

EFFECT OF BERYLLIUM TRACE ADDITION ON THE DYNAMIC SCC BEHAVIOR OF AGED ALUMINIUM-5% ZINC-4% MAGNESIUM ALLOY

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ABSTRACT

The dynamic SCC behavior of a high strength Al-5% Zn-4% Mg-0.01% Be alloy has been studied in 3.5% NaCl solution using a slow strain rate tensile testing set-up. The influence of the presence of beryllium in trace quantities is most significant in the peak-aged condition and not in the under-aged or over-aged conditions. Through minimizing of grain boundary precipitation, avoidance of PFZ and promoting a more uniform and fine scale precipitation, beryllium brings about a change in the brittle intergranular fracture into transgranular ductile fracture and increases toughness and resistance to dynamic SCC.

KEYWORDS

SCC, Dynamic, PFZ, precipitation, trace element, brittle, ductile, fractograph

INTRODUCTION

Among the aluminium based age-hardenable alloys, the Al-Zn-Mg system is known to offer compositions that develop the highest strength (Mondolfo, 1976). However, these alloys suffer from the disadvantage of high susceptibility to SCC in the high strength condition. There have been several attempts (Day, Cornish and Dent, 1969; Latanson and Stahele, 1967; Neilson, 1970; Parkins, 1964; Polmear, 1960; Pugh and Jones, 1961; Sedericks, Slattery and Pugh, 1969; Thomas and Nutting, 1959) to correlate this behavior with the structure and composition of the grain boundary region. There also exists a certain amount of disagreement about the origin and mechanism of SCC in these high strength alloys. Most explanations are based on the role of either the grain boundary structure, or the grain boundary chemistry or both. Subsequent efforts have been aimed at overcoming these limitations by thermal, mechanical or thermo-mechanical treatments or by compositional variations. A singular effort has been the control of microstructure through trace elemental additions. Such additions bring about a change in the precipitate size, morphology and distribution. Since SCC behavior is markedly influenced by the nature and distribution of precipitates, the trace element addition must also exert an influence on the SCC behavior of the alloy.

In the Al-Zn-Mg system, it has been found that if the Zn+Mg content of the alloys is ca. 9%, they develop good strength as well as resistance to SCC

(Polmear and Sargent, 1963; Ryum, Haegland and Lindtveit, 1967). While copper additions have proved futile in this regard, silver additions are very effective (Busby, Cleam and Cudd, 1971; Davies, 1968; Peters, 1971; Truscott and Calvert, 1967), especially in minimizing the occurrence of PFZ. Subsequent studies have revealed that several elements are capable of bringing about a similar influence, including chromium, manganese, indium and zirconium. In a more recent study (Chandrasekar, 1973) it was shown that the elements beryllium and boron bring about a significant change in the SCC behavior of Al-Cu, Al-Mg₂Si and such other aluminium based age hardening alloys. The extent and nature of the influence of beryllium addition had not been studied in the ternary Al-Zn-Mg system. It has been reported that beryllium exhibits a large binding energy (Dwarakadasa, 1970) with vacancies in aluminium matrix. Also it has been shown that the presence of beryllium changed the intergranular brittle fracture into a transgranular ductile one in aged Al-Zn-Mg alloys (Narendranath, 1980). Beryllium also considerably reduced the grain size in the processed alloy. Thus there existed sufficient indications to point to the possible influence on the precipitate morphology due to beryllium addition in the aged Al-Zn-Mg alloys. This project was therefore taken up to study the dynamic SCC behavior of an Aluminium-5% Zinc-4% Magnesium alloy to which 0.01% beryllium had been added. Results obtained are presented in this communication.

