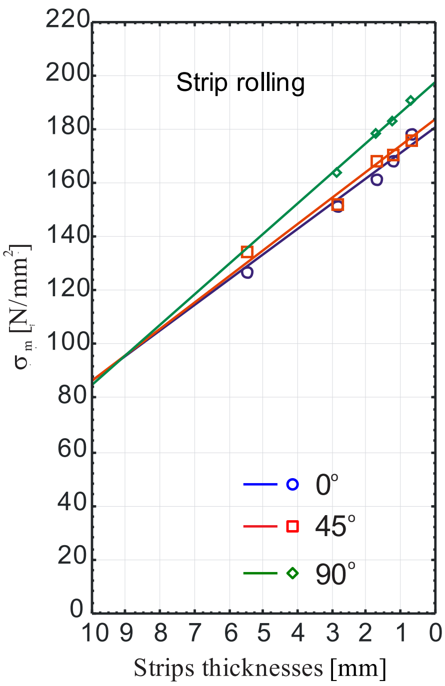


Fig. 7. Tensile strength depending on strip thickness, angles 0°, 45° and 90° compared to strip casting and rolling direction

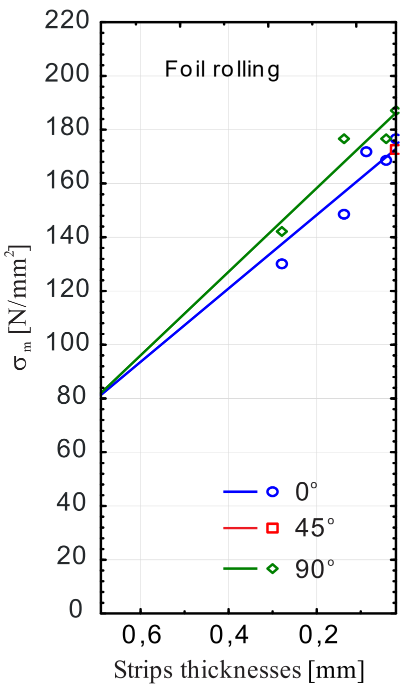


Fig. 8. Tensile strength depending on strip thickness, angles 0°, 45° and 90° compared to foil casting and rolling direction

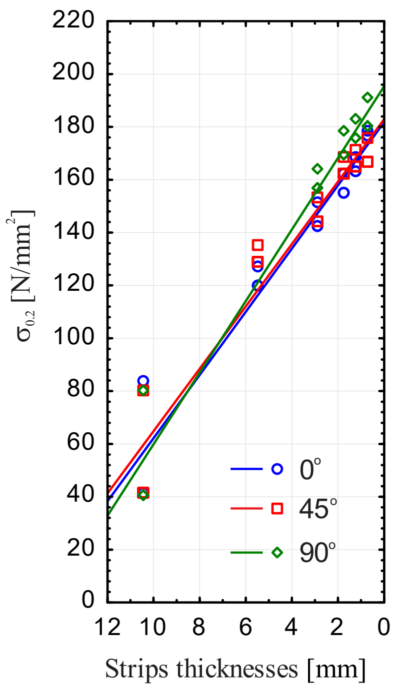


Fig. 9. 0.2% yield point for strips of various thicknesses, angles 0°, 45° and 90° compared to casting and rolling direction

