STUDY OF INCLUSIONS IN TECHNICAL ALUMINIUM

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ABSTRACT

Samples, taken from electrolytic cell and other production lines, were analysed with electron probe microanalyses EPMA and with high resolution Auger electron spectrometry HRAES.
In primary aluminium analyses confirmed the presence of elements like magnesium, copper and molybdenum, which is unknown from the literature. The distribution of inclusions, their number and their size showed that in aluminium, taken from the electrolytic cell, the inclusions are less numerous and coarser compared to inclusions in continuous cast band. After refining the inclusions are smaller and more numerous. Solubility of some components in complex inclusions in water makes metallographic sample preparation as well as quail- and quantitative analysis more difficult.

KEYWORDS

Primary aluminium, technical aluminium, complex inclusions

INTRODUCTION

Aluminium can be produced via two different routes: primary aluminium production from ore, and recycling aluminium from process scrap and used aluminium products. The production of primary aluminium consists of three steps: bauxite mining, alumina production and electrolysis. In reduction plants primary aluminium is extracted from alumina by the Hall-Héroult electrolytic process [1].
Systematic research to discover the origin of inclusions in aluminium is important for the assurance of the quality of products. The quality, that means the usability of aluminium and aluminium alloys, depends on the quantity and type of metallic and non-metallic inclusions as well as on the amount of dissolved hydrogen [2]. An important role is played by the chemical composition of the melt, the solubility of elements in aluminium as well as the conditions during melting, casting and hot working [3, 4].
New technology of primary aluminium production and needs of the customers demands improved quality control of aluminium. The quality control should evaluate the origin of inclusions during production and proposes the action for reduction of their number and size. The quantity of inclusions is a function of chemical composition and solubility of elements in Al, but their size depends on the conditions during casting and hot working [4,5]. Non-metallic inclusions and hydrogen remain in the material as a consequence of production process. They result from oxidation or other external factors (impurity elements in alumina, additives, atmosphere, furnace lining and casting pots) [6,8].

Inclusions in aluminium and aluminium alloys are usually characterized by their quantity and type [9,10]

EXPERIMENTALS

The samples were taken from the whole process that means from the primary melt and from the cast band or slab. The samples were chemical analysed, inclusions were observed by optical metallography and semi quantitative analysed with electron microprobe analyser.
For chemical analysing the following equipment was used for chemical analysing: flame atomic absorption spectrometers and, inductively coupled plasma atomic absorption spectrometer (ICP-AES), Optima 3100 RL.
Metallographic analyses were done by Nikon Microphot FXA optical microscope.
Jeol Scanning Electron Microscope - JSM35 was used for the analysing of coarser inclusions.
As the analysing of the smallest inclusions by micro probe analyser is no more accurate, the analysing of some samples proceed on the Microlab 310 F, a high-resolution field emission scanning spectrometer of auger electrons (HRAES) with Scanning Auger Electron Microscopy (SEM). For analysing the beam of 5 keV and 10 keV and magnifications 2500 x, 5000 x and 15000 x were used.
Samples were ion etched to remove adsorbed carbon and oxygen prior to the HRAES analysis. 1.5 μA ion current of Ar^+ at 3 keV ion energy was used over the whole sample surface, thus producing the current density of approx. 3 μAcm^{-2}. Total etching time was determined by disappearance of carbon peaks from the AES spectrum acquisitioned from the larger area (approx. 200 μm x 200 μm) and was between 15 and 30 minutes in all samples.

During preparation of metallographic samples dissolving of some components of complex inclusions was observed. From that reason different techniques for metallographic sample preparation were tested.

RESULTS AND DISCUSION

Inclusions in aluminium and aluminium-alloys are characterized by their quantity and type, not often by the size. The inclusions of oxide skin or remaining particles of Al_20_3 are small and sharp formed, often in groups together with borides and titanates of aluminium, as well as with other complex inclusions with different composition and size.
In our research the inclusions in the range below 100 μm were observed. Inclusions below 10 μm have not so harmful influence on the thin products as larger inclusions.