MATERIALS AND EXPERIMENTAL PROCEDURE

Large blocks of Al-5% Zn-4% Mg (base alloy) and Al-5% Zn-4% Mg-0.01% Be (Be-containing alloy) alloys were cast, hot forged and then hot rolled to get sheets 1 mm thick as per procedure described earlier (Narendranath, 1980). Tensile samples were milled out from the annealed sheets to have a gauge length of 20 mm. Solutionizing and ageing conditions were obtained from an earlier extensive study (Narendranath, 1980). Samples solutionized for 1 hr either at 570 °C or at 460 °C were quenched into an iced water bath and then aged at 160 °C for different periods to get specimens in the under-aged, peak-aged and over-aged conditions. All the specimens were polished, degreased and dried before mounting on to the SCC set-up. Tests for dynamic SCC behavior were conducted on a hard tensile testing machine using a slow strain rate technique. Strain rates were varied in the range 10^{-6} to 10^{-3} sec⁻¹. Aqueous deaerated 3.5% NaCl solution (pH=5.2 and temperature 25°C constant) and clean laboratory air were the environments chosen. The relative humidity in the vicinity of the test set-up varied in the range of 75-80% during the course of the tests. All the specimens were tested until complete fracture occurred, while automatically recording the load-elongation curve on a strip chart recorder, to enable the evaluation of Ultimate Tensile Strength (UTS), Per Cent Elongation (% El) and the Fracture Energy (E_f). The fracture energy was calculated as the total area under the stress-strain curve. After the specimens fractured, the two pieces of the fractured piece were transferred into the chamber of a Cambridge Stereoscan SEM model S-150, to examine the fractographic features.

RESULTS AND DISCUSSION

The aluminium-zinc-magnesium alloys are well known (Mondolfo, 1976; Pugh and Jones, 1961) to form precipitate-free zones (PFZ) on either sides of the grain boundaries on ageing. Formation of PFZ can, to a certain extent, be prevented by the addition of metals like silver. In the high strength Al-Zn-Mg alloy under investigation here, PFZ were clearly visible in the aged condition (Fig.

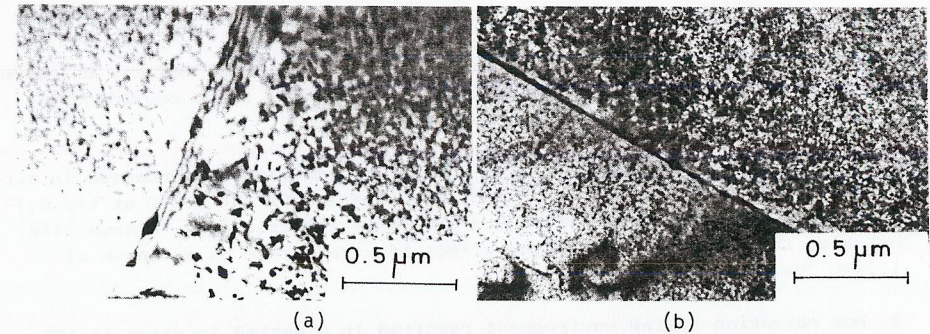


Fig. 1. Transmission electron micrograph of (a) base alloy and (b) beryllium-containing alloy showing presence of PFZ in (a) and its absence in (b)

1.(a). Addition of beryllium in trace amounts removed the PFZ nearly completely as shown in Fig. 1.(b). Also the presence of beryllium decreased the density of grain boundary precipitates indicating a retarded growth of the precipitates. Microstructures shown in Fig. 1. are for the peak-aged condition and were typical of observations made for all other ageing conditions.

The dynamic SCC behavior in air and in 3.5% NaCl studied in different heat-treated conditions and at different strain rates indicated a clear influence brought about by the addition of beryllium. The variation in the UTS of the two alloys as a function of ageing time is plotted in Fig. 2. A similar variation in the per cent reduction in area is plotted in Fig. 3. The effect of strain rate is also brought about in these plots. It is observed that in general increasing the strain rate leads to a reduction in the UTS and per cent reduction in area for all treatments. A better comparison results by considering the variation in the fracture energy values. In Fig. 4 is shown

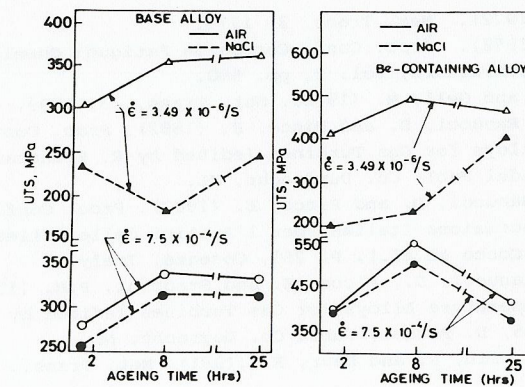


Fig. 2. Variation in the values of UTS as a function of strain rate and ageing time.

