

INTRODUCTION

METALLURGY OF DROSS FORMATION ON AL MELTS

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Dross arising in casthouses is often regarded as a necessary evil. Dross quantities between 15 and 25 kg. per ton of production are regarded as normal; when remelting fine scrap, even 50 - 100 kg/t are still customary.

The costs caused by dross have already been estimated in previous presentations (1), (2); they are roughly just as high as the energy costs in the casthouse. Furthermore the major influencing factors have also already been described which determine the dross quantity during melt treatment, i.e. in particular

- the alloy composition
- the content of trace elements (i.e. Li)
- the kind of fluxing gas in melt purifying
- height of drop and discharge quantity during melt transfer with a free cascade.

However the results of these examinations are entirely empirical. In the following it is to be attempted to analyse a few exemplary operation steps, during which dross arises, on a scientific quantitative basis, in order to contribute in this way to a deeper understanding.

SOURCES OF DROSSThe free cascade

In accordance with Fig. 1, liquid metal has to be filled out of container A (i.e. transport crucible) into container B (i.e. furnace). The difference in level H between both containers is to be overcome by a free drop. To increase the geometrical simplicity, the metal should flow out of a round nozzle.

In the case of low "free drop height" (h), it is possible that the free melt-stream surrounds itself with an oxide skin, the stability of which is sufficient to withstand the friction forces of the liquid flow. Then a tensile force acts on the oxide skin that can be calculated from the viscosity of the melt, the velocity gradient $(dv/dr)_{r=R}$ on the oxide skin and geometrical factors (Fig.1 a) with the aid of the equation

$$K = \eta \cdot (2\pi Rh)(dv/dr)_{r=R} \quad (1)$$

This article scientifically analyses the dross formation in casthouses. The normally complicated procedures are broken down into individual processes, namely:

- oxidation of the surface of the melt
- tearing and pleating of the oxide skin
- afterburning (burn-off).

These elementary processes are considered quantitatively. We show how they can be simulated on a laboratory scale and how important factors can be determined namely:

- the thickness of the oxide skin after short exposure times and
- the tearing strength of the oxide skin

First results are discussed.

Based on these investigations, criteria can be formulated, in compliance with which dross formation can be reduced in casthouses to a minimum. The amount of this minimum value is estimated.

As long as the tensile force does not tear the oxide skin, the following will be valid

$$K \leq R_{\max} d 2 \pi R \quad (2)$$

$$\left(\frac{dv}{dr}\right)_{r=R} \eta \frac{h}{d} \leq R_{\max} \quad (3)$$

(R_{\max} = tearing strength of the oxide skin*, d = thickness of the oxide skin), the oxide skin remains stable, and no dross worth mentioning forms.

Above a "critical" difference in height $h = h^*$ the friction force K exceeds the maximum possible load of the oxide skin, and the latter tears directly at the discharge opening of the nozzle (position A).

Now the conditions are as in Fig 1b : the aluminum atoms on the surface of the cascade move from point A to point B, which requires time Δt . During that time a fresh oxide skin forms on the surface and grows to a thickness d (Δt).

At point B, the oxide coat is pushed in; a ring of wrinkled oxide skin forms around the melt stream. Fig 1b, shows how the wrinkles form; it can be seen that such a dross ring consists of liquid metal, surrounding oxide skins and enclosed air. Fig 2 shows a metallographic microscopic section of a piece of dross, from which this composition is clearly seen.

The quantity M of the oxide in the dross after time t (provided there is no afterburning) can be calculated according to the equation

$$M = 2\rho\pi Rh d(\Delta t) \frac{t}{\Delta t} \quad (4)$$

*) It is assumed here that the oxide skin is stuck so firmly that it is more likely to tear than to be loosened from the nozzle opening due to force K . Otherwise a term describing the bond strength of the oxide skin to the nozzle material has to be introduced in (2).

