Sonderdruck aus dem Heft zum 41. Internationalen Feuerfest-Kolloquium in Aachen
(29.9 und 30.9.1998), Seite 58 - 60

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Abstract

Due to the world-wide increasing rate of consumption and recycling of aluminium, recovered alumina from the processing of aluminium slags (dross and salt cake) will gain an importantance as a cost-effective raw material. In 1997 the annual figure of the German OXITON exceeded 100,000 t. As it is not attacked by molten aluminium and cryolite, OXITON could be used as a recycable bottom lining of aluminium electrolytic cells. In hydraulic bonded monolithics, the fine grained OXITON can replace up to 25 % of the alumina cement as a filler.

Generation and Processing of Aluminium Slags

Recovered alumina from the processing of aluminium slags (dross and salt cake) can be a cost-effective alternative to natural high-alumina raw materials. Aluminium slags are formed during aluminium melting by oxidation of the surface of the melt. Due to environmental and economic aspects, the processing of these slags to recycle aluminium metal and salt is becoming more and more usual procedure in the aluminium industry world-wide. The oxides remain thereby as high-alumina concentrates.

As the rate of consumption and recycling of aluminium metal is permanently growing, the availability of the recovered alumina is expected to increase significantly. Each ton of secondary aluminium results in 0.5 to 0.7 t of salt cake. Each ton of salt slag contains 0.4 t of oxidic aluminium compounds [1].

Aluminium has a very high affinity to oxygen. As difficult as it is to reduce aluminium oxide to metal by aluminium electrolysis with high expense of electrical energy, it is easy to reform aluminium to alumina when it comes in contact with oxygen. This oxidation already takes place at ambient temperature, whereby a freshly mechanically treated metal surface is immediately coated by a thin oxide layer of some nanometers thickness. During melting and pouring aluminium in air at temperatures above 800 °C the metal oxidation is of course much more stronger. The slag thereby formed is a mixture of fine grained particles of oxides and metal. This "dross" can cover the surface of the melt to a thickness of up to of some centimetres. The detailed steps in the generation of aluminium dross were described by I. Alfaro [2].

Recycled aluminium scrap and dross are mainly remelted in rotary drum furnaces. To prevent oxidation, the molten aluminium is covered by a layer of salt consisting of approximately 70 % NaCl, 28 % KCl and 2 % CaF_2. The resulting "salt slag" has a reduced metal content compared with the dross.

Presently, there are approximately 30 aluminium smelting facilities in Germany. For the central processing of salt cake, the company B.U.S BERZELIUS UMWELT-SERVICE AG, Duisburg operates two plants: SEGLmbH in Lünen and HANSE GmbH in Hannover. The central processing guarantees a constant quality of the high-alumina secondary raw material OXITON. In 1997 the output of OXITON exceeded the annual figure of 100,000 t.

The essential steps in the treatment of salt slag by the OXITON-generating German B.U.S process are [1]:

1) dry crushing, milling and separation of metal by screening
2) leaching of salts by water
3) separation of water insoluble oxides by thickening and filtration
4) crystallization and dewatering of the recycled salt
5) cleaning of the off-gases and recovery of NH_3 as ammonium sulphate.

In the USA and Canada a dry treatment of dross is preferred. This is done by burning the dross with a plasma flame. The oxidic residues are

- NOVAL in Canada [3] and
- NMP (nonmetallic product) in the USA [4].

Properties of Recovered Alumina

The chemical compositions of OXITON, NMP and NOVAL are principally very similar (**Tab. 1**), essentially depending on the composition of the manufactured aluminium metal and alloys, with magnesium and silicon as the main additives.

