THE EFFECT OF ZINC ADDITIONS ON THE CORROSION PROPERTIES OF ALUMINIUM-MAGNESIUM ALLOYS

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ABSTRACT : A zinc addition in a Al-Mg alloy is one way of improving the strength of the welded sheet. Besides, a quick literature survey indicates that zinc is beneficial to the resistance to structural corrosion after artificial ageing. Trials on an industrial scale at Pechiney confirmed a better resistance to intergranular corrosion of Al-5%Mg alloys containing zinc. It is due to an homogenisation of the magnesium precipitation and to the reduction of the corrosion potential gap between matrix and grain boundary anodic precipitates. However, severe pitting and exfoliation corrosion is observed after the exfoliation ASSET test on welded specimens, in a narrow region situated on both sides of the weld. This zone seems to correspond to an anodic part of the weld stemming from the solutionising of zinc and magnesium in the heat affected zone.

Keywords *: Aluminium-Magnesium alloys, zinc, corrosion, pitting, exfoliation, intergranular, weld*

1. INTRODUCTION

Aluminium sheets of the Al-Mg series show a good combination of mechanical strength, formability, weldability and exhibit an excellent resistance to corrosion in marine environments. The conventional AA5083 alloy has for instance been used for decades in ship construction, more particularly in High Speed Light Craft.

Answering the requirements of shipyards for an alloy with improved mechanical strength after welding, Pechiney Rhenalu patented [1] a new alloy designated AA5383. Since the resistance to corrosion is one of the key factors for Al-Mg alloys, it was checked that 5383 performs at least as well as 5083, on the base material (see [2] for instance) and on weldments, by accelerated laboratory testing and natural exposure trials.

It is temptating to investigate new ways of improving the strength after welding of Al-Mg alloys, above the level reached by 5383. In particular, the addition of zinc has been cited many times in the literature as a possible solution since zinc and magnesium can form hardening precipitates that increase the strength of the heat affected zone (HAZ) of weldments. Some Al-Mg-Zn alloys have even been registered by the Aluminium Association in 1960-1970 (see AA5080, AA5084 and AA5014 for instance). Some studies on such alloys have also been conducted by Pechiney, in the early eighties [3], but corrosion problems associated with welding caused zinc additions in Al-Mg alloys to be considered dangerous.

In 1997, following the renewal of the marine market interest for zinc containing 5xxx alloys, we investigated the effect of zinc on the corrosion properties of aluminium-magnesium alloys. The objective of this paper is to report on the experimental results that were obtained.

2. QUICK LITERATURE SURVEY

Though Al-Mg alloys are very resistant to corrosion in the as-produced temper, they may become sensitive to intergranular (IGC), exfoliation (EC) or stress corrosion (SCC) when exposed at temperatures ranging from 50°C to about 200°C. For this reason, the use of 5xxx alloys with magnesium content exceeding 3.5 % is generally not recommended above 65°C. The underlying mechanism of sensitisation is well documented : during ageing, magnesium diffuses towards the grain boundaries and precipitates in the form of a thin film of the β-Al_3Mg_2 phase. In a standard saline solution, this phase is highly anodic with respect to the Al-Mg solid solution. Provided that the film formed at the grain boundaries is continuous, it is oxidised in a microgalvanic coupling process which results in the rapid consumption of the Al_3Mg_2 grain boundary compound.

This accounts for the everlasting interest among researchers and aluminium producers for finding minor additions that reduce the sensitivity to ageing of Al-Mg alloys. Zinc, for instance, has regularly been studied since the forties, starting from the early work of Siebel and Vosskühler [4] who suggested that it had a pronounced influence on the corrosion resistance of Al-Mg alloys. Perryman [5] added 0 to 2% Zn to an Al-7%Mg alloy and observed that zinc fosters magnesium precipitation inside the grains, which is beneficial to corrosion resistance after ageing (at 200°C, it is reported that 0.5% Zn lowers Mg solubility from 3 to 1%). The addition of zinc therefore delays the apparition of the microstructure susceptible to SCC. Furthermore, zinc renders the matrix more anodic which reduces the potential gap between the β-Al_3Mg_2 phase and the matrix, decreasing the driving force for structural corrosion.