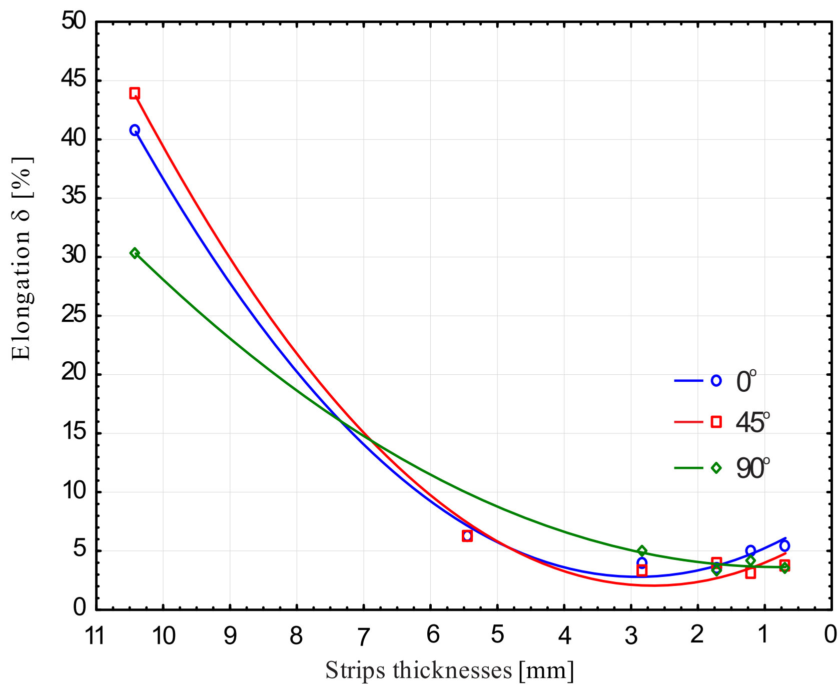


Fig. 10. Elongations for strips of various thicknesses, angles 0°, 45° and 90° compared to casting and rolling direction

3.3. Results of deep drawing test and earing test

3.3.1. Deep drawing

As indicated above, deep drawing was measured at non-annealed samples of unstandardized thicknesses and thermal conditions. Test results are shown in TABLE 3:

TABLE 3

Cup height at Erichsen cupping method

HVT thickness [mm]	5.45	2.93	1.70	1.20	0.69
Deep drawing [mm]	13.0	12.8	8.5	8.0	8.5

3.3.2. Earing test

Earing test was conducted on strips, thicknesses 5, 2.5, 1.4, 0.9 and 0.5 mm, for annealed and non-annealed samples (TABLES 4 and 5).

TABLE 4

Earing of non-annealed samples

Thickness	[mm]	1.4	2.5	5
Ear height	[mm]	2.33	3.57	3.67
Base height	[mm]	27.7	26.8	27.4
Earing	[%]	8.28	12.43	12.88

TABLE 5

Earing of samples annealed at 450°C, T = 3 h

Thickness	[mm]	0.5	0.9	1.4	2.5
Ear height	[mm]	1.82	1.89	2.57	3.71
Base height	[mm]	35.6	40	33.6	34.6
Earing	[%]	5.09	4.73	7.55	10.5

3.3.4. Macrostructure and microstructure

Fig. 11 shows macrostructure of upper surface of continuous cast strip, which is characteristic for its fine-grained structure with equiaxed grains distributed on the entire surface, strip cross-section and lower surface. Such structure remains equiaxed even after 100% reduction without annealing, which is shown on Fig. 12. Microstructure with enormous number of grains is shown in Fig. 13. According to ASTM, the structure can be categorized between class 3 and 4, with approximate grain size of 90 µm.

Fig. 11. Macrostructure of upper surface of continuous cast strip (×10)

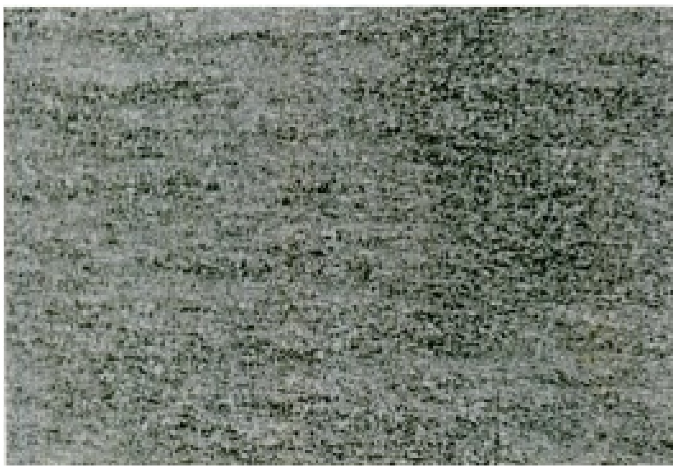


Fig. 12. Macrostructure of cold rolled non-annealed strip 2.5 mm (×10)

Fig. 13. Microstructure of continuous cast strip surface (×100)

4. Result discussion

4.l. Diagnostic criteria

After summarizing the obtained results, the following diagnostic criteria can be defined:

