

High Temperature Oxidation of Extruded Aluminium Alloys

W. VAN RIJSWIJK

Hoogovens Research & Development
P.O. Box 10.000
1970 IJmuiden, Holland.

ABSTRACT- *High temperature oxidation (HTO) of aluminium and the corresponding surface blisters originate in the reaction of water vapour with the surface at temperatures above 300 °C. The paper starts with an overview of the literature from the last decades. Some fluoride salts can be used to control HTO. TGA experiments on the volatility of the salts and on the reaction between vapour products from the salts and the aluminium surface are presented. The sensitivity of aluminium products for HTO is dependant upon the sub-surface structure of the material. This is demonstrated by several examples.*

Keywords: *Aluminium, Oxidation, Blistering, Solution heat treatment.*

1. INTRODUCTION

High temperature oxidation (HTO) of aluminium, often referred to as hydrogen blisters, originates from the reaction of water vapour with the surface at temperatures above 300 °C. It may occur during solution heat treatment in a furnace that has a relatively high moisture content. The reaction may lead to sub-surface blister formation through a mechanism described below. These blisters can be a quality problem that needs to be resolved in the production plant. High-strength extruded products such as for aerospace applications are particularly sensitive to this phenomenon. High temperature oxidation is therefore a familiar problem within this industry.

The paper describes experiments on the mechanism of HTO, and on the mechanisms behind the prevention of HTO using fluoride salts. These salts are sometimes used in production plants, but the use of these volatile fluoride salts should be minimised because of their toxicity.

2. LITERATURE REVIEW

The phenomenon called High Temperature Oxidation (HTO) of aluminium, often referred to as hydrogen blisters, doesn't include all oxidation reactions of aluminium, as might be expected from the name. It is limited here to the reaction of water vapour with the aluminium surface and the resulting blistering phenomenon. Indeed, in aluminium production plants reaction with water vapour is by far the dominant type of high temperature oxidation mechanism. We will follow the common practice in the aluminium industry to use the term HTO to indicate High Temperature Oxidation of aluminium through water vapour and the resulting blister formation.

2.1 Blister formation

It has been postulated already in 1952 by Kostron [1,2] that HTO oxidation originates in the reaction of water vapour with the surface at high temperatures and that the basic mechanism can be divided into the following steps: (1) The water molecules dissociate at the surface giving rise to surface oxidation and hydrogen formation. (2) The hydrogen atoms penetrate the surface and are dissolved in the metal (as proton + electron). (3) Diffusion of the protons into the metal. (4) Going out of solution at an adsorption site within the metal. and recombination as molecular hydrogen. (5) Gas pressure builds up and may lead to formation of visible blisters. The evidence supporting this mechanism has accumulated in the literature [3-17,20,21].

It is important to note that blister formation can only occur when suitable recombination sites for

the hydrogen atoms are present in the metal. Impurities, oxide inclusions, intermetallic phases and the like may act as recombination sites [5,9-11,14-17]. In combination with differences in surface chemistry (particularly the influence of Mg), this forms the basis for the major differences in susceptibility to HTO observed between different alloys and different production routes. In general, the high-strength wrought alloys of the 2000 and 7000 series are the most susceptible [4,12,14,16] and extrusions are more susceptible than forgings or rolled products. Low-strength alloys and clad sheet and plate (two sides) are in practice virtually immune to HTO blister formation. Even so, a major difference in sensitivity to HTO is found even between 99.9% and 99.999% purity aluminium [19]. The process of HTO can be aggravated by the presence of ammonia or sulphur compounds, either in the furnace atmosphere or present as an impurity on the metal surface.

2.2 Kinetics

The kinetics of HTO blister formation was studied by observing the amount of blisters as a function of humidity, temperature and time [5,9,10,12-17] and in more detail by Ibe et al. and Stojanova et al [8,20]. These authors studied hydrogen diffusion and the recombination at an artificially introduced defect. An artificial blister was created which initially is free from gas. The depth and size of the blister are fixed. In a humid atmosphere (humidity corresponding roughly to "ambient" factory conditions) and at high temperature the blister will fill with hydrogen due to HTO. The internal pressure was calculated from the known creep behaviour of aluminium and the size of the blister and on the basis of this, the amount of hydrogen in the blister was determined. Using this technique the authors found the activation energy for hydrogen accumulation due to HTO to be about 140 kJ/mol, which is close to the activation energy for creep of high-purity aluminium at high temperatures. This substantiates the conjecture that creep is the rate-controlling aspect of pore formation by HTO. Others have studied the flux of hydrogen through an aluminium foil with a water-containing atmosphere on one side of the foil [21]. In this study, the activation energy for the hydrogen flux through the foil is surprisingly low, 25 kJ/mol, which is even much lower than the activation energy for hydrogen diffusion in high-purity aluminium, 60 kJ/mol [11].

