

E-12 EMBRITTLEMENT OF SILVER CHLORIDE BY COPPER CHLOROCOMPLEXES

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Abstract

Previous studies have revealed that when polycrystalline AgCl is deformed in aqueous solutions containing silver complex-ions of charge greater than (2-) or (1+), the fracture mode changes from ductile and transcrystalline, as in air, to brittle and intercrystalline. In the present paper it is demonstrated that complexes not containing silver, viz. copper chlorocomplexes, also can induce brittle behavior in polycrystalline AgCl. Thus the phenomenon of complex-ion embrittlement may be more general than hitherto indicated. Observations on the variation in time to failure of statically loaded specimens with applied stress and (i) concentration and type of copper chlorocomplexes present in the testing environment (ii) composition and temperature of the base environment (HCl or H₂O) are described and discussed.

1. INTRODUCTION

When polycrystalline AgCl is deformed in air it is ductile, and extends some 50% before failing in a transcrystalline manner. However, when deformed in certain aqueous environments containing silver complex-ions of charge greater than (2-) or (1+)², it behaves in a brittle fashion, the strain at fracture being reduced to < 5%, and the fracture mode changing to intercrystalline. Studies of this phenomenon of "complex-ion embrittlement" (1-4) have demonstrated that the degree of embrittlement (i) increases with concentration of the critical complex species present in the environment, (ii) increases with charge on the complex-ion, (iii) is a function of the distribution of the charge on the complex, and (iv), for negatively charged complexes, is very sensitive to the applied stress, Fig. 1 (4). It has also been shown that, in an embrittling environment, cracks are formed where slip bands are arrested at a grain boundary of suitable misorientation, and that they propagate in a relatively brittle manner. On the basis of these and other observations, it has been proposed that this type of embrittlement is caused by a localized reduction in cohesion associated with the adsorption of complex-ions of high charge in the vicinity of strained surface bonds (2,4).

Prior to the present studies, however, only complex-ions containing silver, e.g. AgCl₄³⁻, Ag₄Br³⁺, etc., had been shown to embrittle AgCl. It was therefore necessary to determine whether, for AgCl, this phenomenon was specific to environments containing silver complexes, or was

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² For example, 6N NaCl + AgCl₄³⁻, 6N Na₂S₂O₃ + Ag(S₂O₃)₃⁵⁻, and 17N AgNO₃ + Ag₃Cl²⁺.

of more general occurrence such that complex-ions not containing silver also could induce brittle behavior.

This paper describes effects observed when polycrystalline AgCl was deformed in tension in environments containing various copper complexes.

2. EXPERIMENTAL

Specimen Preparation and Testing: Cast and rolled polycrystalline AgCl sheet, 1 mm thick, was obtained from the Harshaw Chemical Company, and tensile specimens, approximately 45 mm x 12 mm in size and having gauge dimensions of 10 mm x 3mm, were stamped from this material. Following chemical polishing for 1 minute in boiling 10N NH₄OH, specimens were annealed at 300°C for 2 hours, and then air cooled to room temperature. This heat treatment produced equiaxed grains 0.5 - 1.0 mm in diameter, with 2-3 grains across the thickness of the specimen. Gauge dimensions were determined optically, and specimens repolished for 1 minute immediately before testing. Tensile tests were performed at room temperature in air and in the various liquid environments described below, utilizing a static loading technique. The variable determined was time to failure, t_F , under specific conditions of applied stress and environment.

Testing Environments - Copper Halide Complexes in HCl and H₂O: The environments used were prepared by adding various amounts of either CuCl or CuCl₂ to water or HCl (1N to 11.8N). In water, these salts form aquocomplexes of the type Cu(H₂O)₄²⁺ or Cu(H₂O)₆²⁺ (5), respectively. When AgCl is added, for example as the test specimen, it interacts with the free Cl⁻ ions to form various silver chlorocomplexes, namely AgCl₂⁻, AgCl₃²⁻ and, in > ~ 3N CuCl₂, AgCl₄³⁻.

