Oxide skin strength on molten AA5XXX aluminum alloy – effect of beryllium and alternatives

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Abstract

This paper present oxide skin strength measurements of AA5XXX alloy with and without 2ppm by weight beryllium. The Pilling-Bedwoth ratio of oxide compounds is used to discuss alternatives for beryllium addition.

Introduction

It has been known for more than 50 years that beryllium has a reducing effect on oxidation of aluminum [1]. By adding a few parts per million of beryllium, the oxidation of high magnesium containing alloys can be reduced significantly. It has also been known for many years that beryllium, and particular beryllium oxide is hazardous. According to HSE-datasheet for beryllium oxide [2], the listed risk phrases are:

- R25 - Toxic if swallowed.
- R26 - Very toxic by inhalation.
- R35/37/38 - Irritating to eyes, respiratory system and skin.
- R43 - May cause sensitization by skin contact.
- R48/23 - Toxic: danger of serious damage to health by prolonged exposure through inhalation.
- R49 - May cause cancer by inhalation.

Therefore it is of vital interest to find alternatives for beryllium as an oxidation reducing agent. Without pure trial and error combined with luck, the search for such an agent will probably take long time.

One parameter which can be useful to study is the strength of the oxide skin. The author has previously published measurements done with an apparatus developed by Dr. Walter Kahl and Prof. E. Fromm [3] and has shown that in addition to the melt temperature, various alloying elements such as sodium and magnesium [4] has effect on the oxide skin strength. In the previous work [4], it was also shown that the oxide skin is about 0.25 second old when it is ruptured. Thus, these measurements are relevant to the situations where the oxide skin is continuously ruptured, such as pouring of liquid metal into a bath or turbulent flow in launders

Early measurements by Kahl and Fromm showed that the torque (which is proportional to the oxide skin strength [4]) is dependent on various alloying elements. For instance sodium, lithium and calcium increases the oxide skin strength significantly, for relatively low concentrations whereas addition of beryllium seems to decrease the strength. The magnesium also gives increased strength, but need much more in order to give the same effect.

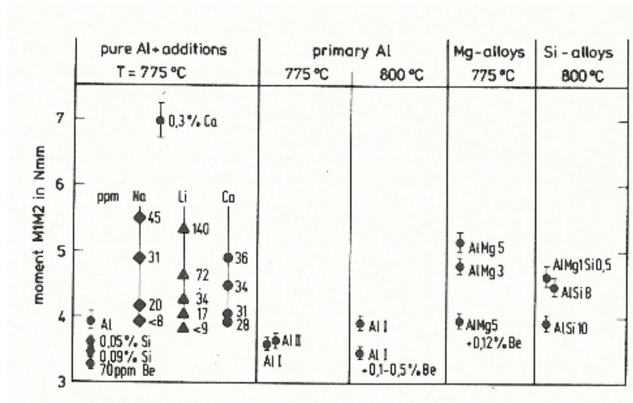

Figure 1: Torque (proportional to oxide skin strength) measurements published by W. Kahl and E. Fromm [3]

Previously the oxide skin strength measurement at SINTEF were done in open atmosphere, with ambient air as the only possible gas in contact with the oxide skin. Lately, the apparatus has been built into a glove box where the atmosphere can be adjusted as shown in Figure 2. The glove box made it possible to do the oxide skin strength measurements on beryllium containing alloys without health risk.

Figure 2: Thermally insulated glove box with oxide skin strength measurement apparatus. The cooling water temperature is adjusted to be able to increase water vapor in the atmosphere.

Experiments and discussion

Pure aluminum produced in a three layer electrolysis process by Vigeland Verk, Norway, is used as a reference. The purity in the metal is better than 99.998% (that is, 4.8N). These reference measurements was previously published by the author in 2006 [4] and are shown in Figure 3. As seen from the figure and discussed in the earlier publication, the oxide skin strength is constant for temperatures below about 720°C and increases slowly for higher temperatures.