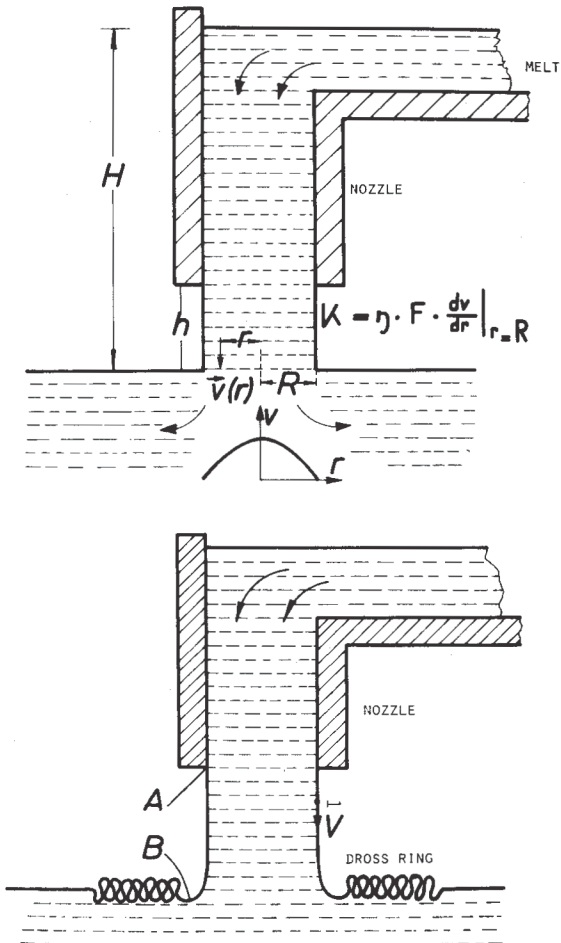


Fig. 1 Dross formation in the case of laminar discharge of liquid aluminum out of a tube (nozzle)

- a) no tearing of the oxide skin. The curve $v(r)$ indicates the distribution of velocity in the outflowing stream in the case of laminar flow.
- b) tearing of the oxide skin. The oxide travels along as closed sheath on the ray surface and collects in a dross ring which surrounds the stream.

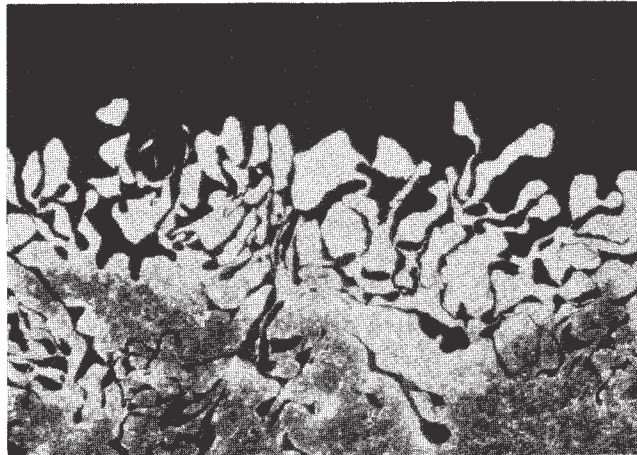


Fig. 2 Microscopic section of a piece of dross that has developed by folding acc. to Fig. 1b (40x).

Dross formation in the case of fluxing gas treatment

The dross formation in the case of gas treatment can be shown schematically acc. to Fig. 3. It is to be assumed that gas bubbles will break through the bath surface at intervals of t seconds so that the oxide skin is pushed aside each time and has to be formed again. Just as in the case of the free cascade, the oxide skin that has been pushed aside forms a dross ring around the rising point of the gas bubbles with the inside radius r .

If the fluxing gas is pure argon, a reaction between the flushing gas and the melt on the bubble surface cannot supply any contribution to the dross quantity, but purely the short time oxidation of the melt surface within the dross ring.

With that, the weight M of the oxide still in the dross after time t can be calculated according to

$$M = \rho \pi r^2 \frac{t}{\Delta t} d \tag{5}$$

The correlation become somewhat more complicated if one assumes that the inside radius of the dross ring becomes smaller in time, i.e. with increasing dross quantity. In fact the dross quantity is not proportional with the time. Rather the increase in the dross quantity will be the smaller, the more dross is already present.