There have been few investigations of the complex chemistry of the CuCl₂ - HCl system, and the predominant complex species existing in any given concentration of HCl cannot yet be stated with certainty. There is evidence that in chloride environments of concentration > 2N, Cu(II) is present as CuCl₄²⁻ (5,6). On the other hand, Jorgensen (7) states that in 1N HCl the complex CuCl(H₂O)₅ predominates; in 8N HCl either CuCl₂(H₂O)₂ or CuCl₃⁻; and in 13N HCl, the predominant species is CuCl₄²⁻. Pavlyuchenko and Lazzerko (8) consider that in HCl of concentration > 5N, the complex CuCl₅³⁻ predominates, rather than CuCl₄²⁻. In acids of low strength (< 1N), the aquocomplexes predominate.

Presumably a similar sequence of complexes to that listed by Jorgensen (7) exists for the CuCl-HCl system. Again, however, the predominant species in any given HCl concentration is uncertain. Cotton and Wilkinson (9) suggest that in 1N KCl (and thus presumably in 1N HCl) CuCl₂ predominates, and that CuCl₃⁻ and CuCl₄²⁻ are formed at higher Cl⁻ ion concentrations. In Malik, Rahman and Ali's (10, 11) work on this system, conductometric studies indicated the existence of CuCl₄²⁻ in HCl solutions of ~ 1N.

Terminology: In view of the uncertainties regarding the complex chemistry of the environments of interest, a particular terminology has been adopted in order to designate a testing solution without specifying the predominant complex species. This is illustrated in the following example. A solution prepared by adding to 11.8N HCl the appropriate amount of CuCl₂ to make up a 3.8N CuCl₂ solution, is referred to as a 3.8N Cu(II) 11.8N HCl solution.

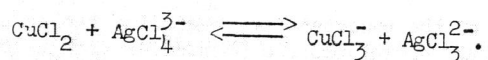
3. RESULTS AND DISCUSSION

3.1. EXPERIMENTS IN HCl ENVIRONMENTS.

Previous studies of complex-ion embrittlement phenomena indicated that embrittlement increases with charge on the complex. Accordingly, experiments were first carried out in concentrated HCl environments (11.8N), since additions of copper halides to such solutions were likely to result in formation of the most highly charged copper chlorocomplexes. Figures 2 and 3 present data from comparative tests performed using polycrystalline specimens immersed either in 11.8N HCl, or in 11.8N HCl to which had been added various amounts of CuCl₂. The significant increases in embrittlement associated with the addition of CuCl₂ are apparent.

Figure 2 also presents data from tests performed in 11.8N HCl presaturated with AgCl to produce the complex AgCl₄³⁻, and it can be seen that the presence of an appreciable concentration of this complex species at the onset of the test also induced a greater degree of embrittlement than that obtained in HCl alone. The possibility arose, therefore, that embrittlement in Cu(II) 11.8N HCl environments might be due to an increased concentration of AgCl₄³⁻ complexes (due to the greater Cl⁻ ion content of the environment) rather than to the presence of Cu(II) chlorocomplexes. To investigate this possibility, tests were performed in 11.8N HCl environments presaturated with AgCl₄³⁻ complexes and to which were added various amounts of CuCl₂. The variation of t_F at 750 gm/mm² with composition of the environment is shown in Fig. 4. It can be seen that the addition of ~ 10⁻⁴N CuCl₂ to the presaturated HCl resulted in inhibition of embrittlement, t_F increasing from ~ 5 sec to > 10⁴ sec. However, when more than ~ 5 x 10⁻³N CuCl₂ was added, the solution again became embrittling, and t_F then decreased gradually with increasing Cu(II) content. Data from similar experiments performed in unpresaturated 11.8N HCl are also included in Fig. 4. For such environments, inhibition effects were not observed, and the solutions became increasingly embrittling with Cu(II) content.

