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# Accompanying phenomena during casting of aluminium alloys

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## Marek Galčík, Ing.\*

Department of Technological Engineering, Faculty of Mechanical Engineering,  
University of Žilina,  
Univerzitná 1, 010 26 Žilina, Slovak Republic.  
E-mail: marek.galcik@fstroj.uniza.sk, Tel.: + 421 41 513 2771

## Marek Brůna, Assoc. prof. Ing., PhD.

Department of Technological Engineering, Faculty of Mechanical Engineering,  
University of Žilina,  
Univerzitná 1, 010 26 Žilina, Slovak Republic.  
E-mail: marek.bruna@fstroj.uniza.sk, Tel.: + 421 41 513 2756

## Martin Medňanský, Ing.

Department of Technological Engineering, Faculty of Mechanical Engineering,  
University of Žilina,  
Univerzitná 1, 010 26 Žilina, Slovak Republic.  
E-mail: martin.mednansky@fstroj.uniza.sk, Tel.: + 421 41 513 2771

**Abstract:** An oxide layer is formed on the surface of a molten aluminium alloy when it is exposed to the surrounding atmosphere. The oxide layer on the surface of the melt is not harmful. The problem occurs when it is entrained into the melt volume and solidifies in the casting. The paper deals with the formation of the oxide layer, its types and the formation of a double oxide layers.

**Keywords:** aluminium alloys, oxide layer, bifilm

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## INTRODUCTION

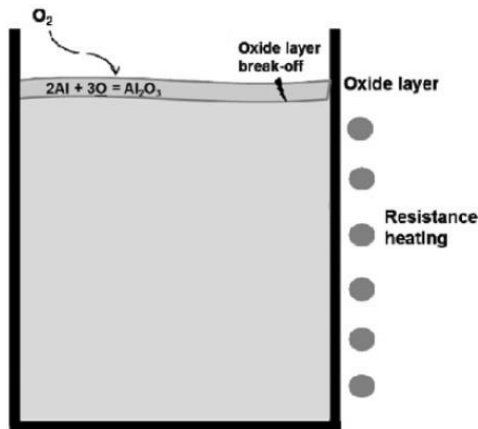
The quality of the used input material significantly determines the final quality of the final castings, as well as the quality of the prepared liquid metal. Just before casting, the prepared melt must be checked and, if necessary, modified in such a way that it meets at least the minimum requirements for its quality and should remove as much impurities as possible from it. To minimize the amount of internal defects in castings, it is necessary to prepare a high quality liquid metal. A high quality liquid metal is considered to be a metal that basically does not contain impurities. Above all, it concerns double oxide layers, as well as elements levelling and opening these layers. In aluminium alloys, such elements are iron, *hydrogen* and other gases. The quality of the liquid metal should not be taken for granted, and without proper processing, this requirement is often not fulfilled. The starting point for achieving a clean and high quality melt is the quality of the input material from which the melt is prepared. Since a combination of primary foundry alloys and secondary foundry alloys made by *remelting* recoverable material is used for melting, care must be taken to increase the iron content of the melt, which leads to an increased amount of harmful intermetallic phases. From the research of recent

years, the presence of *reoxidation* processes and the formation of double oxide layers is considered to be a key problem affecting the final quality of castings from *aluminium* alloys. That is why it is important to understand the causes and mechanisms of their formation, which will make it possible to eliminate a certain amount of them during the casting process by using a suitable technological solution [1-3].

## 1 OXIDE LAYER FORMATION

When liquid *aluminium* reacts with *oxygen*, the equilibrium solubility of oxygen in aluminium is extremely small. Nevertheless, *aluminium* and its alloys contain large amounts of oxides. This is due to the reaction of *oxygen* with the melt surface, as *aluminium* has a high affinity for *oxygen*. Within a few milliseconds (probably 10 ms to 100 ms), a continuous amorphous oxide layer of  $Al_2O_3$  (Fig. 1), several nanometres thick, is formed on the melt surface. This is called primary oxidation. Secondary oxidation, which is the oxidation occurring from the metal being poured until the mould cavity is filled, and tertiary oxidation, which occurs in the casting during solidification, are also called *reoxidation*. Oxidation occurs in both solid and liquid states and the extent of oxidation increases with increasing

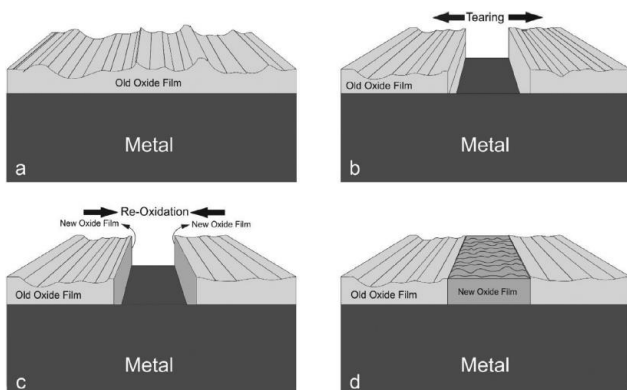
temperature. The formation of oxide layers and the development of *reoxidation* processes have the most significant influence on the formation of defects in *aluminium* alloy castings. Since the melting temperature of the *aluminium* oxide is about 2000 °C, it will only ever be present in the melt in the solid phase [2, 4, 5].



