Factors leading to grain-boundary fatigue crack propagation in Al-Zn-Mg alloys

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Fatigue crack propagation experiments have been carried out at low load amplitudes with a high purity and a corresponding commercial purity AI-Zn-Mg alloy. When the high purity alloy was tested in laboratory air, cracks were often seen to propagate along the grain boundaries. Particularly in the peak aged condition, this alloy is highly susceptible to failure by intercrystalline cracking. However, with dry nitrogen as the test environment, the crack was observed to propagate preferentially along shear bands within individual grains. In the commercial purity alloy, grain-boundary crack propagation was not observed for either laboratory air or dry nitrogen atmospheres. The proportion of intercrystalline cracking in laboratory air could be lowered for the high purity alloy by a thermomechanical treatment.

1. Introduction

The interest in A1-Zn-Mg alloys has intensified in recent years because they possess the highest known yield strengths among the entire series of A1 alloys. The high purity A1-Zn-Mg alloys are, however, susceptible to intercrystalline cracking (ICC) in the age-hardened condition, a fact that leads to low associated ductility. This tendency for brittle fracture has received considerable attention by previous workers, and the main variables responsible for the occurrence of ICC in unidirectional loading appear to be reasonably well established [1, 2]. For example, the higher the yield strength of the alloy, the larger is the observed proportion of ICC. Furthermore, at comparable yield strengths, a larger area fraction of grain boundary precipitate favours increased occurrence of ICC.

That ICC plays an important role during fatigue loading of these alloys has also been indicated by previous workers. McEvily *et al.* [3] have fatigued samples of a high purity A1-5.5 Zn-2.5 Mg alloy and found that the fatigue crack propagation in the age-hardened condition occurs almost exclusively along grain boundaries. Unwin and Smith [1] have investigated the fracture toughness of a high purity A1-6 Zn-3 Mg alloy and found that as much as 85% of the initial fatigue crack area had been formed in an intercrystalline manner.

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Preferential grain-boundary deformation and crack nucleation at the grain boundaries in the overaged condition have been reported from surface observations of test pieces fatigued in torsion by Stubbington [4] in a high purity A1-7.5 Zn-2.5 Mg alloy and by Finney in one consisting of Al–6.3 Zn–2.9 Mg [5]. Ryder and Lynch [6] have observed about equal proportions of transgranular and intergranular crack propagation after torsion fatiguing a high purity A1-6.3 Zn-2.9 Mg alloy aged to relatively high yield strengths (\sim 400 MN m⁻²) and to contain a small fraction of grain boundary T phase $[(A1 Zn)_{49}Mg_{32}]$. Specimens with large fractions of grain boundary T phase showed exclusively intercrystalline fracture. Intercrystalline crack *initiation* was observed for low and intermediate fatigue stresses, regardless of the grain-boundary composition.

It is proposed in this work to formulate more systematically the conditions under which ICC occurs in A1-Zn-Mg alloys containing low $Zn + Mg$ content and which are fatigued at low load amplitudes. Among the factors that will be shown to influence the degree of grain-boundary cracking are the thermal and mechanical treatment, the degree of purity of the alloy, and the test environment. Experiments characterizing the effect of these variables on the crack propagation behaviour will be described.

2. Experimental details

Both the commercial purity Al-Zn-Mg-l* and corresponding high purity ternary alloy (with nearly the same Zn and Mg contents but without the impurity additions) have been employed for the tests. The compositions, in weight per cent, are as given in Table I.

TABLE I Compositions

	(1) Commercial purity alloy	(2) High purity alloy		
Zn	4.7 (2.0 at. $\frac{9}{9}$)	4.9 $(2.1 \text{ at. } \%)$		
Mg	1.2 $(1.3$ at. $\%)$	1.2 $(1.3$ at. %)		
Cr	0.12			
Zr	0.15			
Mn	0.25			
Fe	0.3	0.02		
Si	0.3	< 0.01		

The alloys were obtained in rod form through the courtesy of Vereinigte Aluminium-Werke (VAW). The rods, 10 mm in diameter, were rolled down to 1.5 mm thick strips from which specimens with 6 mm \times 1.5 mm cross-section were machined. A 0.8 mm deep notch was made on one side to reduce the time for crack nucleation and also to predetermine the crack nucleation site.