Inhibition effects associated with the addition of divalent cations to environments containing AgCl₄³⁻ complexes have been observed previously (4). For example, additions of Zn²⁺, Cd²⁺ or Hg²⁺ ions to 6N NaCl + AgCl₄³⁻ solutions prevent the embrittlement of AgCl in these environments. Inhibition of embrittlement can result from (i) association of the inhibitor-ions with the AgCl₄³⁻ complex-ions to produce water-soluble mixed complexes of lower charge, and therefore reduced embrittling capacity (see Introduction), or, from (ii) reaction of the inhibitor-ions with AgCl₄³⁻ complex-ions to produce non-embrittling chlorocomplexes of lower charge, for example:



The latter possibility is considered more likely in this case, since there is no evidence in the literature for the existence of mixed Cu-Ag-chlorocomplexes.

The data of Figs. 3 and 4 reveal therefore, (i) that embrittlement in 11.8N HCl containing substantial quantities of Cu(II) cannot be due to the presence of AgCl_4^{3-} complexes - because embrittlement due to this source is inhibited by the presence of only some 10^{-4}N Cu(II) - and therefore must be associated with the presence of Cu(II) chlorocomplexes (ii) that even low concentrations of Cu(II) ($< 10^{-2}\text{N}$) can induce significant embrittlement, and (iii) that the degree of embrittlement increases with concentration of Cu(II) present.

Effects of Varying the Type of Copper Complex Present: Experiments were performed in which the type of complex-ion predominating in the testing solution was varied by altering the concentration of HCl present. The Cu(II) content itself was kept constant at $7.6 \times 10^{-1}\text{N}$ Cu(II), and the solvents were 11.8N HCl, 5.9N HCl, 1N HCl and H_2O . The data are shown in Fig. 5. While the 11.8N HCl environment was very embrittling, no embrittlement occurred in either the 1N HCl or water environments. Moreover, as will be discussed later, it seems likely that the embrittlement observed in the 5.9N HCl environment was due to AgCl_4^{3-} complexes, and not Cu(II) chlorocomplexes. Thus, since it is known that the charge on the predominant complex species increases with Cl^- ion content of the environment (7,9), it is apparent that only highly charged cupric chlorocomplexes are embrittling; lower complexes are not.

To further investigate the role of charge on the complex, tests were performed in HCl to which CuCl had been added. $7.6 \times 10^{-1}\text{N}$ Cu(I) 11.8N HCl solutions were significantly more embrittling than $7.6 \times 10^{-1}\text{N}$ Cu(II) 11.8N HCl environments, Fig. 5. However, the Cu(I) containing environments incorporate a greater concentration of complex-ions than Cu(II) containing environments of the same normality. When specimens were tested in $3.7 \times 10^{-1}\text{N}$ Cu(I) 11.8N HCl solutions, which contain the same number of gm per liter of copper as $7.6 \times 10^{-1}\text{N}$ Cu(II) 11.8N HCl environments, the data from these two environments were not distinguishable, Fig. 5. On the basis of previous work on the complex-ion embrittlement phenomenon (2,4), this observation can be rationalized if the predominating cupric and cuprous complexes in 11.8N HCl are of identical charge, and the charge is $> 2-$. This appears to be a reasonable hypothesis. For example, from Cotton and Wilkinson (9) and Malik et al. (10) it can be assumed that the predominant cuprous species in 11.8N HCl is CuCl_2^- . There is disagreement about the predominant species in the Cu(II) HCl system, but the most recent experimental work, that of Pavlyuchenko and Lazerko (8) in 1958, suggests that CuCl_3^- is the predominant complex in HCl of $> 5\text{N}$ concentration. Thus the environments $3.7 \times 10^{-1}\text{N}$ Cu(I) 11.8N HCl and $7.6 \times 10^{-1}\text{N}$ Cu(II) 11.8N HCl might be considered to contain identical concentrations of complex-ions of the same charge, and hence be equally embrittling. As noted previously (4), the structure of the complex (cf. CuCl_2^- and CuCl_3^-) appears to be less relevant to the embrittlement process than the magnitude and distribution of its charge.