**Fig. 1. Reaction of oxygen with the melt surface [6]**

Although *oxygen* can only react with the surface of the melt, a large number of oxides are present in the castings. It is for this reason that the surface layer can be entrained into the volume of liquid metal. The presence of *oxygen* in *aluminium* must therefore be understood from a mechanical point of view, as it is a mechanical process and not a chemical one [2].

The entire surface area of the melt is covered with a continuous old oxide layer (Fig. 2a) until it is mechanically disturbed. Mechanical stresses may cause the oxide layer to tear (Fig. 2b), when the melt surface is again in contact with *oxygen* (Fig. 2c). As a result, a new oxide layer is again formed within a few milliseconds (Fig. 2d). It is therefore important to avoid mechanical surface disturbances as much as possible, as this produces an increasing amount of oxides [7].

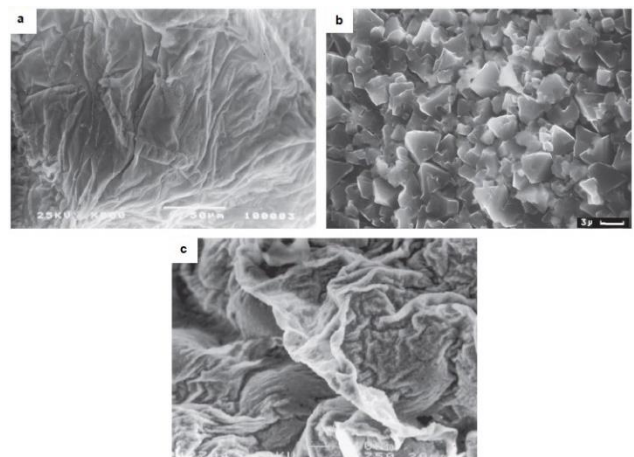


**Fig. 2. Mechanical failure of the surface oxide layer [7]**

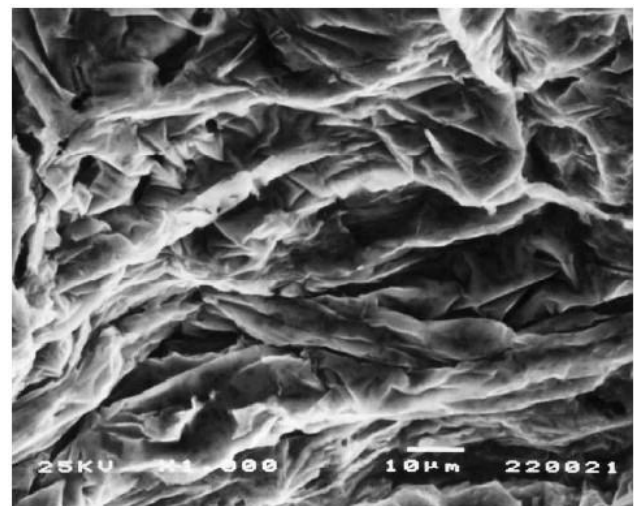
## 2 OXIDE TYPES IN ALUMINIUM ALLOYS

The most commonly occurring oxides in *aluminium* alloys, depending on the chemical composition, are

$Al_2O_3$  oxides,  $Al_2MgO_4$  spinels and *MgO* magnesium oxides. In *aluminium* alloys containing up to 0.005 wt. % Mg, pure *aluminium* oxide  $Al_2O_3$  is formed on the surface. In *aluminium* alloys with a *magnesium* content between 0.005 to 2 wt. %, a layer of  $Al_2MgO_4$ , known as spinel, is formed. At Mg contents above 2 wt. %, pure *magnesium* oxide  $MgO$  is formed on the surface. In fact, most *aluminium* alloys in use contain some *magnesium*, so that the oxide layer of *aluminium* formed almost immediately on the melt surface is converted to spinel over a period of time. The change in the type of oxide layer is also related to its morphology. Under the microscope, these films have characteristic shapes. The newly formed *aluminium* layer is typically 20 nm to 50 nm thin with a relatively smooth surface (Fig. 3a). The morphology of the spinel resembles a large number of crystals or sandpaper grains (Fig. 3b). *Magnesium* oxide films are wavy in shape and are roughly ten times thicker than *aluminium* oxide films (Fig. 3c) [2, 8].



