Vključki v proizvodni liniji bram, kvalitete Al 99,0

On Inclusions in Al 99.0 Grade Slab Ingot Production Line

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Absolutna vsebnost vključkov v aluminiju je večkrat manjša kot v jeklu, vendar pogosto že nekaj vključkov na enoto prostornine lahko poslabša kvaliteto aluminija. Količina, velikost in kvaliteta vključkov pa opredeljujejo njihovo vplivnost in omogočajo ustrezna ukrepanja za njihovo zmanjšanje.

1. UVOD

Kvaliteta aluminija in aluminijskih zlitin je poleg kemične sestave in mehanskih lastnosti odvisna tudi od vsebnosti vključkov, ki so kovinskega in nekovinskega porekla, ter od vsebnosti vodika.

Sistematične preiskave[1] izvora in količine vključkov v procesu proizvodnje aluminija, ki so bile izvršene v TGA — Kidričevo, so že pred leti opredelile kvalitativno in kvantitativno kontaminacijo aluminija v posameznih fazah proizvodnih procesov. Novejši proizvodni postopki in kvalitetne zahteve, ki so se bistveno spremenile, pa so bile povod za ponovne raziskave vključkov v aluminiju. Poudarek našega dela je na nekovinskih vključkih, ki smo jih opazovali v okviru obširnega dela[2], predstavljamo pa delo in rezultate spremljanja vključkov v posameznih fazah proizvodnje, od elektrolize do polproizvoda.

2. IZHODIŠČA IN CILJI

Nekovinski vključki (v nadaljevanju teksta vključki) so nujna, vendar neželjena posledica proizvodnih procesov in nastajajo (oksidacija) ali pa jih vnašamo (elektrolizni procesi, dodatki, atmosfera, obloge peči, loncev in žlebov) v talino od elektrolize do ulitega polproizvoda. Pri danih oziroma razpoložljivih tehnoloških možnostih ter postopkih sta količina in velikost vključkov odvisni predvsem od dosledne izvedbe vseh tehnoloških normativov v procesih proizvodnje. Zaradi tega smo namenoma analizirali kvantiteto in kvaliteto vključkov pri ustaljenih tehnoloških parametrih in izvedbah, ne da bi pri spremljanju in odvzemanju vzorcev kakorkoli vplivali na procese.

V svetu so za določevanje vključkov v aluminiju razvili več metod, vse so specifične in zahtevajo posebno opremo oziroma razvito metodologijo. Njihov cilj je čim enostavnejša in hitra določitev količine, sestave in velikosti vključkov v znani količini kovine.

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Absolute amount of nonmetallic inclusions in aluminium is often lower than in steel, however, a few inclusions per unit of volume can already impair the quality of aluminium. The amount, size and sort of inclusions determine theirs influence as well as the measures to be taken against them.

1. INTRODUCTION

Besides the chemical composition and mechanical properties, the amount of inclusions (metallic, nonmetallic and gas — hydrogen) also influences the quality of aluminium and its alloys.

Systematic investigations (1) of sources and amount of inclusions in aluminium production line carried out a couple of years ago in TGA Kidričevo resulted in qualitative and quantitative determination of the contamination of aluminium in particular production stages. Newer production processes and quality demands, which have undergone essential changes made it necessary to investigate inclusions in aluminium once again. The main object of our extensive work (2) were nonmetallic inclusions. The present report gives description of the work and results of investigation of inclusions in aluminium in particular production stages from electrolysis to semi products.

2. WORKING HYPOTHESES AND AIMS OF INVESTIGATION

Nonmetallic inclusions are unavoidable and undesired consequence of production processes. The inclusions are generated or introduced in aluminium (through oxidation, electrolysis, additions, atmosphere, refractory lining) from electrolysis to cast semi product. The amount and size of inclusions for a given technology and available technical facilities depend mainly on strict obedience of all prescribed technological procedures.

Therefore, the qualitative and quantitative analysis of inclusions was carried out during the time of normal production i. e. at standard production conditions without any special or provisional measures for sampling in order to prevent from interferring with routine production process.

Several methods have been developed for determination of inclusions in aluminium. All the methods are specific and require special equipment and a specially developed technique. The ultimate aim of all these methods is to determine the amount, composition and size of inclusions in a known weight of aluminium as quick and simple as possible.