After homogenization, the grains in the high purity alloy were 0.1 to 0.4 mm in size with large planar boundaries. In the commercial alloy, due to the presence of grain growth inhibiting elements, the grains were relatively small, about 0.04 mm in size, and the grain boundaries were somewhat rough. The high purity alloy was heat-treated in order to produce basically three conditions: (1) underaged (2) aged to peak hardness and (3) overaged. The heat-treatments that yield peak hardness for the pure alloy were derived from the work of Bryant [7]. For the commercial alloy, ageing was carried out at temperatures below 130°C in order to obtain a yield strength of about 252 MN m^{-2} . Some samples were subsequently aged at 170° C to produce a somewhat overaged condition (yield strength of about 228 MN m^{-2}). The details of the heat-treatments are given in Tables II and IV for the high purity and commercial purity alloys, respectively.

The crack propagation experiments with the

high purity alloy were also carried out with samples which were thermomechanically treated. The thermomechanical treatment (TMT) consisted of solution treating, rolling to 50% reduction in thickness and then ageing for about 3 days at 100°C. It was found that after this TMT the samples had a yield strength of about 244 MN m⁻² and an elongation value of about $7\frac{\%}{\%}$ in the longitudinal direction.

Another very important variable investigated in these experiments has been the test environment. Most of the crack propagation tests were carried out either in laboratory air environment or under a flowing nitrogen gas atmosphere which had been dehumidified by cooling to near the temperature of liquid nitrogen. A few samples have also been tested under flowing dry argon (argon dehumidified by cooling to about $-$ 50 \degree C) or dry air (dehumidified by cooling to about -80° C) atmospheres. These four test environments are designated as moist air, dry nitrogen, dry argon and dry air, respectively.

In all cases, after the heat-treatment the samples were electropolished to be able to observe the crack propagation more clearly and were then fatigued under loads varying sinusoidally at 50 Hz (tension-compression). The stress amplitudes were always below one fourth of the yield strength of the heat-treatment under consideration. Plane strain conditions are, therefore, expected to prevail during crack propagation tests. The crack propagation was followed during the experiment with an optical microscope, using stroboscopic illumination. The fatigue tests were interrupted after the crack had attained a length of 2 to 3 mm. In all cases, at the end of the test the sample containing the crack was mechanically polished, etched to reveal the crack path with reference to the grain boundaries, and the broad surface studied with an optical microscope. Subsequently, the samples were pulled in tension to complete fracture and the fatigue fracture surfaces were studied using scanning electron microscopy (SEM).

3. Experimental results

3.1. Crack propagation experiments with the high purity alloy

3.1.1. Normally heat-treated (solution treated and aged) samples

Table II summarizes the results of the various crack propagation experiments.

Sample no.	Heat-treatment	Nature of precipitates and pre- cipitate free zone (PFZ) width	strength $(MN m^{-2})$ mm	0.2% yield % elonga- Test		Crack path (trans- or tion in 31 environment intergranular)
R 10	1 h at 400° C (homo) 153 h at $R.T+$] (ageing) 128 h at 135° C (aged to peak hardness)	Small η' ppt 276 in matrix η at the grain boundaries $PFZ \sim 0.08$		7.4	Moist air	About 50% intergranular (Figs. 1a, 2a)
R ₉	as R 10	μ m as R 10	276	7.4	Dry argon	Predominantly transgranular (Fig. 1b)
R 11	As R 10	as R 10	276	7.4		Dry nitrogen Transgranular (Fig. 2 _b
R 16	as R 10	as $R10$	276	7.4	Dry air	Predominantly transgranular
R 13	1 h at 400° C (homo) 12 days at $R.T+$ 2 days at 135° C+ (ageing) 3 days at $160^{\circ}\mathrm{C}$ (somewhat overaged)	n at grain boundaries	222	8.5	Moist air	Mainly transgranular (Fig. 2c)
R 12	1 h at 400°C (homo) 96 h at R.T+ $\,$ 18 h at 135 $^{\circ}$ C+ (ageing) 96 h at 170°C (overaged)	Essentially η' (large particles) $+$ small amount of η in				
		matrix η at grain boundaries $PFZ \sim 0.08$ µm	171	13.2	Moist air	Mainly transgranular
R 7	as $R12$	as $R12$	171	13.2	Dry argon	Transgranular
R 14	1 h at 400° C (homo)	10 Å radius				
	6 days at R.T (ageing) (underaged)	GP zones in 152 matrix		19.9	Moist air	Mainly transgranular (Fig. 3a)
R 15	as R 15	as R 15	152	19.2		Dry nitrogen Transgranular (Fig. 3b)

TABLE II Crack propagation experiments with the high purity alloy samples (normally heat-treated)