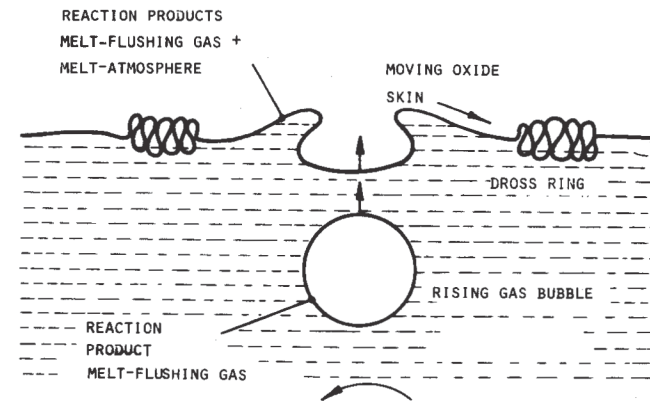


Fig. 3 Dross formation as a result of fluxing gas treatment

Dross formation when melting fine scrap

When melting fine scrap, the metal losses are so high that it is more accurate to determine the input quantity m_1 of the charge and the mass m_2 of the liquid metal molten out of it and with that to calculate the yield

$$A (\%) = \frac{m_2}{m_1} 100 \tag{6}$$

The gross metal loss

$$V = 100 - A \tag{7}$$

consists of various fractions according to

$$V = V_0 + V_1 + V_2 + V_3 \tag{8}$$

These fractions should be defined as follows:

- V_0 (%) of the charge to be melted is already in non-metallic form before melting
- V_1 (%) of the charge is converted during melting to oxidic form by oxidation (burning)
- $V_2 + V_3$ (%) of the charge go into the dross in metallic form
- V_3 (%) of the charge is recovered during dross treatment

Only fractions V_1+V_2 are genuine metal losses which must be evaluated with the metal price, while V_3 has to be assessed with (considerably lower) claiming costs.

In the case of thin strip and foils (gauge d_{Al}) the non-metallic fraction can be directly determined by measuring the thickness of the oxide coat d_{Ox} . Then for $d_{Ox} \ll d_{Al}$ is

$$V_0 = \frac{2 \rho_{Ox} d_{Ox}}{\rho_{Al} d_{Al}} \quad (9)$$

We measured an oxide coat thickness of 0.005 μm in the case of capacitor foils with a gauge of 9 μm so that here $V_0 = 0.11\%$ results. In the case of geometrically less well defined scrap, V_0 can be determined as follows: A representative sample from the charge is crushed by a laboratory shredder to such an extent that small representative samples can be taken from the ground material. The oxide content of these samples is then determined by dissolving the metallic phase in bromide methanol and subsequently weighing the remaining oxidic phase. We determine the V_0 of used beverage cans in this way, in comparison with the actual metal loss. The results can be seen from Table I.

Table I Typical metal losses or non-metallic components of can scrap.

Material	V(%)	V (%)	Al ₂ O ₃ Fraction (%)
Can scrap, condition on delivery	11	6	0.22
Can scrap, delacquered	9	2	0.82

It becomes clear from the examinations that the fraction of Al₂O₃ with V_0 is small and that it increases by means of delacquering.

The fraction of V_1 can be kept at low level if as low as possible a water vapour and oxygen partial pressure is set in the furnace or if one works with covering flux layers and at the same time makes sure that the charged material is not overheated.

The fraction of V_2+V_3 mainly arises due to the fact that the solid metal is surrounded with a layer of oxide and the proper weight of the metal is not sufficient to break through this oxide skin. The liquid metal then remains trapped in an oxide bag, cannot flow out and contributes to the metallic fraction of the dross.

This effect can be observed particularly clearly if a piece of aluminum household foil is heated over a candle. One then observes the melting of the metal, but it cannot drip as the tearing strength of the oxide skin is too great.

If one wishes to develop remelting techniques with increased yield, then one has to understand these procedures even better. Here too the two factors oxidation speed and tensile strength of the oxide coat are of special significance.

Afterburning of the dross

Fresh dross has a very high metal content (often 95%) directly after it arises. However, this metal content drops very quickly while the dross is still floating on the melt. Two processes take place:

1. Part of the metal flows out of the dross and gets back into the bath. This process probably plays a certain role particularly in the case of induction furnaces.
2. Due to its porosity, the dross has a large inner surface which is exposed to the furnace atmosphere. In the case of hearth furnaces the oxygen content in the atmosphere can be kept low by means of burner and furnace chamber pressure control, but on the other hand the thermal insulating effect of the dross leads to an overheating of the surface. This increases aftercombustion partially also through a reaction with the nitrogen in the air. In the case of induction furnaces this overheating does not exist, but the furnace atmosphere has the oxygen partial pressure of the ambient air.

A dross treatment with an exothermal skimming salt accelerates the release of the metal, but at the same time leads to an increase in the fraction of fines, so that the combustion process is accelerated. After removing the dross from the furnace, care must be taken that this combustion process is stopped.