The accumulation of hydrogen is strongly dependant on the type of surface reaction that occurs [8,12,20]. Blistering only occurs above 300°C, where the dehydration of $\text{Al}(\text{OH})_3$ into $\text{AlO}(\text{OH})$ at the surface starts. In the range of 500-550°C the $\text{AlO}(\text{OH})$ starts to convert into amorphous- or gamma Al_2O_3 , releasing water and leading to a rapid increase in the kinetics of hydrogen accumulation in the blister. At higher temperatures the reaction of water vapour and aluminium leads directly to amorphous- or gamma Al_2O_3 formation with the release of hydrogen into the metal. As all the hydrogen now goes into the metal and is not partly retained in the monohydrate at the surface, the hydrogen accumulation in the blister is again increased.

2.3 Fluoride salts

The use of some fluoride salts to prevent HTO is mentioned in the literature [22-26]. Opinions on the amount to be used vary [8,25]. The German Din Norm [25] quotes 0.2-0.5 g of NH_4HF_2 per m^3 of furnace capacity whereas Long [8] gives a range of 5-25 g per m^3 of furnace room for either NH_4BF_4 or NH_4HF_2 salts. The requirement will depend on the total surface area of the aluminium furnace load, amongst other factors. Other preventive measures against HTO are possible and several patents in this direction are given. These methods generally involve an additional processing step with pre-treatment of the surface before solution heat treatment, which makes them expensive. An example is disclosed in a patent [27], describing a surface treatment with a FeCl_3 solution at $\text{pH} = 0.5-2$, prior to SHT.

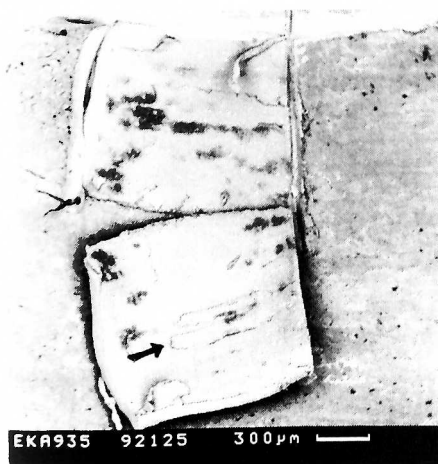
3. EXPERIMENTAL RESULTS

Two types of experiments were performed: analysis of formed blisters and TGA analysis of the reaction of vapour products from fluoride salts with aluminium.

3.1 Blisters

Samples of hydrogen blisters (HTO) were obtained from round bars in medium- to high-strength 6000 series extrusions after solution heat treatment. These extrusions were made with an indirect extrusion press.

First it is necessary to establish the origin of the observed blistering. The HTO type blisters can easily be distinguished from other extrusion blisters (which contain air) and from hydrogen porosity arising from a too-high hydrogen level in the cast material. When the blister is observed in cross-section with a light microscope, the HTO-type blister has a rough inner surface, while the "normal extrusion blister" has a smooth inner surface. Hydrogen porosity is found throughout the material, while HTO is found only near the surface [16]. After establishing the blister origin to be HTO, some blisters were opened with a surgical knife and the inside of the blisters was analysed with an electron microscope (see figure 1).



With energy dispersive element analysis, the inside of the blisters was analysed. It was observed that the blisters contain oxidised areas, the dark spots in figure 1. These areas are thought to be the sub-surface recombination spots for the hydrogen atoms.

Careful inspection showed that many of these samples had layered structures, which were locally peeled-off to reveal a deeper layer.

Figure 1: One of the HTO blisters opened with a surgical knife and observed with backscattered electrons (element contrast) in the electron microscope.

Structures like this can be seen in the blister (see arrow in figure 1). In addition to this, it was shown by element analysis that significant parts of the inside of the blisters were covered with a very thin oxide layer, even aside from the "dark spots". A discussion will be given below.

3.2 Reaction of aluminium with gaseous products from fluoride salts

Samples of NH_4BF_4 and NH_4HF_2 were analysed with Thermogravimetric Analysis (TGA) at heating rates of both $5^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$ (see figure 2). At $10^\circ\text{C}/\text{min}$, the point of 50% weight loss in the TGA experiments was 330°C for NH_4BF_4 and 165°C for NH_4HF_2 .