- Extremely high value of strain hardening exponent (n_1 = 0.45);
- Two different values of strain hardening exponents (n_1 = 0.45 and n_1 = 0.15);
- Linear dependency of $\ln\sigma_m$ - $\ln\varepsilon$;
- Almost complete isotropy of mechanical properties of continuous cast strip;
- Isotropy of mechanical properties of cold rolled strip;
- Linear dependency between tensile strength and degree of reduction at the area of strip cold rolling, as well as at the area of cold rolling of the strip until obtaining a foil;
- Very high tensile strength of continuous cast strip (84 N/mm^2);
- High elongation of continuous cast strip under the angles of 0°, 45° and 90° compared to casting direction (40.8%, 44% and 30%);
- Identical hardness of continuous cast, cold rolled and soft rolled annealed strip d = 0.5 mm (8.5 N/mm^2);
- Very high elongation of cold rolled and soft annealed strip (δ = 48%), measured by extensometer – up to 50%;
- High strength of continuous cast strip (26 *HB*);
- Extreme hardness of cold rolled strip (*HB* = 53.5);
- Extreme tensile strength of cold rolled strip (d = 0 .69 mm, σ_m = 191 N/mm^2);
- Extensive elongation of cold rolled and non-annealed state (δ = 3.5 ÷ 6.0%);
- High tensile strength of 20 μm foil (σ_m = 187 N/mm^2 and δ = 2.0%);
- Short annealing time for achieving compromised mechanical properties (in 1 hour of annealing at 450°C, foil thickness 160 μm reaches σ_m = 99 N/mm^2 and extraordinary elongation of 30%);
- Excellent deep drawing capacity in cold rolled state which is not classified as standardized by ISO;
- Low earing for cold rolled state;
- Low earing for soft annealed and cold rolled state;
- Notable fine-grained macrostructure;
- Fine-grained microstructure, grain size 90 μm in as-cast state;
- Exceptional grain refining and distribution of inclusions;
- Remarkable-brilliant, highly-reflexive surface.

4.2. Discussion of strain hardening mechanism

Even though the results of the above research are not sufficient for a complex discussion of the mechanism of strain hardening and drawing conclusion, the stated research results point out the specific manifestations during plastic procession of strip into a foil. Having in mind the fine-grained and uniform structure of continuous cast strip and other relevant diagnostic criteria, one may assume that the requirements for achieving high plasticity, which is very close to superplasticity, have been met. Not all the necessary requirements for achieving metal superplasticity have been met or analyzed, but a crucial, widely accepted, superplasticity requirement-achieving extremely fine-grained structure has been met. Fine-grained structure with clearly defined boundaries of subgrains and grains is reflected through surface energy located on the boundaries of the grains. As surface energy interacts with stacking fault energy and dislocation energy, it is clear that almost all grain energy is located at its periphery. Consequently, if the grain is very small, all requirements for achieving deformation mechanism through inter-grain sliding, without any further grain twinning or refinement, are met. In this specific case, grain boundary sliding is probably not an exclusive mechanism of aluminum plastic flow, but certainly has an important role in plastic flow process. Aside from the grain size, this is confirmed by extremely high value of strain hardening index (n_1 = 0.45), which is very close to limit value of n_1 = 0.5. This paper has not analyzed strain hardening index in detail, as strain hardening velocity factor is not tested. However, velocity factor is definitely included in strain hardening exponent, with hardening coefficient (m):

$$\sigma = const \cdot \varepsilon^{n_1} \cdot \varepsilon^{m} \quad (3)$$

At regular deformation, coefficient (m) is less than 0.2, while in superplastic flow state the coefficient is $m = 0.3$. Consequently, speed sensitivity of yield strength is one of the crucial requirements of superplasticity. Exponent value (m) emphasizes the tendency of material to form ears, as deformation speed at ear area is much larger than in other parts. Thus, yield strength results in hardening of the material. Providing that it includes coefficient (m), high value of coefficient (n_1) points to the possibility of viscous plastic flow, i.e. confirms its share in the procedure of plastic flow. If dislocation density in polycrystals is $10^8 \div 10^{12}$ cm^{-3}, then the maximum hardening effect ($n_1 = 0.45$) can be explained by dislocation blocking on the developed grain surface and mosaic blocks. As relatively pure aluminum is subjected to microalloying, mechanism of impurity precipitation (adsorption) can be present on grain boundaries, while deposit-free zone may appear along the grain boundary. This results in another type of defect, i.e. Schottky point defect. If this assumption is correct, then sliding and superplasticity could be explained by sharp transitions between the grain interior and grain boundaries which are separated by thin layer of high-plasticity amorphous structure. Therefore, sliding amongst grains is easier than twinning of the grains which are stiffened by grain boundary of extremely high surface energy, resulting in viscous flow and influence of strain rate. This explains the synergy of mechanical properties, i.e. the fact that high tensile strength is accompanied by significant elongation, which is in collision with their usual behavior. Very high tensile strength accompanied by extreme elongation in continuous cast strip, cold rolled strip and foil prove the above stated point. Moreover, during the rolling procedure, strain is localized in the area where the rollers of the rolling mill capture the metal. The condition of aluminum strip surface is crucial and it is achieved by microalloying of aluminum by means of the above stated combination, especially by adding beryllium and providing maximum elastic modulus and compactness of oxide layer. Research results are shown in Fig. 14.