Temperature Dependence of Embrittlement: The data of Fig. 6 demonstrate that the effect of increasing testing temperature over the range $20^\circ\text{C} - 100^\circ\text{C}$ on t_F at a given stress depends on composition of the environment. For the most embrittling environments used, i.e. 3N Cu(II) 11.8N HCl and 1.85N Cu(I) 11.8N HCl, the degree of embrittlement increased slightly with temperature. However, for less embrittling environments, e.g., $7.6 \times 10^{-1}\text{N}$ Cu(II) 11.8N HCl, 2N Cu(II) 11.8N HCl, $3.7 \times 10^{-1}\text{N}$ Cu(I) 11.8N HCl, and also 11.8N HCl presaturated with AgCl_4^{3-} complexes, raising the testing temperature decreased embrittlement, i.e., t_F increased. It can be seen that the variation with temperature is a function of the Cu(I) or Cu(II) content of the HCl environment.

The data of Fig. 7(a) reveal that the temperature dependence of a 6N NaCl environment presaturated with AgCl_4^{3-} complexes is similar to that of the 3N Cu(II), 3.8N Cu(II), and 1.85N Cu(I) in 11.8N HCl environments. Following consideration of Figs. 6 and 7(a), therefore, it does not appear that the observed variations are associated with changes in the stability of the AgCl_4^{3-} or predominating Cu(II) chlorocomplexes with temperature. An alternative possibility is that the HCl environment is primarily responsible, but a mechanism cannot be suggested at this time. Determinations of the variation in dissolution rate of AgCl in 11.8N HCl with temperature revealed a 20% increase in rate over the range $20^\circ - 60^\circ\text{C}$. However, a similar change also was noted for the 3.8N Cu(II) 11.8N HCl environments. Thus it does not seem likely that a temperature-dependent Joffe-effect is involved. Further work on this aspect of the investigation is planned.

Figures 6(a) and (b) also provide other examples of the similar embrittlement behavior of 11.8N HCl environments containing the same number of gm per liter of either Cu(I) or Cu(II) (see previous section). Compare curves for $3.7 \times 10^{-1}\text{N}$ Cu(I) 11.8N HCl and $7.6 \times 10^{-1}\text{N}$ Cu(II) 11.8N HCl; and for 1.85 N Cu(I) 11.8N HCl and 3.8N Cu(II) 11.8N HCl.

Metallographic Observations: The fracture mode of specimens deformed at stresses near to or greater than the macroscopic flow stress of ~ 300 gm/mm² in Cu(II) 11.8N HCl environments was similar to that previously reported for specimens embrittled by silver chlorocomplexes. Cracks were initiated where slip bands were arrested at grain boundaries of large misorientation, as at A in Fig. 8; crack propagation was relatively brittle and intercrystalline, as at B in Fig. 8, and occurred preferentially along those boundaries lying approximately perpendicular to the stress axis. However, as can be seen from Fig. 3, it was possible in 3.8N Cu(II) 11.8N HCl environments to induce fracture in times of order 3000 sec at stresses as low as 50 gm/mm² - that is, at approximately one sixth of the macroscopic flow stress. In such cases, it was not possible to correlate cracks and slip bands, for the latter could not be detected by optical microscopy. However, exposure of unstressed specimens to this environment did not induce cracking, and thus it is considered that cracking at stresses of order 50 gm/mm² is associated with sub microscopic slip in a few grains. Once an intergranular crack was initiated, the stress concentration at its tip ensured continuing embrittlement. In specimens immersed in 3.8N Cu(II) 11.8N HCl solutions and stressed at low levels, failure presumably occurred by propagation of the first crack, for secondary cracks were rarely observed.