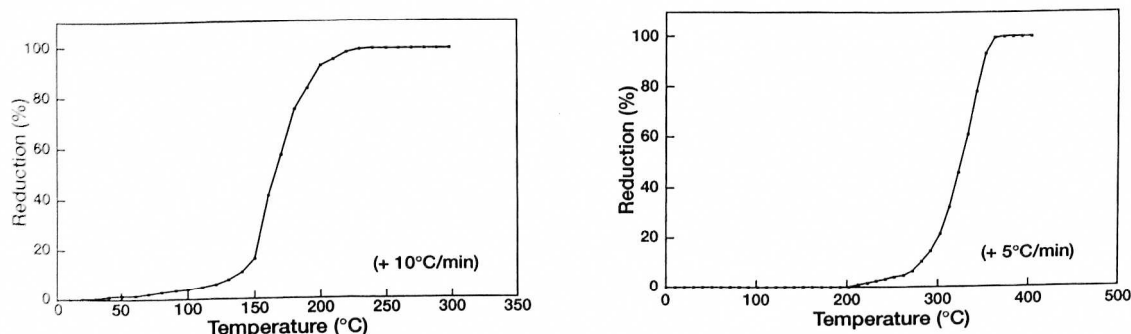


Figure 2: Thermogravimetric Analysis (TGA) of NH_4HF_2 (left) and NH_4BF_3 (right).

The reaction between the gaseous products of these salts and an aluminium foil was measured in

the TGA by determining the increase in weight as a function of time during heating-up at a rate of 10°C/min. The results show (figure 3) that a minimum temperature of about 300°C is required before any significant reaction with the aluminium is obtained. The reaction slows down considerably when the build-up layer exceeds about 70 mg/m², as the layer acts as a diffusion barrier. By analysing the resultant foil with X-ray diffraction, it was established that the surface layer on the aluminium consists of beta-AlF₃.

We found the minimum requirement of NH₄BF₃ in the factory to be 2 g per m³ of furnace room even when release of the dissociation products of the fluoride salt was timed to the furnace load reaching 300°C.

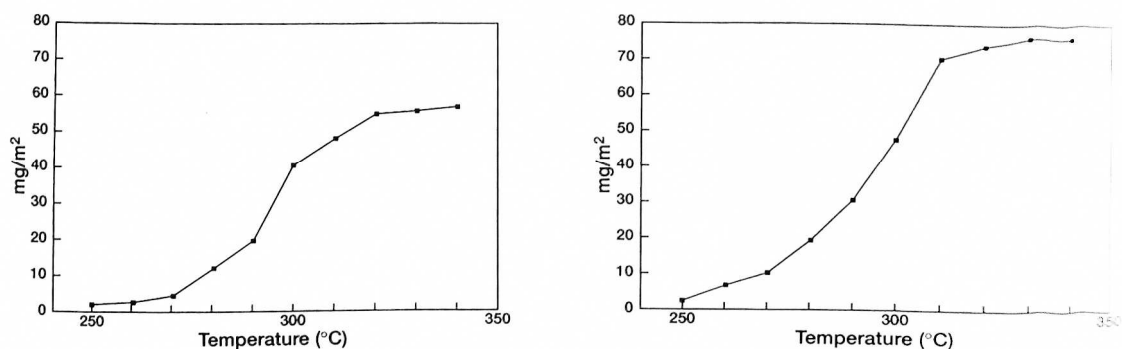


Figure 3: The weight increase as a result of the reaction between an aluminium foil and the gaseous products from NH₄HF₂ (left) and NH₄BF₃ (right) as a function of temperature during heating-up at a rate of 10°C/min.

By calculating the total surface area of the aluminium profiles in the furnace load and assuming a maximum thickness of 70 mg/m² of fluoride, one can estimate the efficiency of the total procedure of coating the aluminium surface with AlF₃ in the furnace. In one particular case, for extrusion profiles with 1.5 m² of aluminium surface area per m³ of furnace load, this efficiency was about 5%.

4. DISCUSSION AND CONCLUSION

High Temperature Oxidation (HTO) can arise during solution heat treatment in a forced-air furnace. As a rule of thumb one may state that for a particular aluminium alloy during solution heat treatment:

$$\text{HTO BLISTERS} = (\text{Sub-surface defects}) \times (\text{Water vapour partial pressure})$$

Thus there are three ways of preventing HTO blisters during solution heat treatment: (1) prevention of significant sub-surface defects and (2) lowering the water vapour partial pressure in the furnace and (3) treatment of the aluminium surface such that reaction with water vapour is prevented.