EXPERIMENTAL

It has become clear in the foregoing that two factors considerably influence the dross formation above all, namely

- the short time - oxidation speed of the melt and
- the tearing strength of the oxide skin.

The thicker the oxide skin can grow before it is pushed aside the higher the oxide content of the freshly removed dross. The greater on the other hand the tearing strength of the oxide skin, the richer in metal must the dross be, since the liquid metal now no longer flows out of the oxide wrapping so easily.

This idea that is also shown in Fig. 4, must remain a working hypothesis as long as these two factors are not measured. In fact no data are available in literature. Various researchers (3), (4), (5) have written on the basis of gravimetric examination i.e. the increase in weight of the melt is determined based on oxidation. It is, however, only measurable after approx. 30 minutes oxidation time.

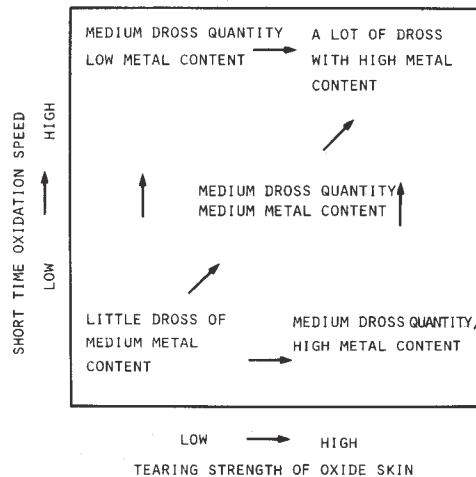


Fig. 4 Criteria for the tendency of alloys to form dross.

Short time oxidation

Aluminum was melted in a flat rectangular mould made of ceramic felt, the melt surface being 200 cm². After that the oxide skin was removed periodically with a graphite rod. As the inside wall of the mould was inclined on one short side, the dross arising was able to be immediately pulled over the edge of the mould where it quickly cooled down in the argon jet stream, so that there was no afterburning of the dross (cf Fig. 5).

After the first removal and disposal of the dross, drawing off took place according to an exact time programme, namely

- a) for two minutes every 5 seconds i.e. 24 times with $\Delta t = 5$ secs.
- b) five times with $\Delta t = 1$ min.
- c) five times with $\Delta t = 10$ min.

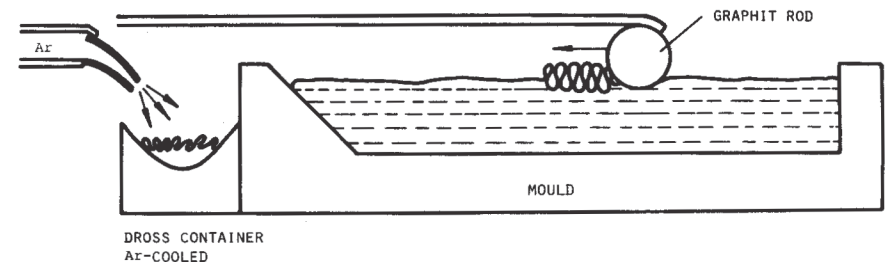


Fig. 5 Test arrangement for determining the thickness of the oxide coat after short time oxidation.

The dross obtained in this way was treated with bromide-methanol, with which the metallic aluminium is dissolved and the oxidic phase is left. This was filtered off, burned, weighed and analysed.

From the oxide quantity obtained in this way one can directly deduce the oxide quantity m_p per cm² melt surface that forms after oxidation time t . It is namely

$$m_p (\Delta t) = \frac{m_o}{F_n} \tag{10}$$

F indicating the bath surface (= 200 cm²) and n the number of times the oxide has been removed. If one finally inserts the density of the oxide (in g/cm³), then the thickness of the oxide layer is obtained as

$$d(\Delta t) = \frac{m_p(\Delta t)}{\rho} \quad (11)$$

Several oxide skins formed under industrial conditions were taken for laboratory examination. They underwent the following tests:

- Thickness measurement by dissolving in bromide-methanol solution and weighing the residue.
- Identification of the phases present by X-ray diffraction.

Table II resumes the main results which were recorded. On that basis, we can draw the graph of Fig. 6, where we can compare the measured oxide thicknesses with Radin ones (3). We can notice a fair similarity through extrapolation.