During the melting of aluminium in air the metal does not only combine with oxygen. It also reacts – to a less degree – with the nitrogen of the ambient atmosphere, forming aluminium nitride. Therefore, in the chemical composition of dross and salt slag, AlN must also be taken into account. If these residues are processed with water, the aluminium nitride decomposes to aluminium hydroxide by releasing ammonia gas. With the dry processed products of the USA and Canada the AlN content comes up to 18 %. In the very intensive wet treatment of the OXITON-generating German process, the aluminium nitride is decomposed to a great extent.

The essential mineralogical components of the high-alumina secondary raw materials are corundum (α-Al_2O_3) and spinel ($MgO \cdot Al_2O_3$). The cause is the intensive exothermic oxidation of aluminium with such high local temperatures, that the developed

Tab. 1. Chemical composition of recovered aluminas

%	OXITON Germany [5]	NMP USA [4]	NOVAL Canada [3]
Al_2O_3	59–66	60–70	53–65
AlN	1–2	1–10	9–18
Al metal	1–5		5–10
MgO	6–9	13–17.5	2–4
SiO_2	6–9	4–9	1–2
CaO	3	1–1.5	3
F	1–2		0.3–0.8
Na_2O	1	2.0	0–3
K_2O	0.5	1.5	0.4
Fe_2O_3	1.4	1–1.9	0.5–2
L.O.I. (800° C)	8–10		

Tab. 2. Sintering behaviour of OXITON (dry pressed at 50 N/mm²)

Temperature [° C]	Thermal Expansion [%]	Bulk Density [g/cm³]	Open Porosity [%]	Apparent Density [g/cm³]
110	+0.1	1.66	43.7	2.95
1100	+1.9	1.47	55.8	3.32
1400	–8.7	2.42	26.7	3.30

alumina transforms into the high-temperature modification corundum. Magnesium reacts even easier and more exothermal with oxygen than aluminium. Therefore, the magnesium oxide formed in the oxide layer immediately transforms with alumina to spinel [5].

The physical properties of OXITON are:

- The true specific density is 2.95 g/cm³.
- The particle size is less than 200 µm, with a medium particle size of about 10 - 20 µm and ultimate particles less than 5 µm.
- The Blaine-surface is about 12,000 cm/g.
- The melting point is higher than 1680 °C.

The sintering behaviour of OXITON is shown in **Tab. 2**. Sintering begins above 1100 °C. This corresponds to sintering investigations with alumina residues from the treatment of aluminium salt slags in Spain [6].

Applications for Recovered Alumina

As these materials are new on the market, their field of applications is still small. Relating to their composition, the recovered aluminas from aluminium slags are proposed for ceramics, refractories, cement, glass, mineral wool, ceramic fibres, foundry and steel mixes and abrasives [1, 3, 4, 6]. In the USA the refractory lightweight aggregate PLASMAL was developed [7]. German research results demonstrated the possibility of manufacturing high-porous sintered grains for light-weight concrete and bricks by using OXITON [8]. In Canada the construction of a new plant for the production of calcium aluminate, using aluminium dross by-products, was completed in 1997 [9].

Up to now, mainly producers of cement take benefit of OXITON as a cost-effective alumina source for the production of clinker, because they adjusted to use the wet filter cake material, resulting from the processing of the salt slags. To develop additional markets, it will be necessary to produce dried and calcined OXITON.

Tab. 3. Refractory mortar and concrete mixes with OXITON

Mortar mixes		1	2	3
Aluminate cement "Secar 51"	%	100	75	50
OXITON	%	0	25	50
Water addition	%	23	31	44
Initial setting time	h	2:40	2.30	3.20
Final setting time	h	4.00	4.10	5.30
Cold crushing strength	N/mm²	90	90	45
Concrete mixes		**1**	**2**	**3**
Aluminate cement "Secar 51"	%	20	15	10
OXITON		0	5	10
Tabular alumina				
0–0.5 mm	%	44	44	44
0.5–1.5 mm	%	36	36	36
Water addition	%	11	11	10
Cold crushing strength	N/mm²	40	40	20

Dried OXITON was tested as a filler in cement bonded building materials. Thereby was found that OXITON can replace up to 25 % of a comparatively more expensive alumina cement in refractory mortars and concretes (**Tab. 3**).