4.1 Sub-surface defects

The best way of solving a HTO problem is thus to ensure that significant sub-surface defects do not arise. In our case this meant looking into the extrusion processing. The clues could be found in the samples such as shown in figure 1. The blisters observed in this study had large sub-surface impurities in the metal, consisting mainly of aluminium oxides (or hydroxides). These defects can be related to the indirect extrusion process, in which the surface of the extrusion billet is more likely to flow into the extruded product than with direct extrusion. Even with scalped billets, as in our case, this may lead to defects. The slightly oxidised layered structures found in our samples indicates that

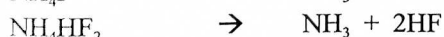
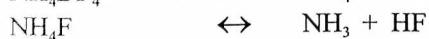
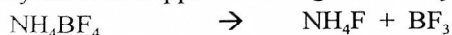
material which had accumulated very close to the extrusion container has flowed into the extrudate. By lowering the container temperature, this problem could be resolved, thus virtually eliminating the occurrence of HTO blisters.

4.2 Furnace atmosphere

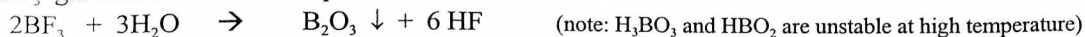
Lowering the partial pressure of water vapour in the furnace is only practical if excess water vapour above ambient concentrations exist in the furnace. As the solution heat treatment furnace is of the forced-air type, any excess water vapour will leak away to the environment. Gasses, such as reaction products from fluoride salts, will also leak into the environment. In our own furnace, typical exponential "decay times" to ambient conditions are of the order of half an hour.

4.3 The use of fluoride salts

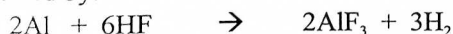
Three compositions are reported as being used successfully in production: NH_4BF_4 , NH_4HF_2 and thirdly the direct application of gaseous BF_3 . The relevant reactions are:



the BF_3 gas reacts with water vapour in the furnace:



followed by:



The AlF_3 then forms a protective layer on the surface that prevents the reaction of water vapour with the aluminium.

Prevention of HTO by the use of fluoride salts should be minimised because of the toxic nature of these salts and their dissociation and reaction products (HF gas!). This minimisation can be accomplished by proper timing of the release of the gaseous products of these salts into the furnace. Ideally, the furnace load should have reached about 300°C before these gases are released, as reactions start only above 300°C (figure 3). It has been shown that NH_4BF_4 dissociates at a higher temperature than NH_4HF_2 , which can be an advantage. The BF_3 gas has the double function of taking away water vapour and the generation of a protective layer. BF_3 gas, when bought separately, is expensive though. Concerning the reaction of BF_3 gas with water vapour in the furnace atmosphere, it is important to note that there is sufficient water vapour in the furnace, even at ambient conditions, for this reaction to be relevant (air with 100% humidity at 20 °C has 17 g/Nm³ of water vapour). A disadvantage of both NH_4BF_3 and BF_3 is that B_2O_3 is formed as a reaction product, which is a solid at all relevant temperatures and which will accumulate in the furnace and possibly its immediate surroundings. There is thus room for improvement in this area.

ACKNOWLEDGEMENT

I would like to thank ir. Louis Tack for stimulating discussions and for gracefully bearing with me in his office over an extended period of time.

REFERENCES

- [1] Hans Kostron, Aluminium und Gas, Band 43, Heft 3, pp 269-284 [in German].
- [2] Hans Kostron, Aluminium und Gas, Teil II: Blasen und Poren im Knetmaterial, Band 43, Heft 3, pp 373-387 [in German].
- [3] D. Altenpohl, "Aluminium und Aluminiumlegierungen", Springer Verlag, 1965, pp 95-99 [in German].
- [4] T. Croucher, "Light Metals pt.2. Solution heat treating of aluminium", Heat Treating vol.14, nr.3, March 1982, pp 18-19.