Examination by optical microscopy of the intercrystalline fracture surfaces of specimens deformed in Cu(II) 11.8N HCl environments did not reveal evidence for discontinuous crack propagation such as previously reported (4) for specimens fractured in NaCl environments. Two possible explanations may be suggested for this variation: (i) the HCl environment dissolved away any evidence of surface "striae" before the acid could be rinsed off, or (ii) the greater concentration of embrittling copper chlorocomplexes present in, for example, 3.8N Cu(II) 11.8 HCl environments (potentially $3.8N \text{ CuCl}_n^{(n-2)-}$), as compared to $\sim 10^{-2}N \text{ AgCl}_4^{2-}$ in 6N NaCl) was sufficient to ensure continuous embrittlement. The latter possibility is considered more likely.

Several tests also were performed under impact loading conditions. In air, polycrystalline specimens extended to failure in a purely ductile manner. When immersed in $7.6 \times 10^{-1}N \text{ Cu(II) 11.8N HCl}$ environments, however, fracture was brittle and intercrystalline, the fracture surfaces revealing no evidence of partial shear failure. In other words, even under impact conditions, it was not possible to deform a specimen more quickly than this environment could embrittle it.

Inhibition of Embrittlement: In previous studies using 6N NaCl + AgCl_4^{2-} environments, it was found that the addition of $\sim 10^{-1}N$ of either K^+ or Cs^+ ions, of $10^{-2}N \text{ Hg}^{2+}$ ions, or of $\sim 1N \text{ Zn}^{2+}$ or Cd^{2+} ions, led to inhibition of embrittlement (4). (Two possible modes of action for inhibitor ions were mentioned above). Experiments were performed, therefore, with the object of finding suitable inhibitors for embrittlement by copper chlorocomplexes. It was observed that the addition of K^+ and Cs^+ ions to Cu(II) 11.8N HCl environments did prevent embrittlement, but this came about as the result of precipitation of the water-insoluble mixed complexes KCuCl_3 (12) (yellow) and CsCuCl_3 (13) (dark red), respectively. In other words, copper chlorocomplexes were effectively removed from the environment, rather than simply prevented from embrittling the AgCl. Such "irreversible" effects might be regarded as examples of the "elimination" of embrittlement, rather than its inhibition. Accordingly, several other ionic species were evaluated as potential embrittlement-inhibiting species for the Cu(II) chlorocomplexes present in 11.8N HCl, namely Li^+ , Na^+ , Zn^{2+} , Ca^{2+} , Hg^{2+} and Fe^{2+} , but an effective means of inhibiting embrittlement by these copper chlorocomplexes remains to be found.

The addition of $\sim 2 \times 10^{-1}N \text{ Cs}^+$ ions to solutions of $7.6 \times 10^{-1}N \text{ Cu(II) 5.9N HCl}$, on the other hand, effectively inhibited embrittlement, raising t_F at 970 gm/mm^2 from 9 sec to $> 10^4$ sec, and no precipitation was observed. Similar inhibition effects were noted for aqueous CuCl_2 environments containing AgCl_4^{2-} complexes, see the following section. Thus it seems likely that embrittlement in Cu(II) 5.9N HCl environments is associated with the presence of AgCl_4^{2-} complexes, and not with Cu(II) chlorocomplexes, for if copper complexes had been present, they would have been precipitated out when Cs^+ ions were added.

3.2. EXPERIMENTS IN AQUEOUS Cu(II) ENVIRONMENTS.

Data from tests performed in Cu(II) H_2O solutions containing silver chlorocomplexes are presented in Fig. 9. Fracture was brittle and intercrystalline, and the characteristic critical stress for embrittlement was