Akeret [6] noticed a reduction in the grain boundary precipitation of an Al-4.5%Mg-Mn containing 1% Zn.

Campbell [7] studied different Al-Mg alloys (Mg : 3.5%-6%, Mn : 0.2%-0.8%, Zn : 0%-1%) in the annealed or cold-worked temper, with or without artificial ageing. It was observed that zinc and manganese additions allowed a higher level of magnesium for a given level of sensitisation.

3. EXPERIMENTS CONDUCTED AT PECHINEY

3.1. Experimental procedure

Industrial type manufacturing was used for this study, involving large scale casting, rolling heat treating steps starting from 450mm x 1450mm x 2400mm ingots. The composition of the 6mm thick sheets fabricated and characterised is given in table 1.

Alloy	Si	Fe	Mg	Mn	Zn	Zr	Cu	Cr
AGZ1.3	0.074	0.11	5.5	0.81	1.33	0.11	0.17	0
AGZ0.7	0.06	0.10	5.4	0.81	0.71	0.11	0.17	-
AGZ0.55	0.11	0.14	5.0	0.82	0.55	0.11	0	0
AGZ0.35	0.10	0.12	5.3	0.85	0.35	0.12	0	0
5383	0,07	0,13	4,55	0,80	< 0,01	< 0,002	0,08	0,1

Table 1 : Chemical compositions of Zn containing Al-Mg alloys studied.

The mechanical and corrosion properties were evaluated on the as-rolled and heat-treated sheets and also after welding. MIG welding was performed with 5183 filler wire.

The sensitivity to intergranular corrosion was assessed on the base material by the so-called Interacid test [8], consisting in the immersion of a sample in a NaCl + HCl solution followed by a mass loss or corrosion depth measurement. The resistance to exfoliation corrosion was evaluated on welded specimens by the ASSET test (ASTM G66).

Corrosion behaviour was studied on the as-fabricated (or as-welded) specimens and also after artificial ageing treatments that entail sensitisation to structural corrosion. In particular, ageing 7 days at 100°C simulates the long-term exposure of Al-Mg alloys [9,10] and is consistent with a thermally activated process for magnesium precipitation. More precisely, precipitation reactions that occur at temperature T_1 for a period of time t_1 is equivalent to accelerated ageing performed at T_0 during t_0 :

$$t_0.\exp\left(-\frac{K}{T_0}\right) = t_1.\exp\left(-\frac{K}{T_1}\right)$$

where K is a constant involving the activation energy of magnesium (or zinc) diffusion, varying in the literature from 10 000K to 13 500 K. Typical (T,t) equivalences are as follows :

7 days at 100°C ≈ 6 months at 60°C ≈ 16 years at 25°C.

The ageing for 7 days at 100°C thus allows for the prediction of the corrosion behaviour at room temperature for periods of time exceeding 5 years.

3.2. Results

Figures 1 and 2 describe the influence of the zinc content on the IGC susceptibility as a function of the artificial ageing treatment. Although the mass loss is lower for 5383 after short ageing treatments, it increases significantly as ageing proceeds whereas the evolution of the mass loss with ageing of Al-Mg-Zn alloys is slower. After 20 days at 100°C, only pitting and uniform corrosion is observed on Al-Mg-Zn alloys whereas 5383 displays intergranular attack. Zinc additions are thus beneficial to the IGC resistance. This is consistent with the data found in the literature and can be attributed to two effects : an homogenisation of magnesium precipitation (preventing magnesium from precipitating exclusively at grain boundaries) and a decrease in the potential gap between matrix and grain boundary precipitate Al_3Mg_2.