- [5] P.L. Lenzi, E. Di Russo, "The effect of heat-treatment furnace atmospheres on some physical-mechanical characteristics of [aluminium] light alloys", *Alluminio* vol. 36, nr 8, Aug. 1967, pp 401-407 [in Italian].
- [6] J.E. Hatch (ed.), "Properties and Physical Metallurgy", *Am.Soc. Metals* (1984), ISBN 0-87170-176-6, pp 156-157.
- [7] "ASM Handbook", vol.4: Heat Treatment, (1991), pp 848-851.
- [8] L. Stojanova, S. Yaneva, N. Stojchev, "Zur Kinetik der Wasserstoffsammlung in Künstlicher Glühblasen bei Oxidation von Aluminium in wasserdampfhaltiger Atmosphäre", *Z Metallkunde* 78 (1987), pp 452-456 [in German].
- [9] N. Kawashima, H. Yamada, Y. Sato, "Study on the blistering of aluminium (2nd report: Blistering caused by aqueous vapour in the heating atmosphere)", *Light Metals (Tokyo)* Vol.13 nr.5, (1963), pp 5-12 [in Japanese].
- [10] N. Kawashima, H. Yamada, T. Yokote, H. Ueno, "Study on the blistering of aluminium (3rd report). Blistering caused by water vapour in the heating atmosphere", *Light Metals (Tokyo)* Vol.14 , nr.4, (1964), pp11-18 [in Japanese].
- [11] H.F. Ades, A.L. Companion, "The interaction of hydrogen with point defects in aluminium metal", *Surface Science* 177 (1987), pp 553-564.
- [12] P.E. Blackburn, E.A. Gulbransen, "Aluminium reactions with water vapor, dry oxygen, moist oxygen, and moist hydrogen between 500° and 625°C", *Journal of the Electrochemical Society*, Dec. 1960, pp 944-950.
- [13] F. Winter, W. Gruhl, "Versuche zur Blasenbildung auf festem Aluminium beim Glühen in wasserdampfhaltiger Atmosphäre", *Metall* 31, Heft 6 (June 1997), pp 595-599
- [14] K.B. Das, E.C. Roberts, G. Bassett, "An investigation of blistering in 2024-T6 aluminium alloy", *Hydrogen in Metals*, Proc. Int. Conf. on the effects of hydrogen on materials properties and selection and structural design, 23-27 Sept. 1973, *Champion, Pa.*, pp 289-299.
- [15] M.R. Louthan Jr., A.H. Dexter, "Hydrogen embrittlement of 1100 aluminium", *Metallurgical Transactions A*, Vol. 6A (Aug. 1975), pp 1655-1657.
- [16] F.D.S. Marquis, "Mechanisms of formation of hydrogen porosity in 7X50 and 2X24 aluminium alloys. Effects on mechanical behavior", *Conf. Gas Interactions in Nonferrous Metals Processing*, Anaheim, 4-8 Feb. 1996, pp 43-62.
- [17] S.A. Levy, R.S. Mapes, "High temperature oxidation of formed aluminium parts", *Hydrogen in metals Proceedings of the Second International Congress on Hydrogen in Metals*, vol. 10, paper 6B4, Paris, June 1977, Pergamon Press.
- [18] ASTM standard B 597-90, "Standard Practice for Heat Treatment of Aluminium Alloys", 1990.
- [19] B. Cao, N. Gao, D. Wang, L. Zhang, "Characterization of defects in hydrogen charged aluminium by PAT and TEM", *Materials Science Forum*, Vols 175-178 (1995), pp 311-314.
- [20] G. Ibe, F. Winter, W. Gruhl, "Ursachen und Kinetik der Bildung von Wasserstoffblasen beim Glühen von Aluminium in feuchter Atmosphäre", *Zeitschrift für Metallkunde*, Vol, 79, Bd. 70 (1979) H. 9, pp 561-566 [in German].
- [21] F. Winter, W. Gruhl, "Wasserstoffaufnahme von festem Aluminium durch Glühen in wasserdampfhaltiger Atmosphäre", *Zeitschrift für Metallkunde*, (Dez. 1975), H. 12, pp 1204-1209.
- [22] T. Croucher, "Light metals Part 2. Solution heat treating of aluminium", *Heat Treating*, Vol. 14, nr. 3 (March 1982), pp 18-19.
- [23] US standard MIL-H-6088F, pp 17 (B-4).
- [24] H.W. Long, Chapter "Metallurgy, heat treatment of alloys", *Non Ferrous Metal Technology*, Technical Services, Madison, Alabama, USA.
- [25] DIN 29.850, "Wärmebehandlung von Aluminium-Knetlegierungen", Juli 1983 [in German].
- [26] ASM Handbook, Vol. 4, Heat Treatment (1991), pp 848-851.
- [27] US patent 4391.655, 1983.