The separation of inclusions is performed by centrifugation (5) or filtering (6) of remelted samples or by

Izolacija vključkov se izvrši s centrifugiranjem[5] ali filtriranjem[6] ponovno raztaljenih vzorcev ali pa s kemičnim raztapljanjem in izolacijo (brom-etanol). V zadnjem času se uveljavlja in ponuja[7,8] posebna preizkuševalna naprava, ki omogoča hitro določitev količine vključkov.

V TGA — Kidričevo so pred našimi raziskavami začeli preizkušati in uvajati posebne metode. Postopek je TGA — Kidričevo predložil dr. J. Langerweger, zato ga poimenujemo kar Langerwegerjeva metoda[3] ali kratko L-metoda. Omogoča[3] makroskopsko opazovanje in razvrščanje vključkov, večjih kot 30 µm po anodni oksidaciji, z diamantnim nožem obdelane večje površine (okrog 150 cm²) na poseben način v bakreno kokilo ulitega vzorca.

Rezultati raziskav[3] količine in velikosti vključkov v kvaliteti aluminija za rondele niso opravičili pričakovane uporabnosti in zanesljivosti L-metode. Zato smo vzporedno preverili njeno zanesljivost v primerjavi s klasično metalografsko metodo, dopolnjeno s kvalitativnimi rezultati analiz vključkov na elektronskem mikroanalizatorju. To metodo, ki je izredno zahtevna (veliko število vzorcev), smo uporabili, ker nimamo drugih aparativnih oziroma izvedbenih možnosti. Za poenostavitev dela in zanesljivejše rezultate smo predvideli določevanje količine, vrste in velikosti vključkov s pomočjo faznega diskriminatorja in računalniške obdelave rezultatov.

Nobena metoda nima absolutne prednosti, saj je v končni fazi potrebna tudi kvalitativna analiza vključkov. Za vse metode velja, da so najpomembnejši pravilno izbrani in ustrezno pripravljeni vzorci, ki morajo predstavljati pravo povprečje. To povprečje, preneseno na velikost posamezne šarže agregata, polizdelka in izdelka, pa lahko zaradi naključnosti dogajanj med procesi ne daje povprečne slike o dejanski kvaliteti.

Po objavljenih podatkih[3,5,6] in po rezultatih naših raziskav sloni ocena vključkov na količini in vrsti, manj pa na velikosti. Pogosto se navajajo odvisnosti med količino vključkov, ki nastopajo v posamezni fazi proizvodnih procesov ali pa po sestavi oziroma vrsti, katero karakterizira značilna oblika in pogosto tudi velikost. Tako se prikazujejo npr. oksidni vključki kot kožice ali delci Al_2O_3, karbidi značilnih drobnih ostrih oblik delcev, ki pogosto nastopajo v skupkih, boridi in titanati aluminija ter preostali kompleksni vključki različnih sestav in velikosti.

Glede na učinke vključkov pri predelavi in uporabi aluminijskih zlitin smo dali poudarek velikosti in številu vključkov. Za mejo smo izbrali velikost vključkov 10 µm, ker manjši vključki tudi pri nadaljnji predelavi v folije ne morejo povzročati značilnih napak in s tem vplivati na kvaliteto. Nadalje smo na osnovi rezultatov kvalitativnih analiz in značilnih oblik nastopanja posameznih vrst vključkov ocenili prevladujoče vrste in vrstni red nastopanja po količini. Za tovrstno predstavitev smo se opredelili šele po kvalitativnih analizah, saj so rezultati značilnih oblik vključkov pogosto pokazali popolnoma drugačno sestavo oziroma vrsto vključkov, kot bi sklepali na osnovi opazovanja v mikroskopu (oblike, barve in pogostost nastopanja). Prav tako je bila pogosto pri kompleksnejših vključkih zaradi različnih sestav onemogočena natančna razvrstitev glede na značilne vrste (oksidi, karbidi itd.), kar še dodatno poveča zanesljivost rezultatov uporabljene metode.

3. DELO IN REZULTATI

1. Podatki o šarži, vzorčevanju in pripravi vzorcev

Na proizvodni liniji bram smo spremljali tri šarže, analizirali pa smo vzorce tretje zaporedne šarže. Za kemične in metalografske analize smo vzorce posameznih

chemical dissolving and separation (with bromine-ethanol). Recently a special equipment has been available (7, 8) for rapid determination of the amount of inclusions.