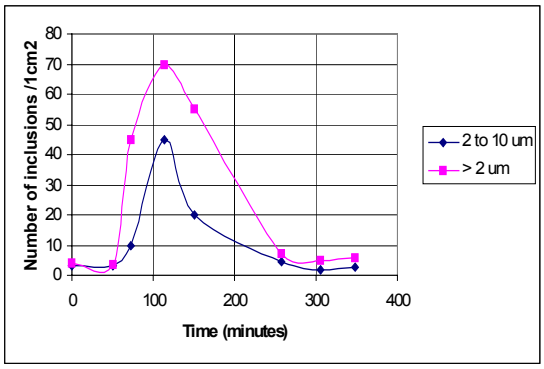
In the test charges beside inclusions also the chemical composition of the melt in the cell and in the semi products was checked.
Analysing of 33 samples taken from the melt in electrolytic cells showed the content of Fe up to 0,20 %, several times up to 0,84 %. The content of silicon was between 0,07 and 0,09 %. The contents of other elements as: Mn, Mg, Cu, Ni, Ti, Zn, V, Cr, B, Pb, Sb and Na were low and constant.

The samples were taken from the electrolytic cells, from cast band and from cast slabs. For sampling the melt was cast into metallic mould, which is used for the analysis on quantometer. The samples were taken from tree different technological lines.

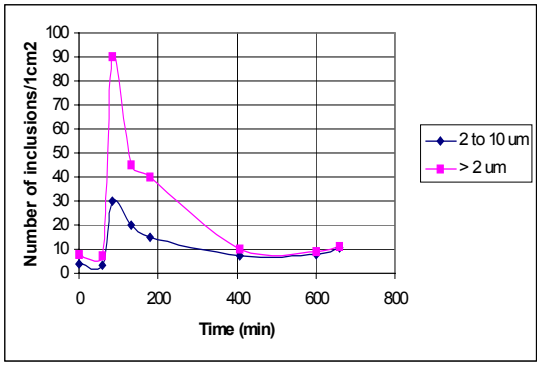
Metallographic analysis of inclusions was done on the cross section of cast sample with diameter of 25 mm. Because of the small size of inclusions several measurements was done by the magnification of 500 x which cause the increased number of observed fields for evaluation of the whole cross section. The results were calculated on the unity of surface (1 cm^2), which gives relative results with higher reliability compared to absolute results.

The quantity and type of inclusions

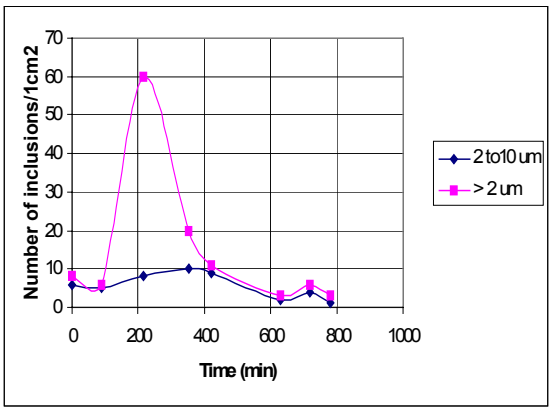
The number of inclusions in two size ranges for individual phases of production are graphical presented in the **Figures 1, 2 and 3**. Measured and calculated average values deviation is ± 12 % at slabs, ± 14 % at wide bands and ± 15 % at narrow bands.