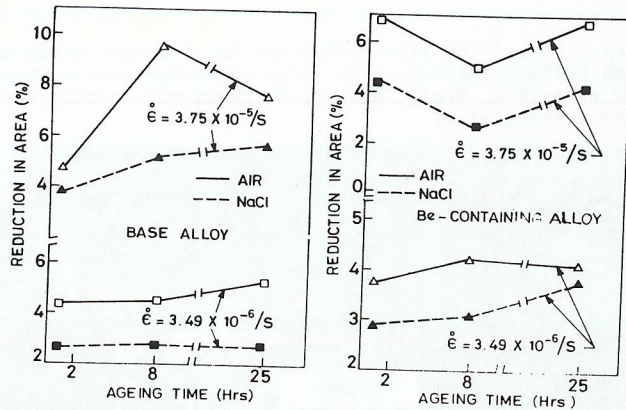


Fig. 3. Variation in the value of % reduction in area as a function of strain rate and ageing time.

the variation of the ratio of fracture energy measured in the 3.5% NaCl environment to that measured in air as a function of strain rate. This ratio was higher for base alloy than for the beryllium-containing alloy at all strain rates and for all heat treatments. Also in the base alloy it increased continuously with increase in strain rate. It was highest for the over-aged condition. In the beryllium-containing alloy the ratio initially decreased with strain rate and then showed an increase so that for strain rates greater than ca. $2 \times 10^{-4} \text{ sec}^{-1}$ this ratio was greater for the peak-aged and under-aged conditions than for the over-aged condition. Thus under dynamic SCC conditions the higher strength peak-aged condition exhibits a better resistance if beryllium is present in the alloy. It is also noticed that at the particular

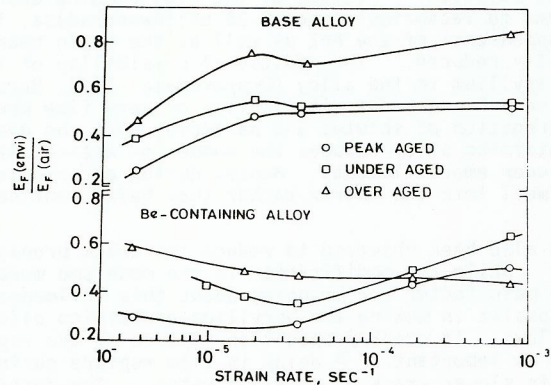


Fig. 4. Effect of strain rate on the ratio of fracture energy measured in 3.5% NaCl to that measured in air for different heat treated conditions.

strain rate of $2 \times 10^{-4} \text{ sec}^{-1}$ the behavior in all the heat treated conditions is the same. It was also observed that the influence becomes stronger as the solutionizing temperature is increased. This is understandable as the solubility of beryllium in the aluminium matrix increases with temperature rather steeply (Hansen and Anderko, 1958).

The influence of the presence of beryllium is also observed on the fracture surface in terms of the fractographic features. In Fig. 5 and Fig. 6 are shown the secondary electron images of fractured surfaces in the two alloys tested at two different strain rates. From these it is evident that in both the alloys a ductile rupture is observed for high strain rates of testing while at lower strain rates a brittle intergranular failure results.