TGA Kidričevo started to test the method proposed by dr. J. Langerweger before our work was started. Langerweger's method (L-method) utilizes macroscopic observation (3) and classification of inclusions larger than 30 micrometers after anodic oxidation of sample surface (about 150 cm²). The sample is prepared by especial casting in copper mould. The surface is cut by diamond tool and subjected to anodic oxidation.

The previous investigation (3) had not confirmed the expected reliability and usefulness of L-method for determination of the amount and size of inclusions. Therefore its reliability was examined by a comparative test with classic metallographic method supplemented with qualitative analysis of inclusions by electron micro probe. This impractical method which requires high number of samples was used since no other was available. To simplify the operation and improve reliability the phase discrimination facility and computerized analysis of results was utilized.

Neither method has definite and absolute advantage since at the end qualitative analysis of inclusions is also needed. Proper sampling and sample preparation are most important for all the methods. Even really representative samples in respect to the weight of heat, semiproduct and product may not offer average data on true quality due to the randomness of variations in process line. According to references (3, 5, 6) estimation of inclusions is based mainly on the amount and type of inclusions and in a lower degree on the size. The amount of inclusions and the type viz. composition of inclusions which is reflected by a characteristic shape and often size observed in a particular production stage are common methods. Oxide inclusions are referred to as films or Al_2O_3 particles, carbides as characteristic fine grained angular particles occurring often in clusters, the presence of aluminium borides, titanates and other complex inclusions of various composition and size have been observed.

As regards inclusion influence on processing and application of aluminium alloys the number and size of inclusions are emphasized. We have taken 10 µm as significant size limit since smaller inclusions can not cause characteristic defects and diminish the quality of Al folia. Based on results of qualitative analysis and characteristical appearance the prevailing type of inclusion was determined. According to the amount inclusions were classified in decreasing order. Very often the results of qualitative analysis did not agree with our expectations based on microscopic observation of shape, color and frequency. Complex inclusions due to different compositions frequently could not be precisely classified in respect to characteristic types (oxide, carbide, etc) which additionally increased reliability of the used method.

3. EXPERIMENTAL

1. Data on the Heat, Sampling and Sample Preparation

Three subsequent heats were investigated from the start to the end of slab ingot production line. Samples cast in cold metal mould for quantometer probe were taken from different production stages of the third heat. Since previous investigation showed that the highest average amount of inclusions were observed on cross-section at 1/3 sample height the same cross-section of all samples were subjected to microscopical investiga-

faz proizvodnega postopka ulili v hladno kovinsko kokilo, ki se uporablja za kvantometrske vzorce (gobice). Na osnovi rezultatov analiz in preverjanj treh značilnih presekov smo vzeli za analize vključkov prečni presek na približno eni tretjini višine vzorca, ker je pokazal največjo povprečno količino vključkov v posameznih vzorcih. Preiskovani presek površine 4,9 cm² je ugoden tudi s stališča meritev, saj smo najpogosteje z 20 vidnimi polji v optičnem mikroskopu, ki pri 200-kratni povečavi obsegajo premer 1 mm, zajeli področja vzorca od sredine do zunanje površine. Pri drobnih vključkih pa smo pri 500-kratni povečavi ustrezno povečali število meritev.

V **tabeli 1** navajamo glavne značilnosti šarže, posamezne faze in oznake. Če v **tabeli 1** ni posebej navedeno, predstavljajo rezultati metalografskih preiskav posamezne faze povprečne vrednosti treh vzorcev, s tem da so bili vzporedno odvzeti vzorci za kemične in metalografske preiskave ter L-vzorci. Načrtovano in doseženo kemično sestavo preiskovane šarže prikazujemo v **tabeli 2**.

Za pripravo metalografskih vzorcev smo uporabili lastni postopek: brušenje, ultrazvočno čiščenje, večkratno predpoliranje in poliranje z diamantnimi pastami brez poliranja z glinico.