3.1.1.1. Peak aged samples: moist air environment. Fig. 1a shows the broad surface observations of crack propagation in the sample R 10 aged in two steps to peak hardness and fatigued in the moist air environment. The crack has propagated preferentially along grain boundaries. Observation with an optical microscope at a magnification of 200 did not indicate any deformation in the vicinity of the crack on the original electropolished surface. Among the various experiments listed in Table II, this set of conditions caused the maximum proportion of intergranular crack propagation. The average crack propagation direction (CPD) remained essentially perpendicular to the loading direction. The grain-boundary weakness was so

pronounced that sometimes the crack was found to propagate a short distance transgranularly and then rather suddenly to by-pass the grain interior and to travel along the nearest grain boundary. It was usually found that transgranular crack propagation occurred when no suitably oriented grain boundary (oriented nearly at right angles to the principal tensile stress) was available.

That the crack propagation in a sample aged to peak hardness occurs to a large extent along the grain boundaries in moist air environment is confirmed by the fracture surface observations. Fig. 2a represents a typical fracture surface appearance. About 50 $\frac{9}{9}$ of the fracture surface is covered with smooth grain-boundary facets.

Figure 1 Broad surface observations of crack propagation in peak aged high purity alloy samples. (a) Sample R 10: moist air environment, (b) sample R 9: dry argon environment.

Examination of these facets at high magnifications (\times 3000) did not reveal the plastic deformation that is normally seen on the grain-boundary facets observed on tensile fracture surfaces.

3.1.1.2. Peak aged samples: dry argon/nitrogen~ air environment. Samples of the high purity alloy heat-treated to peak hardness were also tested in dry argon, dry nitrogen and dry air environments. It was found that the crack propagation behaviour was markedly different from the above case. Fig. lb shows the broad surface appearance of sample R 9 tested in the dry argon environment. The crack has propagated to a major extent transgranularly. The path within individual grains is very straight, and it has been shown [8] that these directions coincide with the traces of crystallographic slip planes. There is

usually a change in CPD at the grain boundaries, and the CPD is sometimes seen to deviate rather strongly from the perpendicular to the loading direction, e.g. at "A" in Fig. lb.

Tests in a dry nitrogen environment have resulted in an exclusively transcrystalline crack propagation as illustrated in Fig. 2b which shows the fracture surface of the sample R 11 aged to peak hardness and fatigued. The fracture surface consists of several smooth facets whose sizes are of the order of the grain size of the alloy, and one gets the impression that fracture is occurring in individual grains along well defined crystallographic planes. Using the etch pit technique it could be shown [8] that these facets are of (1 1 1) orientation and have been produced as a result of shear band cracking in individual grains.

Figure 2 SEM views of fracture surfaces ot high purity alloy samples. (a) Sample R 10: aged to peak hardness; tested in moist air environment, (b) sample R 11 : aged to peak hardness; tested in dry nitrogen environment, (c) sample R 13: overaged; tested in moist air environment.

Fatiguing in dry air yields the same results as for testing in dry nitrogen.

3.1.1.3. Overaged samples. Crack propagation in two overaged conditions was also investigated (samples R 13, R 12 and R 7) in moist air and dry argon environments. In these overaged conditions the crack propagates mainly in a transgranular fashion in either the moist air or dry argon. Fig. 2c shows the fracture surface of the sample R 13 fatigued in a moist air environment. It can be seen that there are only a small number of smooth grain boundary facets on this fracture surface.

3.1.1.4. Underaged samples. In a moist air environment a significant amount of ICC was observed even though the crack propagated mainly transgranularly. Fig. 3a shows the fracture surface of sample R 15 aged to produce GP zones about 10 A in radius. Several smooth grain-boundary facets can be seen. The transcrystalline segments could often be recognized as cracking along shear bands. As in the case with the peak aged samples, this ICC could be completely prevented when the experiments were carried out in a dry nitrogen atmosphere. Fig. 3b shows the fracture surface of sample R 16 similarly heat-treated but in which the fatigue crack propagation occurred in the dry nitrogen environment. No grain-boundary facets could be observed on the fracture surface, and several regions could be recognized where cracking had occurred along shear bands in individual grains.