Slab production



Wide band production



Narrow band production

Fig. 1-3: Average number of inclusions dependent on time at slab, wide band and narrow band production

The results (**Table 1**) show that several complex inclusions appear in aluminium. The following complex inclusions were found, which are not mentioned in the literature:

AlCaSiKNaClSC, AlCaSiOC, AlTiV, CaK(AlSi)ClC. These types of inclusions can be removed during the preparation process. In all phases of process lines the most harmful are different complex inclusions with the content of calcium (**Fig. 4**). Inclusions with the content of calcium (carbides, chlorides, oxicarbides, sulphides) react with water at wet preparation of metallographic samples. This is the main reason of false identification of such inclusions in the past. Beside that, these types of inclusions are brittle and crumble during grinding. There are also inclusions of corundum, which are often combined with the complex inclusions or small particles of amorphous Al_20_3 (oxide skin or foam).
Inclusions with calcium are present in primary aluminium as well as in technical aluminium. Coarser are inclusions with calcium, which originates from primary aluminium. The number of this type of inclusions increases in further phases because the calcium originates from the lining of furnace, from vessels and from casting channel.

Table 1: Qualitative composition of inclusions in samples taken from the slabs, narrow band and wide band

	Production line of slabs	
	Size of inclusions	
	< 10 μm	10 to 55 μm
Electrolytic Al	Al_4C_3 , SiAlC , Al_20_3	CaAlOC, CaSiOC
After addition of alloying el.	AlCa(O)C, AlCaTiOC(FeSi), Al_2O_3 , TiB_2	AlCa(O)C, CaSiOC, AlSiCaC, $CaSiO_3$, Al_2O_3
Middle and end of casting	CaAlC, AlCaSi, Al_2O_3, AlCaKSClOC, AlTiV	Al_2O_3, AlSi, AlCaSiOC

	Production line of wide band	
	Size of inclusions	
	< 10 μm	10 to 60 μm
Electrolytic Al	Al_4C_3, Al_2O_3, SiAl(O)C	CaSiOC, Al_2O_3
After addition of alloying el.	CaAlKSCl(O)C, AlSiC, Al_2O_3, AlTiV	AlCaSiKNaClSC, Al_2O_3
Semiproducts	AlCaKSClO(C), CaSC, AlTiV, Al_2O_3, SiAlC	AlCaNaKSCl(O)C, AlSi, AlSiC, Al_2O_3

	Production line of narrow band	
	Size of inclusions	
	< 10 μm	10 to 100 μm
Electrolytic Al	AlSiO(C), Si, SiC(O), Al_2O_3	AlCaOC, CaAlSiOC
After addition of alloying el.	AlCaSiKNa(ClSOC), AlTiV, CaAlOC	CaK(Al,Si)ClC, Al_2O_3
Semiproducts	AlCaSiKNaClSC, AlTiV, AlCaSiC	CaK(Al,Si)ClC, AlCaSiC, Al_2O_3

In the rest of technical aluminium, taken from the vessel and casting channel the following inclusions were found: corundum , amorphous Al_20_3, CaSiTiFe, AlSiFe, AlTiO and AlOC.

Metallic and nonmetallic inclusions concentrate on the colder places of the way of melt flow. To prevent the contamination of the next melt it is important to clean orderly all this ways.

In the samples taken from the pot during electrolysis, the inclusions are less numerous and coarser compared to inclusions in continuous cast band. After refining phase the inclusions are smaller and more numerous. This confirmed our anticipation that from the inclusions point of view, the refinement of primary aluminium makes it dirtier.
Coarser inclusions were observed by optical microscopy and analyzed by micro probe analyzer (MPA). The samples taken from electrolytic pot consist of Al and C, or Si, Al, C, or Al and O. Inclusions in the sample taken from the continuous cast band consist of Al and C, or Si, Al and C, or Al and O, or Ca, Al, O, C, or Ca, Si, O and C.