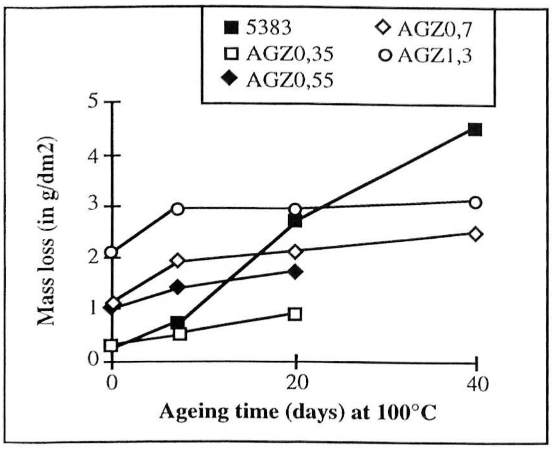

Figure 1 : Influence of composition and ageing on the mass loss after Interacid IGC test.

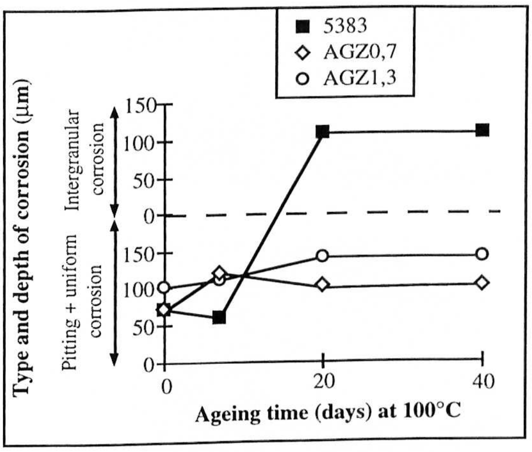

Figure 2 : Influence of composition and ageing on the type and depth of corrosion after Interacid test.

Figure 3 is made of photographs showing welded specimens of the alloys studied, as-welded or aged 7 days at 100°C, after the ASSET exfoliation test. The photographs correspond to the 10% machined surface of the weldments (the corrosion on the original surface is comparable but the photographs are less clear). The behaviour of the non-welded material can be evaluated by considering the metal away from the welded joint.

On 5383, a band of approximatively 5mm wide on each side of the joint, corresponding to the recrystallised HAZ, is free from corrosion. This is consistent with the well known mechanism for exfoliation corrosion (at least for Al-Mg alloys) : exfoliation corrosion occurs when the alloy is susceptible to IGC and has an elongated grain structure. In the recrystallised HAZ, the grain structure is no longer able to entail exfoliation corrosion.

On Zn-containing Al-Mg alloys, the influence of the copper content can be assessed by comparing the photographs : the alloys that contain 0.17% Cu exhibit severe pitting corrosion whatever the location along the welded sample. This detrimental influence of copper on pitting corrosion resistance is well documented in the literature [11].

Especially after ageing 7 days at 100°C, the welded specimens of Al-Mg alloys containing zinc experienced relatively severe pitting and exfoliation corrosion in a narrow band situated in the HAZ, a few millimeters from the joint. This susceptible zone is worrisome because it is a potential initiation site for fatigue or mechanical failures. It recalls the problems that were encountered a few years ago on welded Al-Zn-Mg alloys [12].