One aspect needs to be emphasized in connection with the crack propagation behaviour in the pure alloy samples. Crack propagation was clearly discontinuous. When the grain-boundary cracking was pronounced, crack propagation along the boundaries was generally more rapid than in those regions where it propagated transgranularly. Furthermore, even when transcrystalline crack propagation occurred, a clear

Figure 3 SEM views of fracture surfaces of underaged high purity alloy samples. (a) Sample R 15: tested in moist air environment, (b) sample R 16: tested in dry nitrogen environment.

arrest of the crack was observed at several of the grain boundaries. The propagating crack was seen to run up to a grain boundary and then some time elapsed before the crack started propagating steadily in the next grain.

3.1.2. rhermomechanically treated samples

Table III summarizes the results of the experiments with the thermomechanically treated high purity alloy samples. Fig. 4a shows the broad surface appearance of sample TMT/R 3 thermomechanically processed such that the grains were elongated in the direction of the tensile axis. As a result, very few grain boundaries lie perpendicular to the tensile axis. It is seen that the crack propagates almost exclusively in transgranular fashion. McEvily *et al.* [3] have performed a similar experiment with an Al-5.5 $Zn-2.5$ Mg alloy, and the result of the present experiment is in agreement with their observations.

In order to make sure that the transcrystalline crack propagation is not due solely to the fact that most of the grain boundaries are oriented parallel to the tensile axis, another specimen TMT/R 4 was thermomechanically processed such that the grains were elongated perpendicular to the tensile axis. Broad surface observations indicate again that the crack travels over a major portion of its length through the interior of the grains. Observation of the corresponding fracture surface (Fig. 4b) confirms that the propagation takes place primarily transgranularly. Only about 20 $\frac{9}{6}$ of the fracture surface is covered with smooth grain boundary facets in this case.

Sample no.	treatment	Thermomechanical Mechanical properties in the longitudinal direction			Direction of the Test tensile axis with	environment	Crack path
		Yield strength $(MN m^{-2})$	UTS	% $(MN m^{-2})$ elongation $in 31$ mm	reference to rolling direction		
	TMT/R 3 1 h at 400° C (homo) reduced 50% by rolling 7.3 at 100° C (ageing)	243	378	7.2	Tensile axis parallel to rolling direction	Moist air	Transgranular (Fig. 4a)
	TMT/R 4 as above	243	378	7.2	Tensile axis perpendicular to rolling direction	Moist air	Predominantly transgranular (Fig. 4b)

TABLE III Crack propagation experiments with high purity alloy samples after TMT

Figure 4 Observations with high purity alloy samples after TMT (moist air environment). (a) Sample TMT/R 3: broad surface appearance, (b) sample TMT/R 4: SEM view of the fracture surface.

3.2. Crack propagation experiments with the commercial purity alloy

Table IV summarizes the results of the crack propagation experiments with the commercial purity alloy. The first two entries in the table give the results of experiments done with samples aged at temperatures below 130° C, while the third refers to an experiment with a sample which has also been aged at 170° C (somewhat overaged condition). The tests were performed in moist air and, in all cases, crack propagation occurred in a transcrystalline fashion. The fracture surface was found to be fairly smooth macroscopically and to be perpendicular to the loading direction.

Crack propagation experiments were done

with the sample T 7 aged to 250 MN m^{-2} yield strength and T 9 aged to 228 MN m^{-2} yield strength, first in the moist air environment and then, during the experiment, the test environment was changed from moist air to dry nitrogen. This change resulted in a dramatic reduction in propagation velocity (from about 13 to 2 μ m min⁻¹ in the sample T 7). Fig. 5a shows the fracture surface of the sample T 7 after the crack had propagated successively in moist air and in dry nitrogen environments. Notice that the crack has continued to propagate in a transcrystalline manner in the dry nitrogen environment; however, the fracture surface appearance has changed drastically. Whereas in the moist air environment, it is macroscopically smooth and lies perpendicular to the loading axis, in the dry nitrogen environment it consists of several smooth facets whose sizes are of the order of the grain size. One gets the impression that in the dry nitrogen fracture occurs along crystallographic planes within individual grains. Etch pit experiments have once again shown that several of these facets have formed due to shear band cracking [8]. The propagation behaviour in sample T 13, heat-treated in the same way as sample T 7 but tested in the dry argon environment, was found to be similar to the behaviour in dry nitrogen environment. In the somewhat overaged sample T 9, it was observed that a change in test environment from moist air to dry nitrogen leads to a change in the fracture surface appearance as can be seen in Fig. 5b. The crack path in both environments is transgranular.