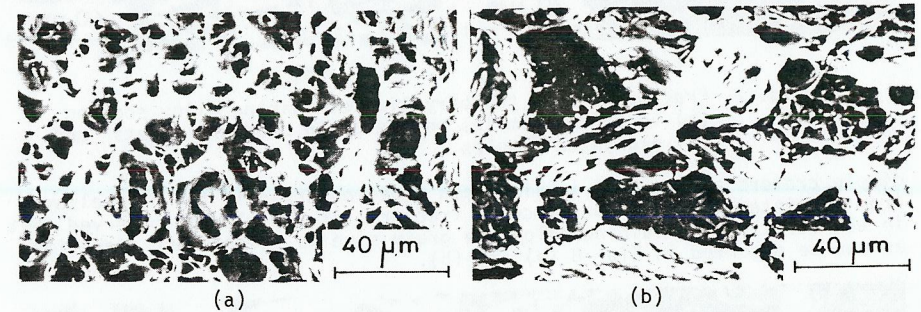


Fig. 5. Secondary electron images of fractures in specimens tested at a strain rate of $7.5 \times 10^{-4} \text{ sec}^{-1}$. (a) base alloy showing ductile dimples; (b) beryllium-containing alloy showing an intergranular ductile failure.

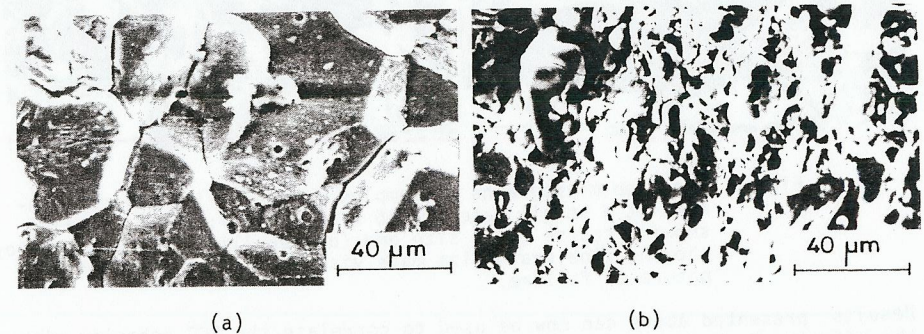


Fig. 6. Secondary electron fractographs of specimens tested at a strain rate of $3.5 \times 10^{-6} \text{ sec}^{-1}$; (a) base alloy showing brittle intergranular failure; (b) beryllium containing alloy showing ductile failure features.

On a comparative basis the beryllium-containing alloy exhibits a greater amount of ductile features at all strain rates of testing. Even when the failure is intergranular the grain boundary surface is filled with a large number of very

fine dimples reminiscent of an intergranular ductile failure (Fig. 7(a)). Also, the dimples in the beryllium containing alloy appear rather elongated (Fig. 7(b)). The presence of precipitate particles that appear in the

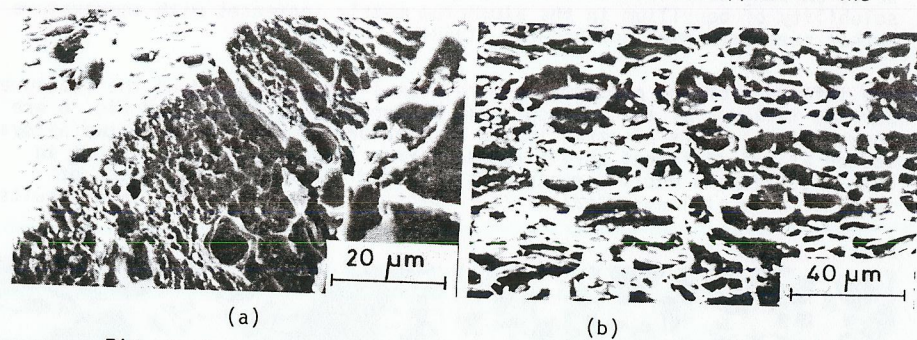


Fig. 7. Fractographs of the beryllium-containing alloy showing (a) very fine dimples on the grain boundary facets and (b) elongated dimples.

dimple craters are smaller in size than those observed in the base alloy. From the intergranular appearance of fractures it can also be observed that in the beryllium-containing alloy the grain size is refined and stabilized as can be observed in Fig. 8 (a) and (b).