Tabela 1: Faze tehnoloških procesov in podatki za linijo proizvodnje bram. kvalitete Al 99,0 (AF 10)

Oznaka faze in vzorcev	Obrata: Elektroliza in Livarna Šarža št. 4898, masa 6—7 t
0	**Elektroliza:** Med črpanjem 6 loncev iz 6 elektroliznih celic Rezultati faze 0 na sliki 1 so povprečne vrednosti 6 × 3 = 18 vzorcev Prevoz taline v livarno
1	**Livarna:** Pred izlitjem taline v rafinacijsko-livno peč so bili iz loncev odvzeti po trije vzorci Rezultati faze 1 na sliki 1 so povprečne vrednosti 9 vzorcev
2	Po legiranju Fe/Si = 1/3,0—3,5
3	Po rafinaciji
4	Po degazaciji
5	Po odstajanju 2ʰ in na začetku litja bram
6	Približno na sredini litja
7	Na koncu litja

Tabela 2: Kemične analize aluminija

	Vsebnost elementov v mas. %						
	Si	Fe	Mg	Mn	Zn	Ti	B
Predpis max.	0,13—0,20	0,40—0,60	—	0,05	0,07	—	
TGA	0,14	0,47	sled	0,006	0,009	0,002	
Faza 5-Ml	0,15	0,47	0,001	0,003	0,021	0,002	0,0010

2. Rezultati, količine, velikosti in vrste vključkov

Količino, vrsto in velikost vključkov smo poskušali določiti s pomočjo faznega diskriminatorja in računalniške obdelave rezultatov. Po več poskusih in določitvi optimalnih parametrov se je izkazalo, da so rezultati nezanesljivi zaradi nemogoče zagotovitve enake kvalitete površine vseh vzorcev (raze in sekundarni vključki — zrna brusnega papirja in ostanki diamantnih past, prašni delci in ostanki topil). Predvsem pa smo to metodo opustili zaradi slabe razločitvene sposobnosti pri razmejitvi med fazami, to je med kovinskimi in nekovinskimi vključki.

tion. The cross-section area of 4.9 cm² is favorable since 20 observation fields which at 200 X magnification means 1 mm diameter were often enough to cover the whole distance from sample centre to the outer surface. When dealing with fine inclusions the number of observation fields was adequately increased to correspond to 500 X magnification applied. The main characteristics of the heat, particular production stages and marks used are given in **Table 1**. Results of metallographic investigation are average values of three samples taken from each production stage if not otherwise stated. The parallel sampling for chemical, metallographic and L-method of investigation was used. Aimed and actual composition of the heat can be seen in **Table 2**.

Metallographic samples were prepared without the use of alumina as polishing means. The method we have developed includes grinding, ultra sound cleanning, multiple prepolishing and final polishing with diamond paste.

Table 1: Technologic stages and data on slab ingot production line — Al 99,0 (AF 10) grade.

Stage and sample mark	Works: Electrolysis and Foundry, Heat Nr. 4898, weight 6—7 tons
0	**Electrolysis** Transport of melt from 6 cells by 6 ladles to foundry Results in fig. 1 are mean of 6 × 3 = 18 samples
1	**Foundry** Before pouring to refining furnace. Three samples from each ladle were taken. Results presented in fig. 1 are mean value of 9 samples.
2	After alloying Fe/Si = 1/3.0—3.5
3	After refining
4	After degassing
5	After 2 hrs stay before of slab ingot casting
6	Approx. in the middle of casting
7	At the end of casting.

Table 2: Chemical composition (wt. %)

	Si	Fe	Mg	Mn	Zn	Ti	B
Prescribed maxim.	0.13— 0.20	0.40— 0.60	—	0.05	0.07	—	—
TGA	0.14	0.47	traces	0.006	0.009	0.002	—
Stage 5-Ml	0.15	0.47	0.001	0.003	0.021	0.002	0.0010

2. Results

After determination of optimum parameters and a number of tests to determine the amount, type and size of inclusions by the use of phase discrimination facility and computer analysis it was found that reliable results could not be obtained because of different quality of sample surfaces (imperfect polishing, secondary inclusions — grains of emery paper, remnants of diamond pastes and solvents, powder particles, etc.). However, the method was abandoned mainly because of poor resolution of phases i. e. its inability to differentiate metallic from non-metallic inclusions. The amount and size of inclusions for particular production stage and in dependence on time are given in **Fig. 1**. Deviation of the measured and calculated average values of samples for a particular stage was ±12 %. Because of time dependence the number of inclusions per cm² for particular stage in **Fig 1**. is given in a continuous form, i. e. as a curve, although they are not continuous naturally. The most frequent composition of the characteristic inclusions which were qualitatively analysed are given in **Table 3** in decreasing order of frequency. The given