As the primary particles of OXITON have its origin from the direct contact with molten aluminium and salt, it is obvious that OXITON ought to be a refractory raw material for applications in the aluminium industry, especially for the bottom lining of aluminium reduction pots.

A typically bottom lining of aluminium reduction cells consists of about 3 layers of dense fire-clay bricks in the hotter zone and about 2 layers of highly porous diatomite bricks or calcium silicate slabs in the colder zone underneath. The joints between the bricks and slabs are weak zones through which electrolyte and metal can penetrate easier than through the compact material. Investigations of deteriorated pots, lined with fire-clay bricks, showed the attack progressing from the joints of the bricks [10]. Low dimensional tolerances and the use of mortars can minimize this problem, but increases the labour and the costs.

Monolithic linings are an alternative solution. Therefore metallurgical alumina, readily available in all aluminium smelters, is used in some plants. It is easier to install than bricks, simply poured into the empty steel shell and levelled. After the useful life of the electrolytic cells has expired, this lining can be removed more easily than a brick lining and can be recycled, even penetrated with electrolyte components, as alumina feed material into the electrolysis. The handicap of this lining is the decreasing heat insulation by penetration of electrolyte. Recent developments are olivine based monolithic materials, forming a barrier to the penetration by cryolite.

To investigate the suitability of OXITON for applications in aluminium refractories, cup tests were carried out at the DIFK-Institute in Bonn. Typically installed refractory materials for the bottom lining of aluminium electrolytic cells (fire-clay bricks ALUBAR 1100 and a monolithic, olivine based barrier material DRYCAST) together with primary aluminium metal and cryolite bath melt were made available by the VAW smelter plant in Neuss.

In the cup tests pressed tablets of OXITON or DRYCAST respectively, with a diameter of 50 mm and a heigth of 25 mm, were filled in drilled bores of fire-clay bricks (50 mm diameter and 60 mm depth). The tablets were covered with pieces of aluminium metal or pressed tablets of powdered cryolite bath melt. The cups were closed by sawed fire-clay slabs.

From the cup test with aluminium melt (800 °C / 72 h) was seen no attack to OXITON. Resistance towards molten metal is a question of thermodynamic stability and wettability. The main components of OXITON, the corundum and the spinel, are thermodynamically stable against aluminium metal. The minor component fluorspar CaF_2, a non-wetting additive in refractories for contact with liquid aluminium [11], is in this case an additional advantage of OXITON.

The result of the cup test with OXITON and cryolite melt (950 °C / 24 h) is shown in **Fig. 1**. Below the dissolved area of the fire-clay brick the OXITON is penetrated, but only partially and not attacked. This corresponds to the behaviour of metallurgical alumina. That means, as in the bottom of a reduction pot is

Tab. 4. Monolithic lining materials for aluminium reduction pots (dry pressed at 50 N/mm²)

material	bulk density [g/cm³]	open porosity [%]
metallurgical Aluminia	1.1	70
OXITON	1.7	42
DRYCAST	2.3	25