The following laboratory test was conducted to determine the compactness of the surface of nano oxide film obtained by Be microalloying: samples of modified and unmodified strips, approximate thickness 0.1 mm were immersed in separate flasks containing water solution 1 mole NaCl, for 24 h. The samples were then washed off and dried, and surface porosity was examined on a microscope with maximum magnification of 100×. Unmodified strips showed substantial changes in stability and shine, with dominant grey surface. On the other hand, modified microalloyed strips showed excellent compactness, stability and shine. Therefore, compactness was directly reflected through low porosity, which was achieved by adding 25 ppm Be. The importance of compactness in foil rolling process shall be discussed in more details in the chapter below. Two values of hardening coefficient pointed to the two stages of strengthening-hardening. The occurrence of the second hardening stage was most probably the result of formation of mosaic blocks of predominantly hexagonal section with minimum dislocation density. Consequently, transversal sliding and further fragmentation of crystals were completely disabled. Under such conditions, ultimate grain size for the given thermomechanical parameters of plastic procession was achieved. Even though plasticity was quite satisfactory, further strengthening was negligible. This was one of the reasons for making synergy of mechanical properties during the process of rolling microalloyed strip into a foil. Therefore, regardless of high strength and extreme thickness of the foil, the possibility of achieving certain-final elongation was still open. The result of the process was obtaining 9 μm foils, i.e. the highest known foil strength worldwide. However, the remaining elongation would enable enhancement of the rolling procedure until obtaining foils which would be thinner than 9 μm (4 or 5 μm).

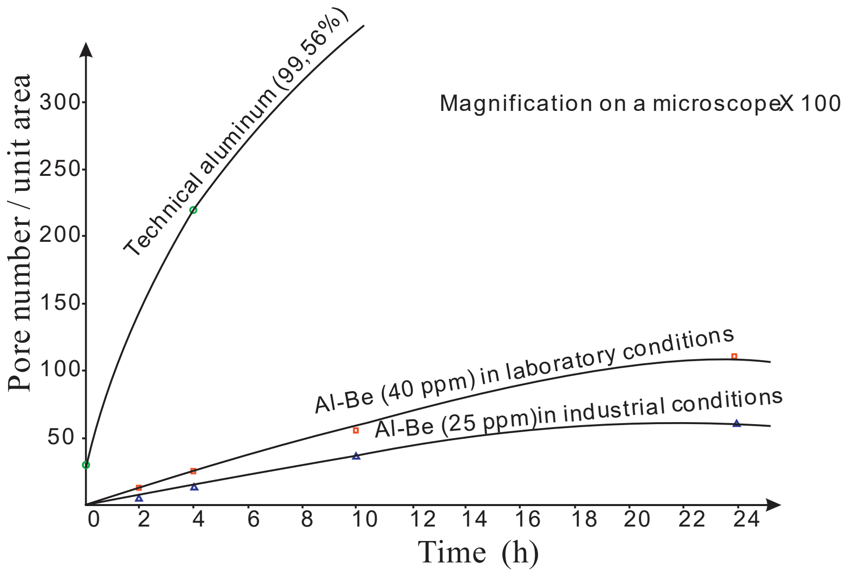


Fig. 14. Porous surface of modified and unmodified technical aluminum

4.3. The effect of dimensions on foil rolling regime

The effect of dimensions on foil rolling regime has not been elaborated to the full extent. Practical problems of aluminum foil rolling refer to uniformity of thin section rolling, especially because elastic deformation of the rollers overcomes the deformation by the rolling process. The physics of thin metal and oxide layers, which has been the subject of extensive scientific research since 1972, points out numerous phenomena and processes that cannot be applied to bulk materials, which makes this scientific field very interesting. As previously stated, elastic deformation of the rollers which overcomes the deformation by rolling process usually results in high deformation resistance, and thus inadequate regulation of front and back tension of the foil and rolling speed result in foil undulation, wrinkling and cracking. High deformation resistance is the consequence of brittle fracture of oxide layer on the foil surface, especially when **cumulative thickness of oxide layer (at top and bottom surface of the foil) is proportional to the thickness of aluminum layer of specific structure, in composite sandwich structure Al_2O_3 (film)-Al-Al_2O_3 (film)**. During the procedure of rolling 9μm or thinner foil, the effects of dimensions are displayed if thickness of oxide film is less than 0.1μm. Composite structure Al_2O_3 (film) – Al-Al_2O_3 (film) in which the thickness of oxide film is negligible, i.e. not more than 100 nm, is achieved by microalloying of aluminum. Fig. 14 clearly shows that oxide layer is very compact, with **maximum elastic modulus which can "sustain" stress during plastic deformation and provide minimum deformation resistance**. During the procedure of doubling at foil rolling, it is crucial that the surface of the foil be compact, due to capillary effects of oil wettability.