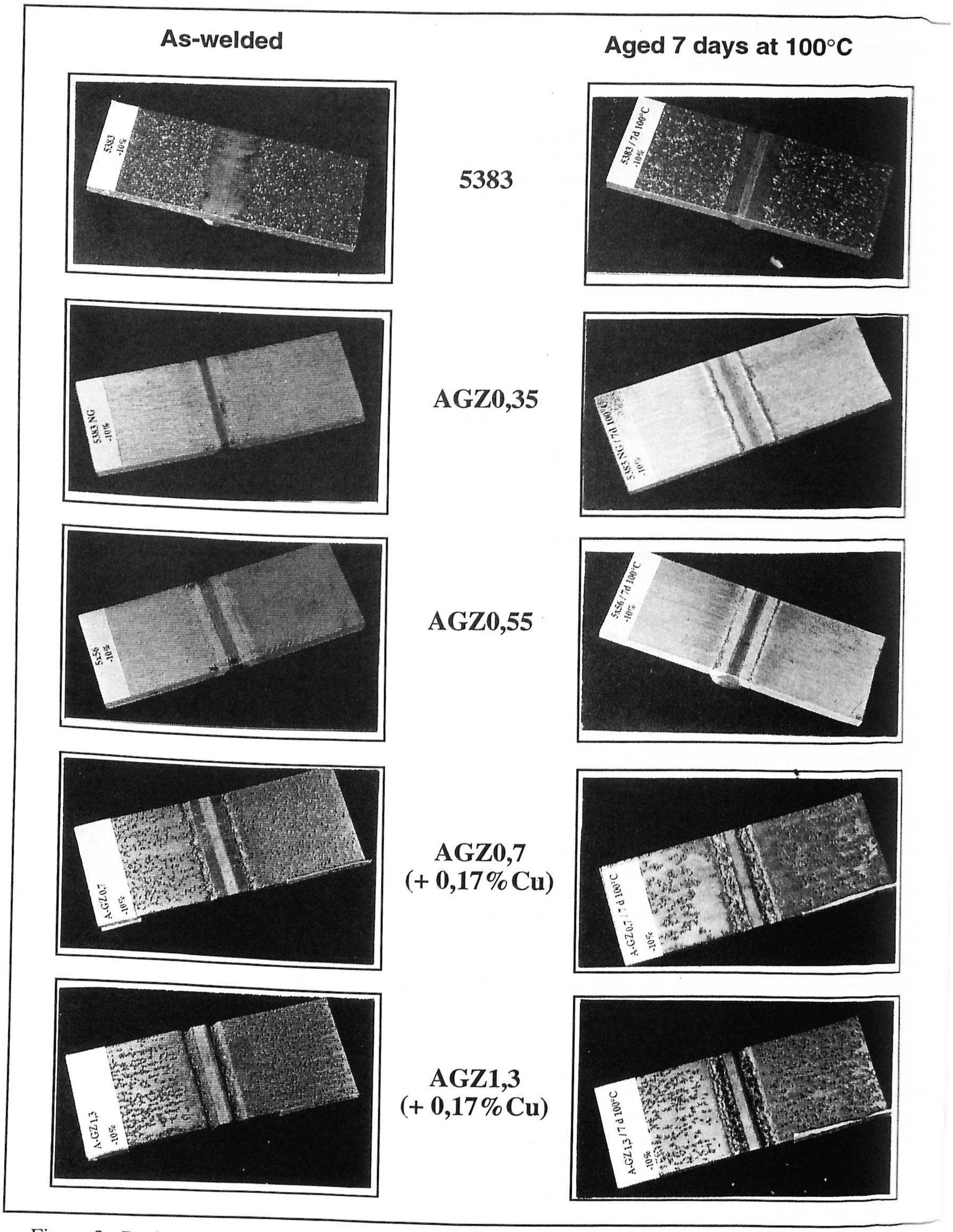

Figure 3 : Resistance to exfoliation of welded Al-Mg alloys containing various amounts of Cu and Zn compared to 5383. ASSET tests conducted before and after ageing 7 days at 100°C.

4. A TENTATIVE EXPLANATION OF THE EFFECT OF ZINC AFTER WELDING

It must be firstly recalled that Zn in solid solution renders aluminium anodic whereas Mg has almost no effect on the corrosion potential. After welding, zinc will be solutionised in the heat affected zone. Artificial ageing will then complete zinc precipitation on the work hardened structure away from the HAZ and the zinc concentration profile can be schematically described by figure 4. This entails corrosion potential gradients as shown by figure 5. In this galvanic cell, heat affected zones with maximal Zn solutionising will behave like small anodes faced with an infinite cathode, and rapid corrosion will occur.

It is generally believed that a potential gradient of 40 mV is sufficient to give rise to microgalvanic corrosion in aluminium alloys. This corresponds approximatively to 0.5% Zn. It is therefore not surprising to observe this detrimental behaviour for Zn contents as low as 0.5%.