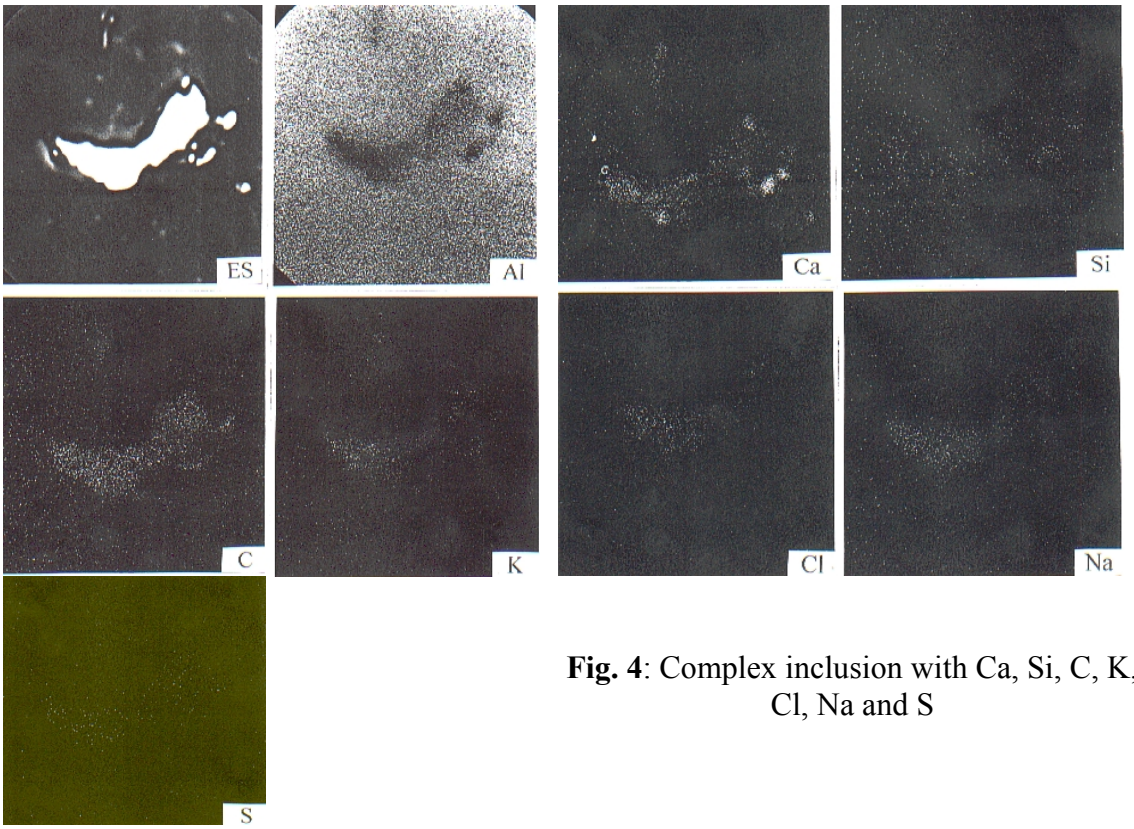


Fig. 4: Complex inclusion with Ca, Si, C, K, Cl, Na and S

Samples from the electrolytic pot were also analyzed on the Microlab 310 F, a high-resolution field emission scanning spectrometer of auger electrons (HRAES) with Scanning Auger Electron Microscopy (SEM). For analyzing the beam of 5 keV and 10 keV and magnifications 2500 x, 5000 x and 15000 x were used. The results of HRAES analyses are shown in **Table 2.**
In smaller combined inclusion (sample Al 1 P1-P3), with the size below 10 μm, the spectrum of kinetic energy confirmed the presence of C, Ca, O and Al. Beside the inclusions one can observe small islands of eutectic like phase which consists of two phases, gray phase and white lamellae phase. Analysis of both phases showed the presence of Al and O in gray phase and presence of C, Al, O, Fe, and Cu in white phase.
Analysis reveals that gray phase consists of O and Al but white phase is more complex and consists of C, Ca, O, Fe, Cu and Al.