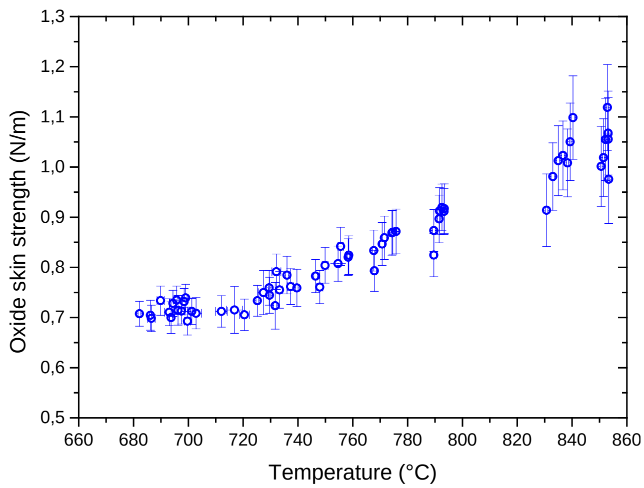

Figure 3: Reference oxide skin strength measurements [4].

The oxide skin strength on an industrial AA5XXX alloy containing 4.7% magnesium with and without beryllium was measured in the apparatus in the glove box. The measurements without beryllium are shown in Figure 4 together with the reference. The magnesium seems to increase the oxide skin strength for the major part of the measurements. During the oxide skin strength measurements of the AA5XXX alloy, it was observed that more oxide was building up around the measuring probe than the case for the pure aluminum. In addition to larger uncertainty in each measurement, this also gave larger variation between the measurements.

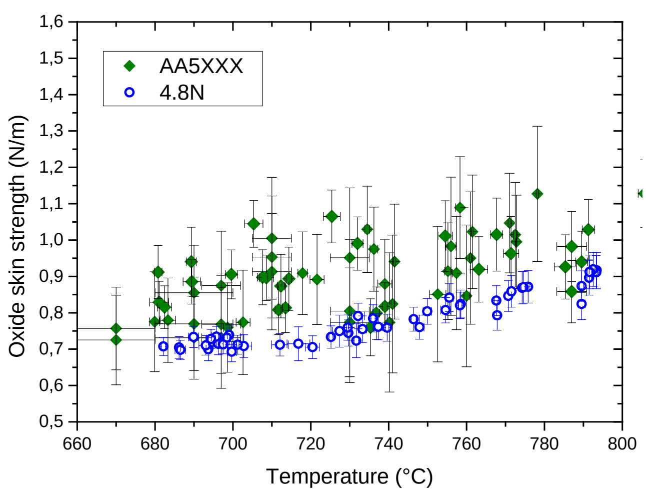

Figure 4: oxide skin strength of high magnesium containing alloy (4.7%) compared to pure aluminum.

The oxide skin strength measurements of AA5XXX with and without 2 ppm beryllium are shown in Figure 5. There is no significant difference between the oxide skin strength of these to alloys. This can partly be explained also from the measurements presented by Kahl and Fromm [3] as shown in Figure 1. They added 1200 ppm beryllium to an alloy containing 5% magnesium giving a reduction in the oxide skin strength of about 30%. If the effect is linear, this will be shadowed by the large variation between the measurements for a high magnesium containing alloy.

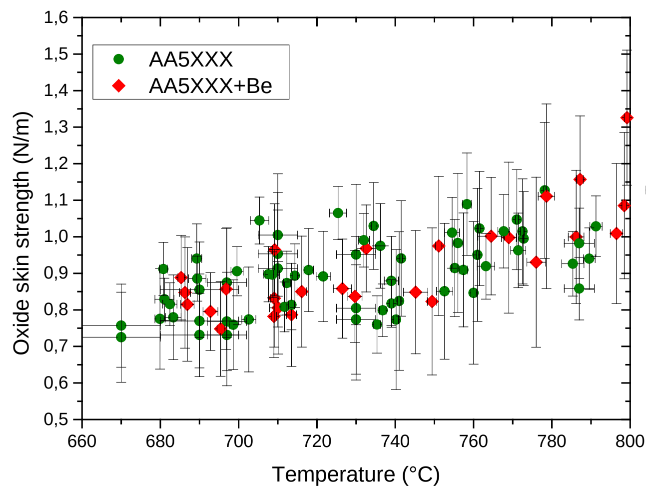

Figure 5: Oxide skin strength measurements on high magnesium containing alloy (4.7%) with and without 2 ppm beryllium.