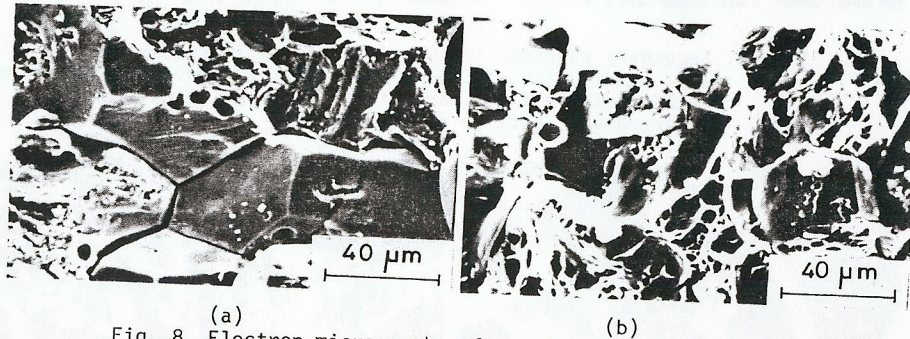


Fig. 8. Electron micrographs of samples fractured in NaCl environment at a strain rate of $3.5 \times 10^{-6} \text{ sec}^{-1}$; (a) base alloy showing coarse grain size and (b) beryllium-containing alloy showing fine grain size made visible by the intergranular nature of failure.

Results presented above can now be used to correlate the SCC behavior with the effects of changes in solute concentration near the grain boundary region and the consequent changes in the morphology of precipitates brought about by the trace addition. The base alloy exhibits a nearly continuous grain boundary precipitate with a wide PFZ (Fig. 1(a)) whereas in the beryllium-containing alloy PFZ is absent for all the ageing periods (Fig. 1(b)). Addition of beryllium also decreases the number of grain boundary precipitates thereby increasing the interparticle spacing. Thus the preferentially corroded paths would be large but widely spaced in the presence of beryllium

in the alloy. Beryllium also influences the fracture mode; while at low strain rates brittle failures with large corrosion debris were exhibited by the base alloy (Fig. 9(a)), ductile features were predominant in the beryllium-containing alloy.

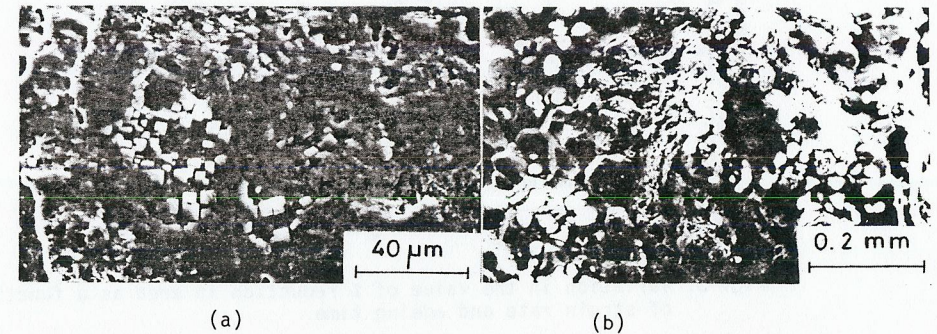


Fig. 9. Fractographs of samples tested in the NaCl environment at a strain rate of $3.5 \times 10^{-6} \text{ sec}^{-1}$. (a) base alloy showing heavy damage due to corrosion attack and the debris (b) beryllium-containing alloy showing predominantly ductile features on an otherwise intergranular failure.