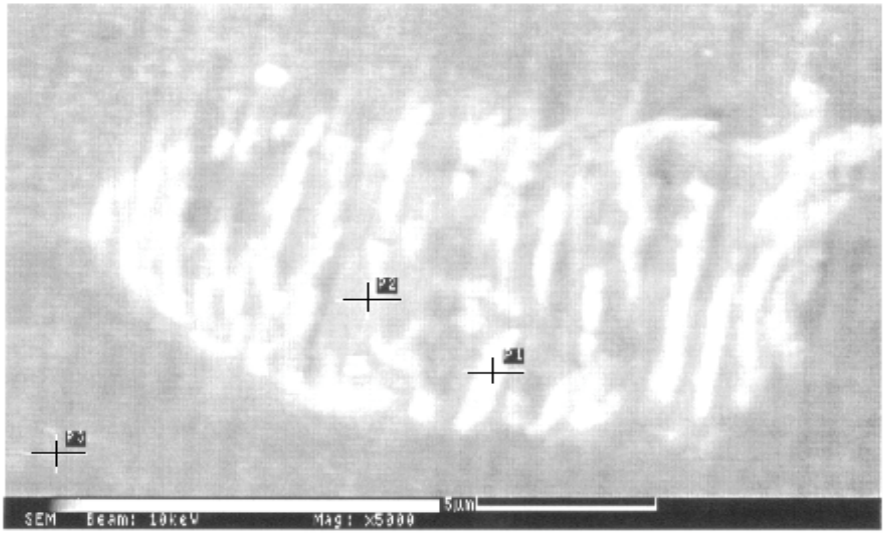
All analyses in Table 3 show in inclusions from 38,5 to 46,2 at. % of aluminium and from 53,8 to 61,5 at. % of oxygen. We suspect that the presence of oxygen is due uncomplete removing of adsorbed oxygen by ionic etching of the surface of the sample.
The analysis on several points shows that multiphase eutectic or complex inclusion consists of the matrix (P2) and most probable of Fe_3Al combined with unknown combination of copper, calcium, carbon and molybdenum. First time the analyses showed on several places increased concentration of copper and in one measurement the presence of magnesium. It looks that in the point P2 in the sample Al 2, copper is present together with iron-aluminium phase, which is present in more complex inclusions (samples Al 3P1, P3, P4 and Al 4P1). The complex inclusions based on calcium (lining and casting channels) include also oxicarbides and at the sample Al 3P4 the presence of copper and magnesium was detected.
Marked analysed points P1, P2 and P3 and the kinetic energy spectra of the analysing points in segment Al 4, representing the multiphase eutectic or complex inclusion, are shown in **Figure 5 and 6**.

Table 2: Content of elements in at. % in different points on samples of primary aluminium

Segment and analysed point	**Content of element (at. %)**							
	Al	**O**	**Fe**	**Cu**	**C**	**Ca**	**Mg**	**Mo**
Al 1								
P 1 – inclusion	19,1	28,5	8,3	2,7		41,2		
P 2 – base metal	39,9	60,0						
P 3 – base metal	41,3	58,6						
Al 2								
P 1 – eutectic	31,5	44,9	23,5					
P 2 – eutectic	41,7	19,5	28,7	9,9				
P 3 - base metal	39,6	60,3						
P 4 - base metal	43,6	56,3						
P 5 - base metal	39,3	60,6						
P 6 - base metal	46,2	53,7						
Al 3								
P 1 - inclusion	28,7	26,7	20,0	13,6	10,8			
P 2 - base metal	42,6	57,3						
P 3 - inclusion	14,6	31,6	30,7	7,4	15,4			
P 4 - inclusion	14,1	20,0	12,1	2,9	13,6	31,6	5,4	
P 5 - base metal	43,6	56,3						
Al 4								
P 1 – eutectic	10,6	18,3	20,4	13,5	10,8	4,6		21,5
P 2 - base in eutectic	41,9	58,0						
P 3 - base metal	40,9	59,0						
Al 5								
P 1 - inclusion	24,1	48,6			11,3	15,7		
P 2 - base metal	39,4	60,5						
P 3 - base metal	38,4	61,5						

The kinetic energy spectra confirm the presence of molybdenum, carbon, calcium, oxygen, iron, copper and aluminium. The presence of molybdenum is surprising. There is no data on the source of molybdenum in primary aluminium. The only possible origin of molybdenum is alumina, like for other elements in primary aluminium. There are no data on the content

of molybdenum in different alumina. From the literature [2] we can see that solid solubility of molybdenum in aluminium is 0.25 wt. % or 0.056 at. %.