Nicholas Smith and coauthors [6] used a tube furnace to oxidize the same AA5XXX alloys and studied the produced oxide layer with FIB and EDS. They found that on time scale of 10, 30, and 120 minutes (prior to breakaway oxidation [1]), there is a thin and dense layer aluminum oxide, with a high magnesium containing granular layer above. This granular layer is significantly reduced for the beryllium containing alloy. Since this granular layer is porous it will probably not contribute to the mechanical strength of the oxide layer, and therefore also not the measured oxide skin strength.

Alternatives for beryllium

As stated in the introduction, the beryllium oxide is considered to be very poisonous. Therefore, a non-toxic alternative to beryllium is highly desired. When looking at the table of elements shown in Figure 6, the elements close to magnesium such as calcium could be an alternative.

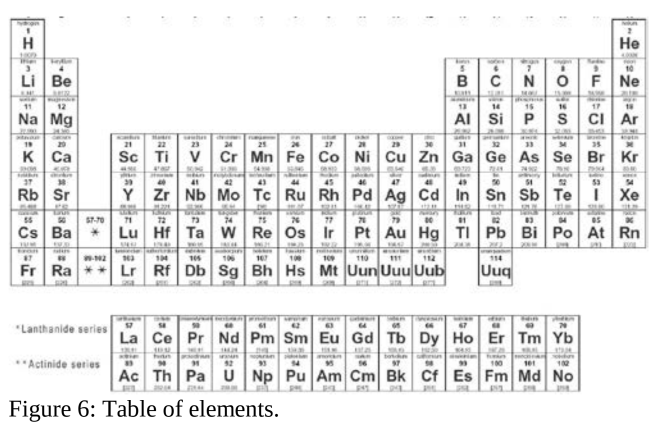

Figure 6: Table of elements.

However, Kahl and Fromm [3] showed oxide skin strength measurements for increasing calcium addition to pure aluminum, while Figure 7 shows measured oxide skin strength on an A356 (cast alloy containing 7% silicon and 0.3% magnesium). The calcium addition increase the oxide skin strength for both alloys.

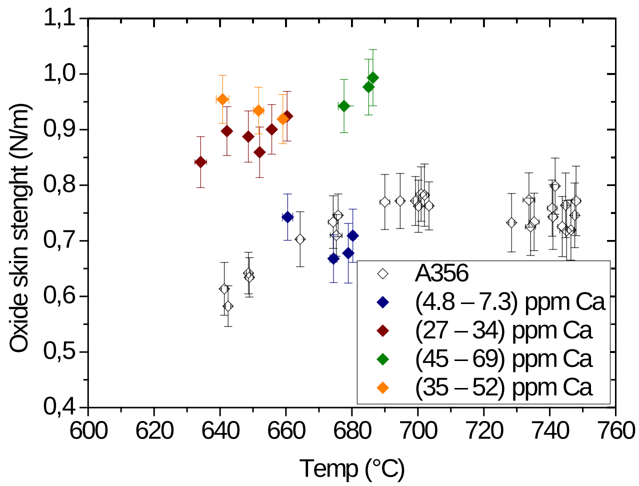

Figure 7: Oxide skin strength as function of temperature on an A356 alloy with varying amount of calcium additions.

One parameter which can be useful in the search for alternatives can be the Pilling-Bedworth ratio [7]. This number gives the ratio between the volume of an oxide component and the volume of the total number of metal atoms in that oxide. Mathematically it is expressed as:

$$PBR = \frac{M_{ox}/\rho_{ox}}{n \cdot M_{met}/\rho_{met}}$$

Where M_{ox} and M_{met} are molar masses and ρ_{ox} and ρ_{met} the densities of the oxide compound and metal atoms respectively, and *n* the number of metal atoms in the oxide compound. Table 1 shows a list of *PBR* values for some selected oxides.