**Fig. 3. Oxide layers: a)  $Al_2O_3$ , b)  $Al_2MgO_4$ , c)  $MgO$  [2]**



**Fig. 4. REM image of the surface of a new oxide [9]**

Depending on the thickness and growth time, two types of oxides are known, young oxides (thin) and old oxides (thick). The extremely fast reaction of the *aluminium* alloy melt with air allows oxide layers to form during the filling process. During filling, the free

surface of the melt may be unstable or expand and tear. These areas are then exposed to air and moisture in the mould. This results in thin oxide layers called young oxides. Unlike old oxides, young oxides have a very short exposure time to air. Therefore, young oxides are referred to as amorphous  $Al_2O_3$  oxides with thicknesses of only a few nanometres. Such thin oxide layers can easily be folded by turbulence and enter the melt. The morphology of the young oxides shows a large number of thin and sharp edges (Fig. 4). If adhered to the melt, some of these oxides can bond to each other and trap air between the layers [9].

Old oxides develop by the thickening of the oxides that originally existed on the surface of the ingots during melting and also during the transport of the melt from the furnace to the crucible. As the name implies, old oxides are formed when exposed to an oxidizing atmosphere for a long period of time, so they have time to thicken. Old oxides are less sensitive to deformation due to turbulence during filling as they have a higher solidity than young oxides. As a result, they have a less wavy surface compared to the surface of young oxide (Fig. 5) [9].

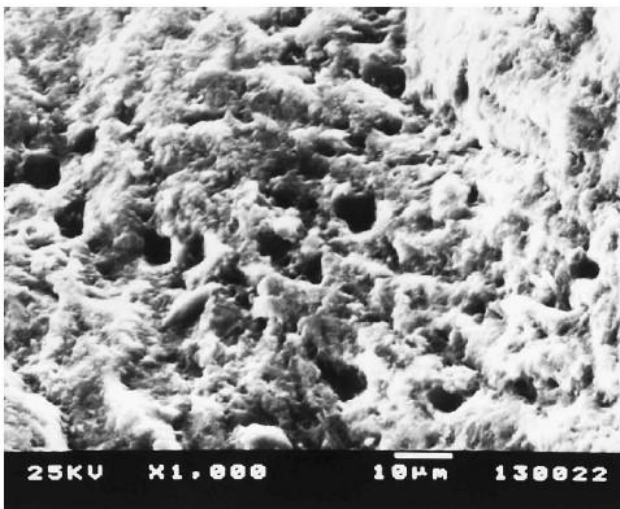


Fig. 5. REM image of the surface of an old oxide [9]

The types of oxide layers formed as a function of time and thickness are shown in Tab. 1. Layers of the 'new' oxide type in the form of thin layers are formed during mould filling. The 'old 1' type oxides in the form of flexible surface layers are formed during melt transfer.

Tab. 1. Oxide types formed on the melt surface of aluminium alloys [8]

| Oxide type           | new          | old 1o         | old 2             | old 3               |
|----------------------|--------------|----------------|-------------------|---------------------|
| Layer thickness [µm] | 1            | 10             | 1000              | 1000                |
| Layer formation time | 0.01 s to 1s | 10 s to 1 min. | 10 min. to 1 hour | 10 hours to 10 days |

Thick and almost inflexible 'old 2' oxides are likely to be formed in melting furnaces and solid 'old 3' oxide in plate form is most likely to be formed in holding furnaces [8].

The differences in the structure of new and old oxides due to the difficulty of analysing nanometre layers are not fully understood. However, there are studies that shed light on the evolution of oxides. Nyahumwa *et al.* have suggested that the structure of the oxide layer evolves from amorphous to  $\gamma$  and then  $\lambda$  phase. Upon contact of the melt surface with air, an amorphous layer of  $Al_2O_3$  forms almost immediately as it does not have sufficient time to crystallize. This layer, a few tens of nanometres thick, covers the entire surface. It is this amorphous layer that is considered to be the new oxide. The thin amorphous layer of  $Al_2O_3$  starts to crystallise into  $\gamma-Al_2O_3$  within five to ten minutes. The crystallization is influenced by the melt temperature, the exposure time and the thickness of the amorphous  $Al_2O_3$ . It is because of the longer time of formation that this oxide is called old oxide. During crystallization, thermal and volume expansion occurs and tensile and transformation stresses are generated within the layer. The tensile stresses cause local distortions of the layer and surface cracks are formed. The melt at the crack location reacts again with the air and a new amorphous layer is formed at the crack location, which grows in the same direction. Over a longer period of time, a transformation occurs at the melt surface, which involves a further reduction in the volume of the oxide as  $\gamma-Al_2O_3$  transforms to  $\alpha-Al_2O_3$  (corundum). This transformation process requires a longer time at a higher temperature, e.g. in a holding furnace. Due to the high hardness of corundum, its presence in the casting is undesirable as it causes worse machining. The transformation of the amorphous  $Al_2O_3$  layer to  $\gamma-Al_2O_3$  and then to  $\alpha-Al_2O_3$  leads to a 24 % reduction of the oxide volume. This volume reduction caused by the transformation causes further cracks and the formation of new amorphous layers. This growth cycle continues until the layer is strong enough to withstand the stresses generated at the surface [4, 8, 9].