4.4. Discussion of the effects of microalloying on the structure of continuous cast strip

Bearing in mind the objective of the paper and the scope of experimental research, comprehensive consideration of the effects of microalloying improvers on the strip structure has not been elaborated to the full extent. Microalloying of aluminum strip is the result of extensive analysis of all parameters of continuous strip casting using 3C machine. Regardless of the addition of grain size modifiers, such as titanium and boron, using the usual content of these elements (up to 150 ppm Ti amd 100 ppm B) results in obtaining typical zebra-stripe structure, i.e. strictly oriented structures with large grains of bicrystals [4]. On the other hand, additional microalloying by manganese (Mn) and beryllium (Be) under the same temperature-speed casting conditions results in achieving fine-grained structure on upper and lower strip surface, as well as on strip cross-section. Theoretical analysis shows that the content of modifiers is reduced from central to peripheral zone of dendrite because of interdentritic liquation [5] which occurs due to depletion caused by peritectic reaction with titanium and boron. This prevents the completion of modification process and causes the formation of dendritic structure which is netted with eutectic alloy of Al Si Fe phase. On the other hand, the content of the modifier can be reduced in another direction-from peripheral zone towards the dendrite interior, if eutectic reaction is present in peripheral zone. Therefore, one peritectic reaction should be accompanied by one eutectic reaction, with the aim of obtaining a very small-grain structure. In this particular case, **aside from** titanium and boron, manganese is added.

Manganese should regulate the flow of eutectic reaction in peripheral zone of dendrite and initiate dispersive segregation of intermetallic in the zone. Overall result implies obtaining finer and more even distribution of particles in the matrix, which reduce the possibility of formation of large-scale grain structure. Regulation of Fe/Si ratio facilitates the "battle" between titanium and iron in peripheral zone of dendrite (phase Al Si Fe). The recommended ratio is Fe/Si = 3:1. Additionally, manganese redistributes iron and silicium by forming Al_6Mn (Si, Fe) phase.

The actual **effect of beryllium is much more complex.** First of all, beryllium regulates the dimensions of most frequent non-metallic inclusions, i.e. dispersed particles Al_2O_3. Beryllium shows higher affinity for oxygen than aluminum and thus tends to eliminate it from the oxide. Of course, this cannot be done to the full extent, but oxide significantly degrades and changes particle morphology, so that they act as other dispersive particles and intermetallic. Applying such procedure undoubtedly results in achieving the best possible strengthening effect, as, at specific point in time, all particles segregate on the formed boundaries of the grains, either after crystallization or after plastic flow (without destructive particles). Aside from the stated effect of beryllium on the morphology and increase of aluminum oxide layer, beryllium indirectly affects the process of crystallization of aluminum strip. Namely, due to poor metal wettability with upper 3C roller, i.e. slow cooling in the zone of peritectic reaction, the effect of modification is reduced or completely eliminated, which results in zebra-stripe structure. In the presence of beryllium, there is no slow cooling zone due to exceptional wettability of microalloyed aluminum and upper roller. Additionally, improved heat transfer and increased cooling capacity are decisive for creating larger number of crystallization centers with almost identical conditions for growth.

5. Conclusions

1. Research of the phenomenon of plasticity of microalloyed aluminum should be continued.
2. The results of this scientific undertaking and analysis of plasticity phenomenon should motivate scientists and researchers to develop and improve aluminum microalloying process.
3. In terms of practical aspect of the obtained results, microalloying of continuous cast strip and strip rolling until obtaining the finest foil (4-5 μm) are highly recommended.
4. Further research should be based on the elaboration of the procedure of deep drawing of cold rolled strip using extreme initial strength.

5. The choice of thermomechanical regime of formation by deep drawing can result in reduced earing, thus avoiding low metal extraction rate.
6. The surface of the rollers of 3C machine for continuous casting and rollers of all rolling mills must be adequately treated in order to achieve maximum compactness and surface reflectance during plastic treatment of strip into foil.
7. The major drawback of the batches used for the paper research was surface roughness which was the result of 3C machine print. The results would have probably been more satisfactory if the surface had been treated in a more appropriate way.

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