The *PBR* values explain why molten magnesium metal will burn in air while aluminum does not. The volume of magnesium oxide is smaller than the volume of the metal atom from which it is formed, thus exposing more magnesium to air; while the volume of aluminum oxide is larger than the volume of the two aluminum atoms from which it is formed. The table also explains the breakaway oxidation as shown by Thiele in 1962 [1]. The initial aluminum oxide formed is γ-Al_2O_3 and will after some time transform to α-Al_2O_3. This transformation is a shrinkage in the oxide which expose new aluminum for further oxidation.

Comparing the *PBR* values in the table with the oxide skin strength measurements earlier presented one sees that oxides with PBR value less than 1 gives an increase in oxide skin strength (Na, Ca, Li, Mg) while Be has a *PBR* value of 1.76 and at least for high concentration (> 70ppm), the oxide skin strength is reduced as seen in Figure 1.

Table 1. PBR values for some oxides. Values for molar mass and densities are found in standard chemical tables.

Element	Oxide	*PBR*
Fe	Fe_2O_3	2.16
Fe	Fe_3O_4	2.09
Fe	FeO	1.77
Be	BeO	1.76
Se	SeO_2	1.69
Ge	GeO_2	1.62
Ti	TiO_2	1.59
Zr	ZrO_2	1.54
Sn	SnO_2	1.32
Al	γ-Al_2O_3	1.27
Ga	Ga_2O_3	1.24
Sn	SnO	1.20
Sc	Sc_2O_3	1.18
Y	Y_2O_3	1.14
Al	α-Al_2O_3	1.12
Mg	MgO	0.78
Ba	BaO	0.69
Ca	CaO	0.68
Sr	SrO	0.65
Na	Na_2O	0.59
Li	Li_2O	0.54
K	K_2O	0.47

Then in addition to beryllium, also the oxides from tin, zirconium, titanium, germanium, selenium, and iron have PBR-values larger than aluminum oxide and should be possible candidates as an alternative for beryllium.

The relation between PBR values and effect on oxide skin strength is also confirmed with addition of iron. Figure 8 shows oxide skin strength on an alloy with 1.3% magnesium and 0.4% iron. As shown earlier, the magnesium addition increase the oxide skin strength, then it can be concluded that iron decrease the oxide strength.

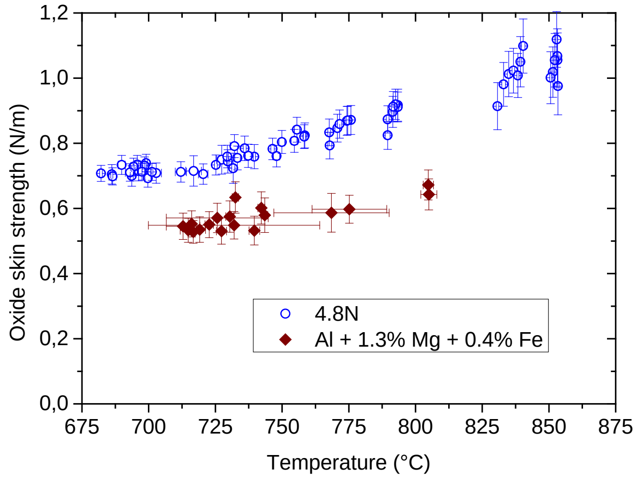

Figure 8: Oxide skin strength as function of temperature for an alloy with magnesium and iron compared to pure aluminum.

Conclusion

- Beryllium oxide is considered very poisonous
- 2ppm Be is too low concentration to measure any change in oxide skin strength
- Promising alternatives for compounds with *PBR* > 1 are Sn, Zr, Ti, Ge, Se, Fe etc.
- Fe addition does reduce oxide skin strength.

Acknowledgements

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