### 3 MECHANISM OF DOUBLE OXIDE LAYER FORMATION

The formation of an oxide layer on the surface of the melt is not harmful, as long as the layer remains on the surface of the melt as it prevents further oxidation. The problem only occurs when this layer is submerged in the melt volume. The oxide layer of the aluminium alloy melt exposed to turbulence in the furnace, in the crucible or during the casting process in the gating system and in the mould cavity can be folded or cracked due to turbulence. The turbulence induced wave causes the oxide layers to be folded into each other and the folded double oxide layer is

entrained into the melt volume (Fig. 6). In this process, gas (mixture of  $O_2$ ,  $N_2$ ,  $Ar$ , etc.) is trapped between the interfaces of these layers. Such a double oxide formed by folding of the layers is known by the term bifilm, which was introduced by Prof. Campbell. Once the bifilm is formed in the melt volume, the internal atmosphere between the halves of the bifilm is consumed by continued oxidation and nitridation, which is controlled by diffusion of ions through the layer. The folding and entraining of the double oxide layer does not necessarily occur solely by wave formation, as shown in Fig. 6. It can also occur due to contraction of the free surface of the liquid metal, while the oxide layer itself, which is solid, is not capable of contraction, and so the excess surface area of the oxide layer must be folded. As the melt stream front advances (Fig. 7a), the oxide layer is trapped against the mould walls and tearing of the oxide layer occurs at the thinnest point of the front. As the melt stream front recedes (Fig. 7b), the solid oxide layer is entrained into the melt [2, 8, 10].

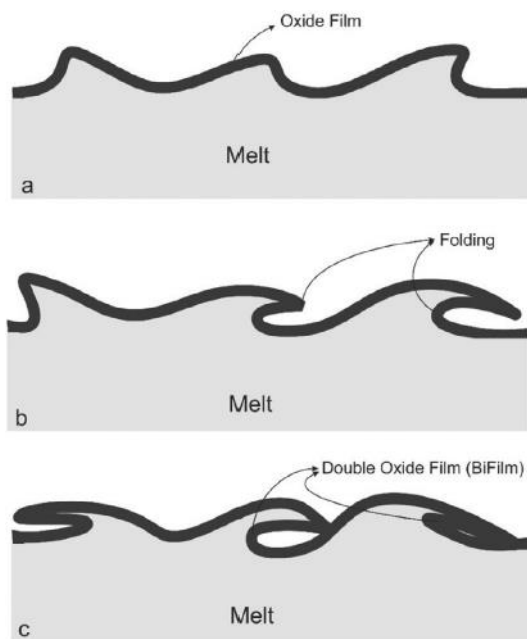


Fig. 6. Formation and entraining of a double oxide layer into the melt volume [7]

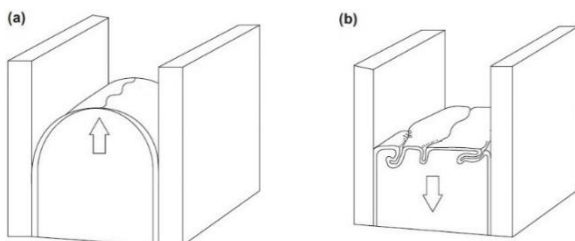


Fig. 7. Free surface liquid metal contraction and oxide layer entraining [2]

## CONCLUSION

The greatest impact on the final quality of the castings is when the oxide layer is entrained into the melt and solidifies in the casting. Several studies in recent years

have shown that entrained oxide layers in the casting act as initiators of porosity, and hydrogen contributes to pore formation by its diffusion between the layers, thereby enlarging the pore. Therefore, it is necessary to focus on minimizing the melt surface turbulence during the casting process. By reducing the amount of these, it can be assumed that there will be fewer pores in the casting and hence better quality.

## Acknowledgement

This article was produced within the UNIZA Grant System Project 01/2022 (17375).

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