Table II Results.

Metal Quality	Temperature	t (s)	d (t) μm
Al 99,5	700°C	5	0,024
Al 99,5	700°C	60	0,044
Al 99,5	700°C	600	0,11
Al 99,5	800°C	5	0,044
Al 99,5 + 130 ppm Zn	700°C	5	0,33
Al 99,5	700°C	5	0,083
Al Mg 3	700°C	5	0,66
Al Mg3	700°C	300	1,5
Al Mg3	700°C	3000	4,1

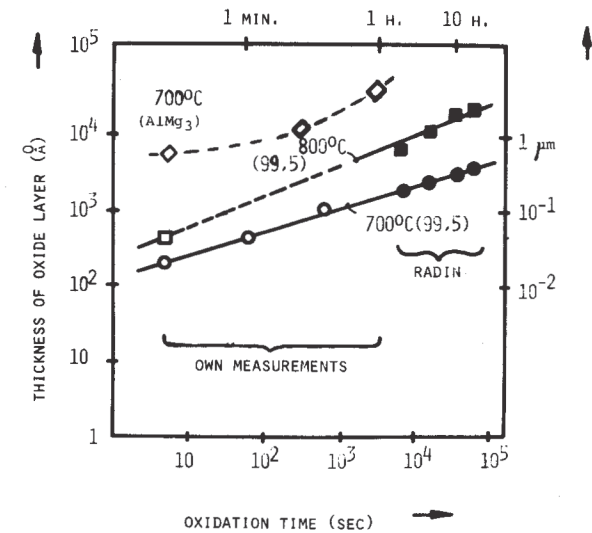


Fig. 6 Dependence of the thickness of the oxide layer on Al melts from the oxidation time. Comparison of some results with results from RADIN (3).

These investigation show that:

- in the first few seconds a doubling of the oxide layer thickness roughly corresponds to a ten times longer oxidation time,
- an increase in the melt temperature by 100°C doubles the thickness of the oxide layer,
- the addition of 3% Mg increases the short time oxide layer thickness almost to thirty times as much,
- small additions of contaminants (i.e. Pb, Ga in the ppm-range) can cause a significant increase in the short time oxide layer thickness.

Table III X-Ray diffraction results.

Metal	t (s)	Phases
AlMg3	300	~amorphous
AlMg3	3000	MgO, MgAl ₂ O ₄ traces of αAl ₂ O ₃

Mechanical properties of the oxide skin

Here, some interesting measurements have been started by FROMM (6) at the "Max-Planck-Institut für Metallforschung" in Stuttgart. The properties are measured in situ by sensitive dynamometer. First results could already confirm the well-known influence of Lithium and Beryllium, and influence of the oxidation time in a reproducible way.

CONCLUSIONS FOR CASTHOUSE

The abovementioned considerations and results supply a basis for answering the question important for operation,

- in how far the quantity of dross can really be reduced in the casthouses
- what a casthouse with minimum dross arisings would have to look like.

There is no doubt that the quantity of dross in a smelter casthouse that only produces pure aluminium can be reduced most consequentially. Here it is a matter of ensuring that the oxide skin is not torn when filling the potroom metal into the mixing furnace. That can take place for example by countertilting the furnace and transferring the potroom metal via a crucible tilting device. In the case of stationary furnace, filling can be done with a syphon or with a filling well that makes it possible for the metal to flow in under an existing oxide layer.

All melt cleaning in the furnace must be dispensed with. This can be attained in that by precleaning the potroom metal i.e. by means of coke bed filtration, the alkaline content in the potroom metal is reduced to such an extent that at best an inline cleaning is necessary ahead of the casting machine in order to safeguard the required metal purity as regards hydrogen and inclusions. If one assumes that in a 25 ton furnace the melt of pure aluminum remains 6 hours in the furnace (during filling and casting), then an oxide layer thickness of approx. 0.8 μm forms at a bath temperature of 750°C according to Fig. 6, which means that per cm^2 1.25 mg aluminum are converted into oxide. With that only 125 g of aluminum burn up with a bath surface of 10 m^2 per charge i.e. 5 g/t, no doubt a negligible quantity compared to other sources of loss. As the modern inline cleaning process produces dross quantities of 0.5 kg/t, such casthouse could be brought to dross quantities of less than 1 kg/ton i.e. less than one tenth of the present amount.

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