Količino in velikost vključkov za posamezne faze in odvisnosti od časovnega poteka predstavljamo na **sliki 1**. Izmerjene in izračunane povprečne vrednosti so odstopale pri vzorcih posamezne faze ± 12 %. Na **sliki 1** smo število vključkov posameznih faz zvezno povezali zaradi časovne odvisnosti, čeprav so podane odvisnosti nezvezne. V tabeli 3 navajamo po vrstnem redu najpogostejše sestave značilnih vključkov, ki smo jih kvalitativno analizirali. Sestava vključkov v **tabeli 3** je relativna. Glede na ugotovljene kompleksnosti sestave in različne porazdelitve elementov v samih vključkih ter pogosto majhno velikost je bilo v večini primerov (razen pri enostavnih, toda redkih vključkih, npr. Al_2O_3, Al_4C_3, TiB_2) nemogoče določiti natančno sestavo. Zato smo označili sestave kar po ocenjeni količini in zaporedju nastopanja elementov v posamezni vrsti vključka. Nekatere sestave vključkov bi lahko priredili poznanim stehiometričnim razmerjem spojin. Takšni prikazi pa bi lahko zavajali, saj natančne mineraloške sestave ni mogoče izračunati, ker ni na razpolago ustreznih kalibracijskih standardov. Pri pogostih kompleksnih vključkih smo ugotovili, da včasih aluminij in kalcij močno nihata ter vzstni red ali pa da eden od obeh manjka. Podobne primere smo našli tudi pri drugih vključkih, kjer v oklepaju navajamo mejne koncentracije elementa, določene s točkovno analizo.

Tabela 3: Zaporedje pogostosti nastopanja in sestave vključkov proizvodne linije bram

	Vključki, velikosti	
	do 10 μm	od 10 do 55 μm
Elektrolizni aluminij, faza 0 in 1	Al_4C_3 SiAlC Al_2O_3	CaAlOC CaSiOC
Po dodatku legirnih elementov, faza 2	AlCa(O)C AlCaTiOC(FeSi) Al_2O_3 TiB_2	AlCa(O)C CaSiOC $CaSiO_3$ Al_2O_3
Sredina in konec litja, fazi 6 in 7	CaAlC AlCaSi AlCaKSClOC Al_2O_3 AlTiV	Al_2O_3 AlSi AlCaSiOC

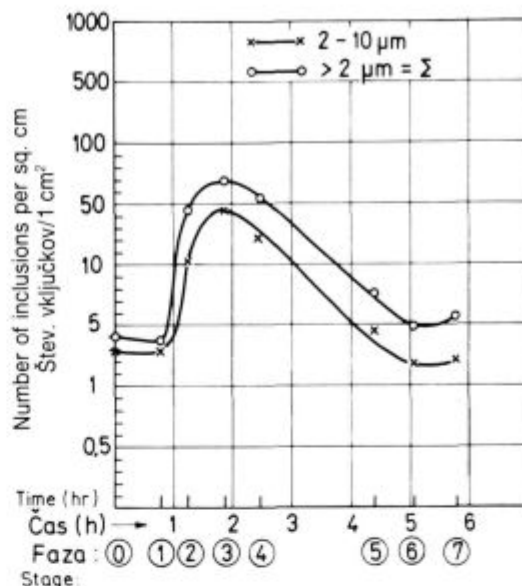**Opomba:** Rezultati predstavljajo kvalitativne analize površine presekov vzorcev (4,9 cm²) posamezne faze. Vključki Al_2O_3 so večinoma amorfni do velikosti 10 μm (delci ali skupki), nad to velikostjo pa korundni in so le redko združeni z manjšimi delci amorfnega Al_2O_3 (oksidne kožice ali glinice).

3. Rezultati L-metode

Od številnih vzorcev, ki so bili pripravljeni v TGA, pri nas pa analizirani, smo lahko samo v nekaj primerih določili primarne vključke. Ocena rezultatov opravičuje trditev, da L-metoda ni dala pričakovanih rezultatov, čeprav smo dodatno osvojili tudi tehniko kvalitativne analize vključkov v anodno oksidirani plasti. V TGA so s to metodo dobili že dobre rezultate[4] o vsebnosti vključkov v različnih fazah proizvodnje. Vzrok za razliko so lahko tudi kompleksne sestave vključkov, ki jih literatura[3] ne omenja.