noted for both 6N and 8N environments. For higher concentrations of Cu(II), however, the form of the t_F versus stress curves was quite novel. To investigate the cause of this peculiar variation, experiments were performed with specimens designed to differentiate between crack initiation - and crack propagation-dependent effects. Such specimens were heat-treated to develop grains approximately 3 mm in diameter extending completely across the gauge section, and whose boundaries lay approximately perpendicular to the tensile axis of the specimen. When a crack was initiated at a grain boundary in such specimens, it immediately propagated to failure. Thus the time to initiate a crack, t_I , and t_F were essentially identical; the time to propagate a crack being $< 1 \text{ sec}$. The data obtained from such specimens when tested in 11.7N Cu(II) H_2O solutions is included in Fig. 9 (dashed line). The form of the t_F versus applied stress curve is that normally observed in very embrittling environments (compare the curve for a 3.8N Cu(II) 11.8N HCl environment in Fig. 3), and the peculiar variation noted for the standard specimens is not present. It is evident, then, that the latter variation is associated with the crack propagation process, and possibly results from difficulties in propagating cracks past triple points and along unfavorably oriented grain boundaries under low applied stresses. Examination of intercrystalline fracture surfaces from specimens tested in 11.7N Cu(II) H_2O environments at stresses between 150 and 400 gm/mm^2 revealed the surface "striae" previously shown to be associated with discontinuous crack propagation (4, 14).

It was also noted that concentrations of CuCl_2 of $< 3N$ did not induce brittle behavior in polycrystalline AgCl, Fig. 9, and that the addition of $\sim 10^{-1}N \text{ Cs}^+$ ions to an 8N Cu(II) H_2O environment inhibited embrittlement, raising t_F at 700 gm/mm^2 from 7 sec to $> 8 \times 10^3 \text{ sec}$. In short, in most respects, the embrittlement behavior of AgCl in aqueous CuCl_2 environments resembled that in aqueous solutions of the Group IA and IIA metal chlorides (4), and thus is considered to be associated with the formation and adsorption of AgCl_4^{2-} complexes (4). However, two interesting variations in behavior from that noted in NaCl environments were observed. First, presaturation of 6N and 8N aqueous CuCl_2 solutions with AgCl did not significantly affect t_F , Fig. 9, whereas t_F was reduced in 6N NaCl environments, Fig. 1, and also in 11.8N HCl environments, Fig. 2. This variation has not been investigated, but it is of interest to note that the form of the t_F versus stress curves for fresh 6N and 8N CuCl_2 solutions are remarkably similar to those for presaturated environments. Presumably it is possible to presaturate unstirred aq. CuCl_2 environments with AgCl_4^{2-} complexes, at least in the vicinity of the surface of the specimen, within 10 sec. Second, t_F at 500 gm/mm^2 in 11.7N Cu(II) H_2O environments increased markedly with temperature (compare Figs. 7(a) and (b)). The behavior illustrated in Fig. 7(b) could result from some temperature-sensitive variation in the state of the Cu(II) ions in solution (e.g., a reduction in number of water molecules attached in hydration shells), allowing increased interaction with the AgCl_4^{2-} complex-ions at higher temperatures. However, more work will be required before any mechanism can be proposed.

4. CONCLUSIONS

The principal conclusion from this work is that polycrystalline AgCl can be embrittled by charged complex-ions not containing silver. The phenomenon of complex-ion embrittlement is therefore seen to have possibilities of more general occurrence than hitherto indicated. The experimental results also are in accord with the view (1-4) that embrittlement results from the adsorption of highly charged complexes at regions of stress concentration in the lattice, for example, where slip bands are arrested by a suitably misoriented grain boundary, illustrated in Fig. 8, or at a crack tip.

Specifically it has been shown that (i) only the most highly charged copper chlorocomplexes are embrittling (probably CuCl_4^{2-} and CuCl_5^{3-}) (ii) the degree of embrittlement increases with concentration of critical species present in the environment (iii) the degree of embrittlement is a sensitive function of stress, and (iv) stresses as low as 50 gm/mm^2 (one sixth of the engineering yield stress) can induce brittle failure in $< 1 \text{ hr}$ in 3.8N Cu(II) 11.8N HCl environments. The observations that, in $7.6 \times 10^{-1}\text{N Cu(II)}$ 11.8N HCl solutions, it was not experimentally practical to deform a specimen sufficiently quickly to prevent brittle failure, and that the fractured surfaces provided no indication of discontinuous crack propagation, demonstrate the severity of embrittlement that can be achieved in the presence of highly charged copper chlorocomplexes.