4. Discussion

As already noted in the introduction, ICC in high purity AI-Zn-Mg alloys occurs even in uni-

Sample no.	Heat-treatment	Yield strength $(MN m^{-2})$	$\frac{6}{6}$ elongation in 18.3 mm	Test	Crack path/macroscopic environment fracture surface appearance
T ₁	1 h at 400° C (homo) 5 days at R.T+ $\}$ (ageing) 37 h at 90°C	253	19.7	Moist air	Transgranular/smooth
T ₇	2 h at 450° C (homo) 4 days at R.T+ $\}$ (ageing) 24 h at 130°C	250	17.8	Moist air	Transgranular/smooth (Fig. 5a)
T ₉	2 h at 450° C (homo) 4 days at $R.T+$ 24 h at 130° C + $\left\{$ (ageing) 24 h at 174°C	228	16.5	Moist air	Transgranular/smooth (Fig. 5b)
T ₇	(somewhat overaged) 2 h at 450° C (homo) 4 days at R.T+ 24 h at 130° C $\left\{ \right\}$ (ageing)	250	17.8		Dry nitrogen Transgranular/rough (Fig. 5a)
T ₉	2 h at 450° C (homo) 4 days at $R.T+$] 24 h at 130° C+ $\left\{$ (ageing) 24 h at 174°C (somewhat overaged)	228	16.5		Dry nitrogen Transgranular/smooth (Fig. 5b)
T ₁₃	2 h at 450° C (homo) 4 days at R.T+ $\}$ (ageing) 24 h at 130°C	250	17.8	Dry argon	Transgranular/rough

TABLE IV Crack propagation experiments with the commercial alloy samples

directional loading tests. Previous workers have offered explanations as to why this should occur, using microstructural considerations. Lynch [2], for example, has analysed the problem along the following lines. In the solution treated condition, the difference in the strength between the grain-boundary regions and the interior of the grains is small. In view of the fairly large grain size, a large fraction of tbe crack should propagate through the interior of

Figure 5 SEM views of the fracture surfaces of commercial alloy samples. (a) Sample T 7: aged to 250 MN m^{-2} yield strength, (b) sample T 9: overaged to 228 MN m^{-2} yield strength. 522

the grains. In the peak aged condition, however, the difference in strength is likely to be large due to (1) soft precipitate free zones (PFZs) adjacent to the grain boundaries and (2) relatively weak grain-boundary precipitate/matrix interfaces. Thus the crack path could be expected to be largely intergranular. In the overaged samples, even though the area fraction of the grainboundary precipitates is large, which contributes to the weakness of the grain boundaries, the matrix yield strength is also low. As a result, the preference for the grain boundaries to crack need not be pronounced.

This type of analysis, however, could not be directly extended to interpret the present results for two reasons: (1) experiments with the peak aged as well as the underaged high purity alloy samples have shown that the grain-boundary cracking during fatigue at relatively small load amplitudes in moist air environment could be prevented by the use of dry nitrogen environment; (2) even though the yield strength of the underaged samples was fairly low $(\sim 152$ MN m⁻²), a significant amount of ICC was observed. Thus, it seems necessary to consider, in addition to microstructural aspects, the reaction of the material with the environment to account fully for the present observations.

It has been well established that AI-Zn-Mg alloys suffer from a high degree of stress corrosion cracking (SCC) [9]. The susceptibility is more pronounced in the peak aged condition than in the solution treated or overaged conditions and usually manifests itself as ICC. Even room temperature ageing makes the alloys highly susceptible. That both the peak aged and room temperature aged conditions suffer from pronounced intercrystalline weakness and that this weakness could be alleviated by using dry nitrogen environment seems to be a direct consequence of SCC playing a role in the material separation. The fact that both dry argon and dry nitrogen yield similar results indicates that it is not any specific reaction between nitrogen in the test environment with the clean, unpassivated aluminium surface generated during crack propagation that is responsible for the observed effects. Further, one could deduce from the observation that the crack propagation behaviour is similar in dry air and dry nitrogen

environments that the water vapour in the environment is the agent responsible for the stress corrosion as has been indicated by previous investigations with aluminium alloys [10].

The observation that small traces of water vapour present in the laboratory air could be important in causing stress corrosion in AI-Zn-Mg alloys receives support from the work of Watkinson and Scully [11]. These authors have carried out unidirectional loading tests with Al-6% Zn-3% Mg alloy. Times to failure of specimens loaded to 80% of 0.2% yield stress in laboratory air at 50% relative humidity and in vacuum were compared. The specimens fractured in 2 to 3 h in air; whereas, there was no cracking in vacuum even after 240 h. Large area fractions of the fracture surfaces in air consisted of bright, mirror-like intercrystalline facets. The agehardened condition was found to be the most susceptible to ICC.