The solubility of beryllium in the aluminium alloy matrix is considered to be an important factor which greatly influences the SCC behavior of the alloy. The solid solubility of beryllium in aluminium (Hansen and Anderko, 1958) is ca. 0.5% at the eutectic temperature of 645°C and decreases to less than 0.01% at 500°C and less than 0.001% at room temperature. When quenched from the solutionizing temperature above 500°C, a larger quantity of beryllium would be retained in solution. Because of the high binding energy exhibited by beryllium atoms to vacancies (of ca. 0.25 eV) (Dwarakadasa, 1970) in aluminium matrix, the appearance of the PFZ as well as the grain boundary precipitates are both greatly reduced. The additional possibility of independent precipitation of beryllium in the alloy (Dwarakadasa, 1970; Narendranath, 1980) results in a very homogeneous distribution of very fine precipitates. This decreased segregation of solutes and particles into the grain boundary in the beryllium containing alloy reduces the number of active sites for SCC and any possible hydrogen embrittlement. Hence, during deformation, strain fields are extended well into the matrix rather than being confined to the narrow PFZ.

Beryllium has also been observed to reduce the crack propagation rates (Chandrasekar, 1973). While the modification in the mode and morphology of precipitation is the main factor for bringing about this influence, several other factors also assist in making the beryllium-containing alloy more resistant to SCC as follow: In crack propagation rupture of the repassivating film at the crack tip is important. A delay in film rupture during slow straining could result in slower crack propagation rates. The ductility of the beryllium-containing alloy is higher. Higher ductility and a protective film would mean that the effect of stress concentration at the tip of the crack would be reduced. This follows directly from the fact that ductile materials possess low stress concentration factors (Forrest, 1962) thus increasing the probability of plastic blunting of the crack tip. Also stress accelerated dissolution and hydrogen entry are slowed down to result in lower crack propagation rates.

SUMMARY

Addition of trace amounts of beryllium to high strength Al-Zn-Mg compositions results in an increase in ductility through modification of precipitate distribution and formation. The resistance to dynamic SCC and to crack propagation are greatly enhanced as a consequence.

REFERENCES

- Busby, J., Cleam, J. C. and Cudd, R.C. (1971). J. Inst. Metals, 99, 419.
- Chandrasekar, R. (1973). SCC Behavior of Age Hardened Al-Zn-Mg Alloys, Ph.D. Thesis, Indian Inst. Sci.
- Davies, A. L. (1968). Metallurgica, 77, 51.
- Day, M. K. B., Cornish, A. J. and Dent, T. P. (1969). Met. Sci. J., 3, 174.
- Dwarakadasa, E. S. (1970). Clustering and Solute Vacancy Interactions in Aluminium-Zinc-X Alloys, Ph.D. Thesis, Ind. Inst. Sci.
- Forrest, P. G. (1962). Fatigue of Metals, Pergamon Press, London.
- Hansen, M. and Anderko, K. (1958). Constitution of Binary Alloys, McGraw Hill Book Co., New York.
- Latanson, R. W. and Stahele, R. W. (1967). Fundamental Aspects of SCC, Eds. Stahele, R. W., Forty, A. J. and Van Rooyen, D., NACE, Huston, Texas, 28.
- Mondolfo, L. F. (1976). Aluminium and Its Alloys: Structure and Properties Butterworths, London.
- Narendranath, K. R. (1980). Age Hardening, Deformation and Fracture Characteristics of Al-5Zn-4Mg Alloy, M.Sc(Engg.) Thesis, Ind. Inst. Sci.
- Neilson, N. A. (1970). J. Mater. Sci., 5, 102.
- Parkins, R. N. (1964). Met. Rev., 9, 201.
- Peters, B. C. (1971). J. Inst. Met., 99, 354.
- Polmear, I. J. (1960). J. Austr. Inst. Met., 89, 19.
- Polmear, I. J. and Sargent, K. R. (1963). Nature, 200, 669.
- Pugh, E. N. and Jones, W. R. D. (1961). Metallurgica, 63, 3.
- Ryum, N., Hegeland, B. and Lindtveit, T. (1967). Zeit. Metallkde., 58, 28.
- Sedericks, A. J., Slattery, P. W. and Pugh, E. N. (1969). Trans. Amer. Soc. Met., 61, 238.
- Thomas, G. and Nutting, J. (1959-60). J. Inst. Met., 88, 81.
- Truscott, J. M. and Calvert, D. S. (1967). J. Inst. Met., 95, 289.