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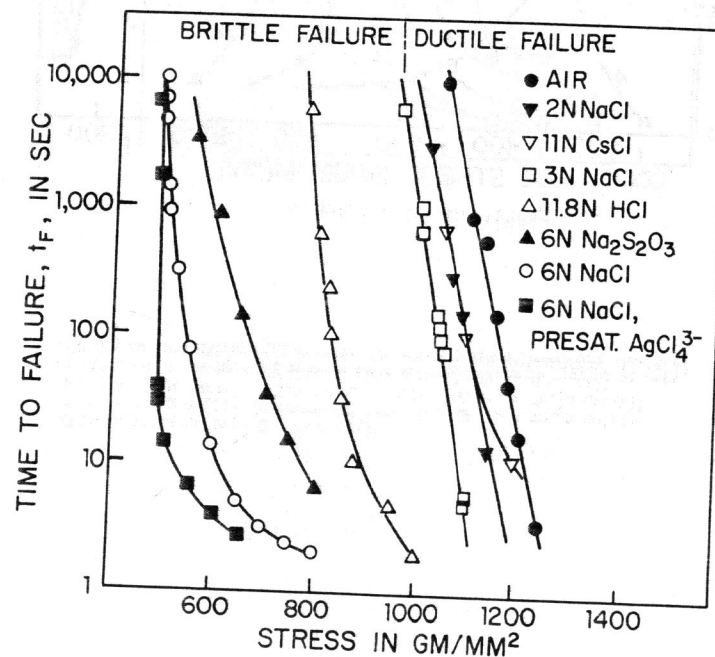


Fig. 1.- Effects of applied stress and environment on the time to failure of polycrystalline AgCl at room temperature. Note variation in degree of embrittlement with concentration of aq. NaCl, and also the effect of pre-saturating 6N NaCl with AgCl_4^{3-} complexes.

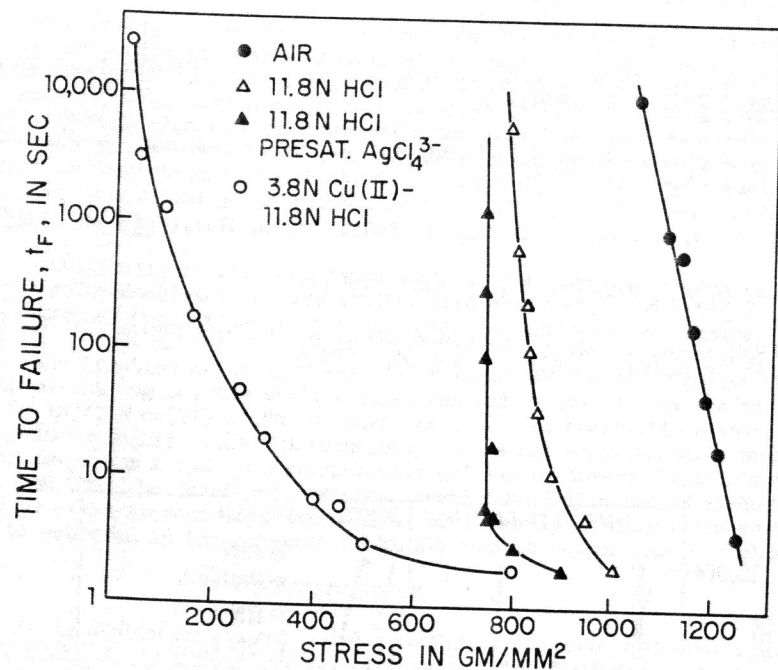


Fig. 2.- Effects of applied stress and various HCl environments on the time to failure of polycrystalline AgCl at room temperature.