4. Analiza rezultatov

Vsebnosti in velikosti vključkov na **sliki 1** ne moremo direktno primerjati z literaturnimi podatki, ker le-ti v večini veljajo za vključke, večje od 30 μm iz različnih faz in določeni po različnih postopkih. Številčnost in natančnost naših rezultatov pa dovoljuje naslednje ugotovitve:

Slika 1:
Povprečna vsebnost vključkov na enoto površine vzorcev preiskovanih faz proizvodnih postopkov izdelave bram
Fig. 1:
Average amount of inclusions per sq. cm of sample surface

compositions are relative since in the majority of cases, except for simple but rare (Al_2O_3, Al_4C_3, TiB_2) inclusions it was not possible to determine the exact composition because of fine size, complex composition and different element distribution. Therefore, the compositions are marked on the basis of estimated amount and order of appearance of elements in particular inclusion. Some compositions established in this way could be associated to stoichiometric formula of known compounds. However, it would be misleading since precise mineralogic composition can not be calculated (e. g. nonstoichiometric compositions) and because of nonavailability of calibration standards. In complex inclusions strong variations in Al/Ca ratio was frequently observed. In extreme cases one of the elements was even absent. Similar phenomena were observed at other inclusions also. In that case boundary values determined by spot analysis are given in brackets.

Table 3: Type of inclusions in decreasing order of the frequency of occurrence

Production stage	Inclusion size	
	< 10 μm	> 10< 55 μm
Electrolytis Al *Stage 0 and 1*	Al_4C_3 SiAlC Al_2O_3	CaAlOC CaSiOC
After alloying *Stage 2*	AlCa(O)C AlCaTiOC(FeSi) Al_2O_3 TiB_2	AlCa(O)C CaSiOC $CaSiO_3$ Al_2O_3
Middle and end of casting Stage 6 and 7	CaAlC AlCaSi AlCaKSClOC Al_2O_3 AlTiV	Al_2O_3 AlSi AlCaSiOC

Remark: *Al_2O_3 inclusions of < 10 μm size are mainly amorphous (particles or clusters), > 10 μm are corundum rarely associated with finer amorphous Al_2O_3 (oxide film). Results were obtained by qualitative analysis of samples taken from particular production stage. Cross-section area of samples was 4.9 sq. cm.*

— Absolutne vsebnosti vključkov v vseh preiskovanih fazah so višje, kot jih zasledimo v literaturnih podatkih, ki pa ne zajemajo vseh velikosti niti kvalitet. Večje vsebnosti lahko pripisujemo tudi specifičnemu vendar enakemu načinu odvzemanja vzorcev pretežno od površine talin in od stene peči, loncev oziroma žlebov.

— Količina vključkov je po vseh proizvodnih fazah višja kot v aluminiju iz elektrolize, predvsem pa se poviša vsebnost večjih (škodljivejših) vključkov, ki večinoma sledi znanim zakonitostim.

— Relativno visoka vsebnost vključkov na začetku ulivanja je najverjetneje posledica premajhnega časa odstajanja, ki podaljšan rezultira v najmanjši količini v sredini ulivanja. Ponovno povečanje na koncu ulivanja (šarže) pa je najverjetneje posledica večje koncentracije vključkov v zadnji talini.

— Največji vpliv na zmanjšanje vključkov ima čas odstajanja, kar potrjuje tudi manjše zmanjšanje števila vključkov neposredno po rafinaciji in degazaciji (fazi 3 in 4). Upravičeno bi bilo podaljšanje odstajanja vsaj na tri ure.

— Prevoz taline iz elektrolize (stresanje) zmanjša količino vključkov, v kasnejših fazah pa se vsebnost vključkov poveča in se zmanjšajo pod začetno količino le drobni vključki (pod 10 μm) v sredini in na koncu litja.

— V vseh fazah tehnoloških proizvodnih postopkov so v najbolj škodljivi velikosti in količini zastopani razni kompleksni vključki, ki vsebujejo kalcij (**tabela 3**). Na drugem mestu so vključki kurunda, ki so pogosto združeni s kalcijevimi kompleksnimi vključki in manjšimi delci ali gručami amorfnega Al_2O_3 (oksidna kožica ali pena). Sestavine vključkov, ki vsebujejo kalcij (karbidi, kloridi, oksikarbidi, sulfid) reagirajo z vodo pri mokri pripravi vzorcev in je to verjetno poleg njihove krhkosti glavni razlog netočnih identifikacij v preteklosti. Dodatni razlog pa je lahko, da tovrstnih vključkov tudi ne navaja strokovna literatura.