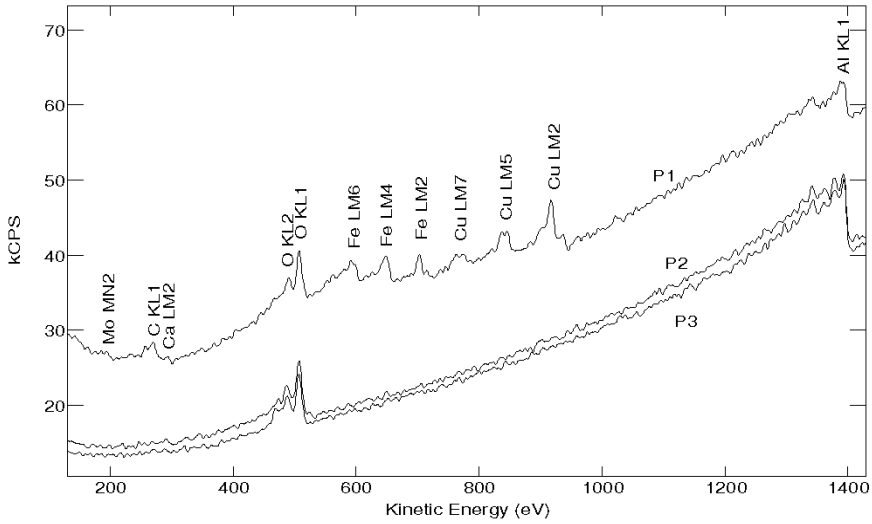


Fig. 5 and 6: Segment Al 4 in primary aluminium with marked analysed points P1, P2 and P3 and spectra of kinetic energy for the analyzed points.

Repeated analysis of primary aluminium confirmed the presence of molybdenum in the melt of primary aluminium. The determined concentrations of trace elements in wt. % are as follows: Fe – 0.015 %, Si – 0.018 %, Zn – 0.002 %, Mn – 0.0005 %, Mg – 0.001 %, Cu – 0.001 %, V - < 0.005 %, Cr - < 0.003 %, Pb < 0.002 %, Sb < 0.003 %, Na < 0.003 % and Mo – 0.001 %.

CONCLUSIONS

- Calcium was found in the inclusions in all three production lines.
- With the EPMA analysis the following complex inclusions were found, which are not mentioned in the literature: AlCaSiKNaClSC, AlCaSiOC, AlTiV, CaK(AlSi)ClC and similar. These complex inclusions can be removed during the wet metallographic sample preparation process.

- One part of inclusions with calcium originates from primary aluminium. The number of this type of inclusions increases also in further process phases and they originate from the lining of the furnace, vessels and casting channel.
- Metallic and nonmetallic inclusions concentrate on the colder places of the way of melts flow. To prevent the contamination of the next melt it is important to clean orderly all this ways.
- The analysis shows that inclusions (particles or agglomerates) below 10 μm are amorphous Al_2O_3. In inclusions above this size prevail corundum, which is seldom combined with small particles of amorphous Al_2O_3. At rolling they crumble into smaller particles.
- Research of inclusions with HRAES confirmed the high sensitivity of Microlab 310 F for qualitative and quantitative analysis of surfaces. Results show the presence of different elements and reveal some unusual combinations of elements.
- Surprising was the presence of molybdenum in eutectic like phase in primary aluminium. The only possible source is alumina. There are no data on content of molybdenum in alumina.

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