It is believed that the reaction of the material in the peak aged condition with the environment manifests itself in two ways: (1) the grain boundaries which are already weak because of the presence of weak grain-boundary precipitate/ matrix interfaces suffer a further loss in cohesive energy*; (2) extensive cracking along straight slip bands, as occurs in dry nitrogen environment, is a relatively low energy process. In the moist air environment, however, such a process is made difficult as will be discussed elsewhere [8]. All the present experiments have been carried out at relatively low stress amplitudes, consequently the crack propagation velocities were generally lower than 30 μ m min⁻¹. This fact allows SCC to assume a significant role in the experiments under consideration.

The observation that the commercial alloy does not suffer from ICC is consistent with its established low susceptibility to SCC [9]. Presence of Cr, Zr, Ti etc. in small quantities in the commercial alloys results in a small grain size with "rough" grain boundaries as opposed to the case with the larger grains with smooth boundaries in the high purity alloy. This fact is expected to make the intercrystalline crack propagation in commercial alloys difficult. Further, the incoherent intermetallic particles in the matrix might also be responsible for the cracks assuming a transcrystal!ine path by

^{*}The exact mechanism of stress corrosion in AI-Zn-Mg alloys leading to ICC has been a subject of controversy. For the purpose of the present discussion, it is implicitly assumed that the mechanism is one of a reduction in the cohesive energy of grain boundaries either by the diffusion of hydrogen into the material along the grain boun the adsorption of some species at the crack tip [13].

providing crack nuclei within the grains ahead of the growing crack. It might be recalled that even in unidirectional loading, the commercial alloys show no ICC. It is not as though the commercial alloys are completely immune to SCC. There is a distinct difference in the fatigue fracture surface appearance in the moist air and dry nitrogen environments. The extensive slip band cracking in the aged sample T 7 occurs only after changing from moist air to dry nitrogen environment. Even after overageing, which should result in a further drop in susceptibility, changing to dry nitrogen environment results in a change in fracture surface appearance (sample T 9, Fig. 5b).

The results of the experiments with the thermomechanically treated samples seem to indicate that TMT markedly lowers the degree of ICC. In both the samples TMT/R3 and TMT/R4 with the grain boundaries oriented perpendicular and parallel to CPD, respectively, the crack propagates predominantly in transgranular fashion. According to McEvily *et al.* [3, 141 TMT destroys the PFZs and introduces jogs into the grain boundaries. Grain boundaries with no PFZs are expected to be associated with smaller amounts of grain-boundary precipitation and hence should be tougher. TMT is also expected to homogenize the deformation in the grain interiors by introducing more dislocation sources [15]. One could in this way account for the decreased proportion of ICC in the thermomechanically treated samples.

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References

- 1. P. N. T. UNWIN and G. C. SMITH, *J. Inst. Metals* 97 (1969) 299.
- 2. s. P. LYNCH, *Met. Sci.* J. 7 (1973) 93.
- 3. A. J. MCEVILY, JUN, J. B. CLARK and A. P. BOND, *Trans. ASM* 60 (1967) 661.
- 4. c. A. STUBBINGTON, *Acta Metallurgica* 12 (1964) 931.
- 5. J. M. FINNEY, *Mat. Sci. Eng.* 6 (I970) 55.
- 6. s. 1,. LYNCH and D. A. RYDER, *Aluminium* 49 (1973) 748.
- 7. A. J. BRYANT, *Z. Metallk.* 58 (1967) 684.
- 8. M. NAGESWARARAO, G. KRALIK, V. GEROLD, to be published.
- 9. M. O. SPEIDEL, "The Theory of Stress Corrosion Cracking in Alloys" edited by J. C. Scully (NATO, Brussels, 1971).
- 10. n, P. WEI, *Eng. Fract. Mech.* I (1970) 633.
- 11, F. E. WATKINSON and J. c, SCULLY, *Corrosion Sci.* 11 (1971) 179.
- 12. w. GRUHL and D. BRINGS, *Metall.* 23 (1969) 1020.
- 13. J. c. SCULLY, Proceedings of the Third International Conference on Fracture, Munich, Germany (1973) Vol. 11.
- 14. A. J. MCEVILY, R. L. SNYDER and J. B. CLARK, *Trans. Met. Soc. AIME* 227 (1963) 452.
- 15. F. OSTERMANN, *Met. Trans.* 2 (1971) 2897.

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