— Večji vključki s kalcijem izhajajo že iz elektroliznega aluminija (Tabela 3) ter se z nadaljnimi procesi povišujejo. Zato sklepamo, da je najverjetnejši dodatni izvor teh vključkov iz obzidav loncev, peči, žlebov in livnih nastavkov.

4. ZAKLJUČEK

V tem delu smo preiskali in določili količino, velikost in sestavo vključkov, ki nastopajo v posameznih fazah proizvodnih postopkov izdelave bram, kvalitete Al 99,0, iz elektroliznega aluminija klasične elektrolize v TGA Kidričevo.

Rezultati preiskav so pokazali, da se je iz dosedaj nepojasnjenih razlogov L-metoda izkazala neuporabna v vseh fazah dela. Nekoliko nepričakovano smo našli v vključkih predvsem mnogo kalcija oziroma vključkov s kalcijem, pogosto kompleksnih in različnih sestav, ki jih strokovna literatura ne navaja. Zanimivo je, da smo le poredko zasledili enostavne vključke (oksidi, karbidi, boridi, titanati itd.), ki se normalno navajajo v literaturi.

Elektrolizni aluminij s tehnološkimi procesi očistimo oziroma zmanjšamo samo drobne vključke (pod 10 μm), onečistimo pa ga predvsem z večjimi škodljivejšimi vključki.

3. Results of L-method

In samples prepared at TGA primary inclusions were determined in a very few cases. It was concluded that results of L-method were far from expectation. However, it helped us to develop the technique of qualitative analysis of inclusions in anodic oxidized layer. It should be mentioned that L-method gave satisfactory results in previous investigation (4) at TGA. Consequently one among reasons for poor success of L-method in this investigation can be the complex composition of observed inclusions not mentioned in literature (3).

4. Analysis of Results

The amount and size of inclusions seen in **Fig. 1** can not be directly compared with reference data since they hold for inclusions from different phases, larger than 30 μm and investigated by various methods. However, the number and accuracy of our results make it possible to draw following conclusions:

— Absolute amount of inclusions in all production stages are higher than reported in literature, which do not include neither all sizes nor all grades. Higher amounts can be attributed to the specific sampling method-samples were always taken mainly from melt surface and in the vicinity of furnace and ladle walls.

— The amount of inclusions in all production stages is higher than in electrolysis. First of all the amount of larger (harm) inclusions increases which follows the known rules.

— Comparatively high amount of inclusions at the start of casting is probably due to short staying of melt in ladle before casting. Longer staying results in the lowest amount of inclusions in the middle of casting. A rise at the end of casting is most probably caused by a higher concentration of inclusions in melt at the end of casting.

— The staying of melt in ladle before the casting exerts strongest influence on decrease in the amount of inclusions. Only slight decrease in the number of inclusions is observed immediately after refining and degassing (stages 3 and 4). An increase in staying to at least 3 hrs should be justified.

— Transport of melt from electrolysis diminishes the amount of inclusions due to associated shaking. However, in later stages the amount of inclusions increases except for fine inclusions (< 10 μm) the amount of which decreases in the middle and at the end of casting.

— In all technologic stages various complex inclusions containing CaO (**Table 3**) are present in the most harmful size and amount. Second are inclusions of corundum type which are often bonded with calcium complex inclusions and finer particles or clusters of amorphous Al_2O_3 (oxide film or foam). Compounds of calcium based inclusions (carbides, chlorides, oxycarbides, sulphide) react with water during wet sample preparation which is probably main cause, besides their brittleness, for inaccurate identification in the past. Another reason can be that this kind of inclusions has not been reported of in literature.

— Bigger inclusions with calcium come from electrolytis aluminium already (**Table 3**). Their amount further increases in the course of technological process. Therefore, it can be concluded that the most probable additional source of this inclusions is refractory lining of ladles, furnaces, nozzles, spouts etc.

4. CONCLUSION

The amount, size and composition of the inclusions occurring in particular technologic stages of Al 99.0

grade slab ingot production line from electrolytic Al (classic electrolysis) at TGA have been investigated and determined.

Results have shown that L-method, for unknown reasons, was not successful in all investigation stages. Somewhat surprisingly calcium type inclusions, frequently of complex and various composition not mentioned in literature were found. Simple inclusions (oxides, carbides, borides, titanates, etc) described and considered in literature were rarely observed.

The amount of only fine ($< 10\,\mu m$) inclusions is reduced through technologic processing of electrolytic aluminium, however, the amount of bigger and more harmful inclusions is increased.

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