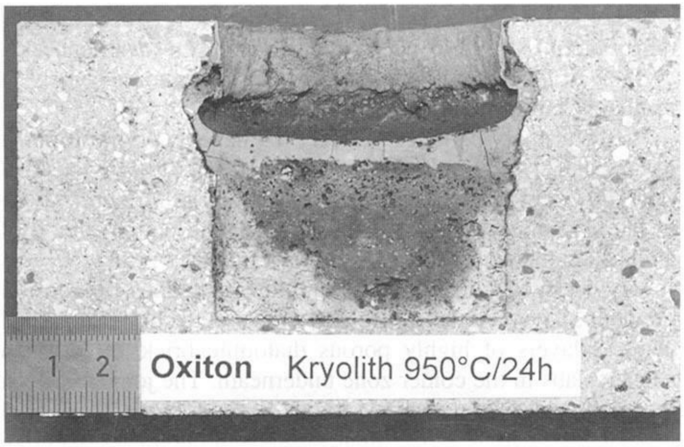

Fig. 1. Cryolite test with OXITON

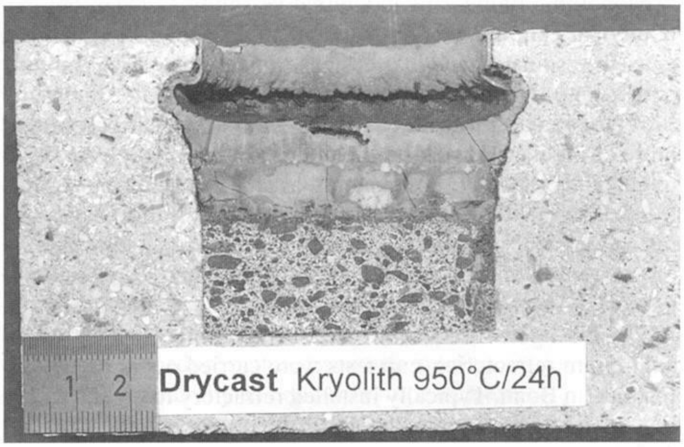

Fig. 2. Cryolite test with DRYCAST

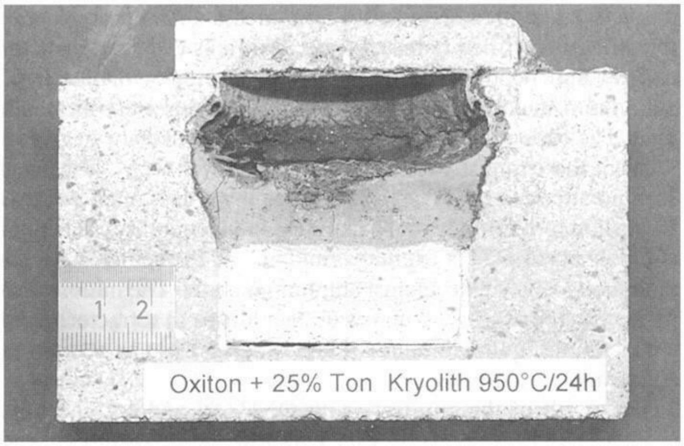

Fig. 3. Cryolite test with OXITON and clay binder

a gradient of temperature, in contrast to the cup test, the electrolyte would solidify at the latest at the eutectic point (about 700 °C) with no deeper infiltration. The advantage of OXITON compared to metallurgical alumina is the significantly less open porosity of the stamped material, so that less cryolite can infiltrate (**Tab. 4**).

With DRYCAST a clear barrier zone is visible (**Fig. 2**). This barrier zone is built up by sodium aluminium silicate from the reaction of the cryolite melt with the clay mineral binding phase in the DRYCAST material. For comparison a mixture of 75 % OXITON and 25 % clay binder was tested. As demonstrated in **Fig. 3**, the penetration of the electrolyte is stopped as well as with DRYCAST. The advantages compared to DRYCAST are the lower density (less material needed) and the higher porosity (better thermal insulation).

Conclusions

The results of the cup tests confirm the suitability of OXITON as raw material for aluminium refractories, especially in the bottom lining of reduction pots. In the technical realisation, the pot lining could be a monolithic stamping consisting of a mixture of OXITON and clay, formed to pellets, briquettes or bricks. The shaped bodies should be thermally pre-treated (up to 700 °C), so that the moisture and the crystalline water are reduced sufficiently, and they are mechanically stable to be transported, but not solidly sintered, so that they can be stamped. The consumed bottom lining could then be recycled into the OXITON-generating processing of aluminium salt slags. (F 043)

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