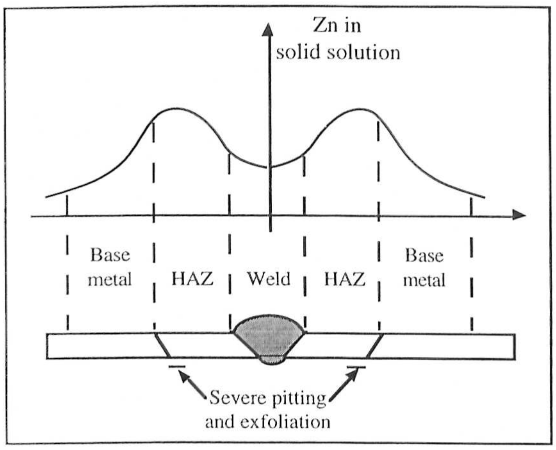

Figure 4 : Gradient of Zn content in solid solution across a welded Al-Mg-Zn alloy.

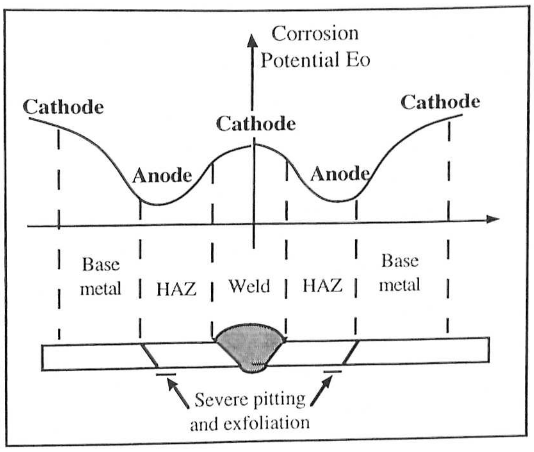

Figure 5 : Gradient of corrosion potential across a welded Al-Mg-Zn alloy.

Again, the localisation of the susceptible region at the end of the HAZ stems from the fact that the metal in this region has undergone zinc solutionising but no recrystallisation, which allows exfoliation to take place. On the contrary, the region of the HAZ that is next to the joint has undergone both zinc solutionising and recrystallisation : the grain structure no longer allows exfoliation.

5. CONCLUSIONS

1 - In Al-Mg alloys, a zinc addition improves the intergranular corrosion resistance of the base metal, which is attributed to homogenisation of the magnesium precipitation and to the decrease of the potential gap between grains and grain boundaries.

2 - However, we also observed that zinc additions have a detrimental effect on the corrosion resistance of weldments, especially after ageing. We explain this observation by considering the process of resolutionising and precipitation of magnesium and zinc in the non recrystallised part of the HAZ, which probably entails galvanic coupling between the anodic HAZ and the cathodic weld bead.

REFERENCES

[1] International patent application WO 96/26299. Pechiney Rhenalu.

[2] R. Dif, T. Warner, G.M. Raynaud. 6th International Congress on Aluminium Alloys. 1998.

[3] Unpublished results. Pechiney CRV. R. Vignaud, G. Pillet, C. Bommier. File 3344. 1986.

[4] G. Siebel, H. Vosskühler. Z. Metallkunde, 32. 1940.

[5] E.C.W. Perryman, S.E. Hadden. J. Inst. Metals, 77. 1950.

[6] R. Akeret. Mémoires Scientifiques Revue Métallurgique, 3. 1980.

[7] C.H.S. Campbell. Proceedings of "The Metallurgy of Light Alloys", Loughbourough, UK. March 1983.

[8] Journal Officiel des Communautés Européennes (13/09/74) N° C104-84 to 89.

[9] E.H. Dix, W.A. Anderson, M. Byron Shumaker. Proceedings of the 4th Annual Conference of NACE, San Francisco. 1958.

[10] K. Van Horn. "Aluminium, Vol. 1". ASM, Metals Park, Ohio. 1967.

[11] M. Reboul, T. Warner, H. Mayet and B. Baroux. Corrosion reviews, vol. 15, N°3-4. 1997.

[12] M. Reboul, J. Bouvaist. Revue de l'Aluminium. Janvier 1980.

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