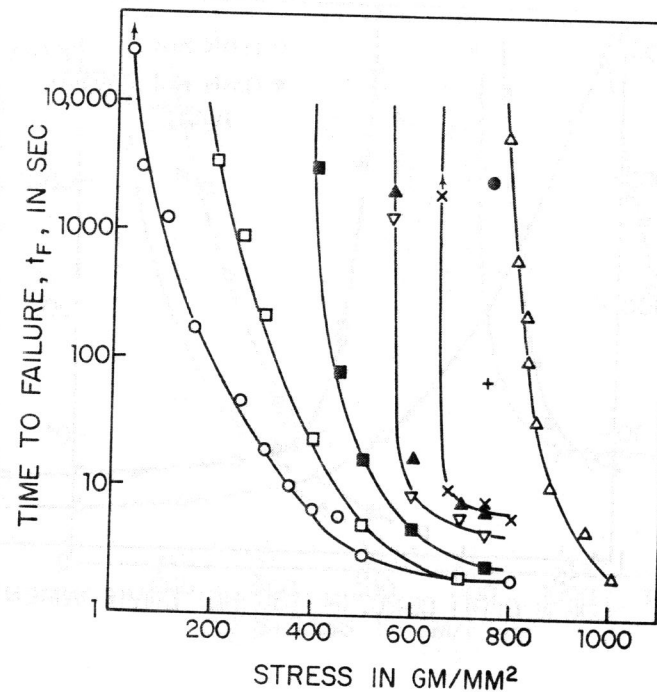


Fig. 3- Variation of t_F with applied stress and concentration of Cu(II) in 11.8N HCl at room temperature; ▲ HCl only; ● 10⁻²N Cu(II); + 7.6 × 10⁻³N Cu(II); × 7.6 × 10⁻⁴N Cu(II); ▼ 7.6 × 10⁻⁵N Cu(II); ▲ 7.6 × 10⁻²N Cu(II) presaturated with AgCl; ■ 7.6 × 10⁻²N Cu(II); □ 7.6 × 10⁻¹N Cu(II); ○ 3.8N Cu(II).

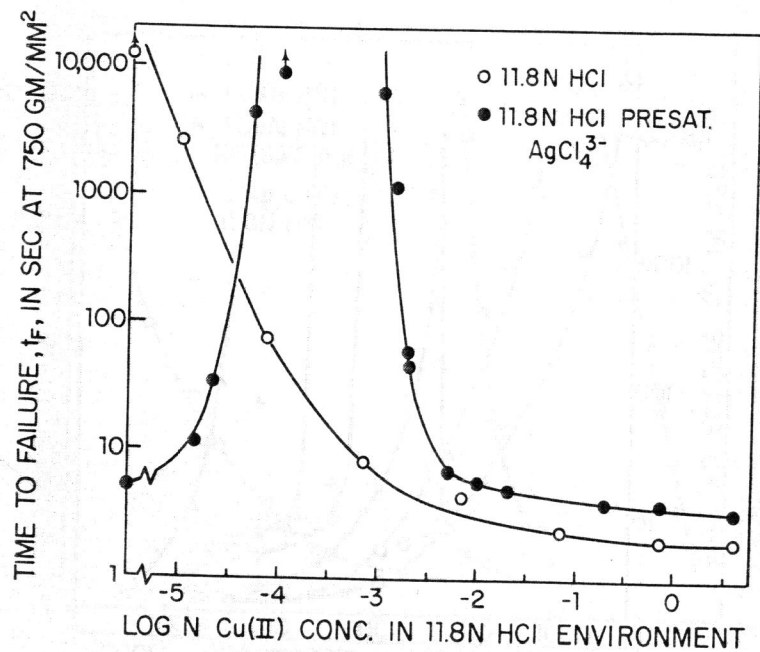


Fig. 4.- Variation in t_f at 750 gm/mm² with Cu(II) content of 11.8N HCl, and 11.8N HCl presaturated with AgCl₄³⁻. Note inhibition of embrittlement in pre-saturated HCl for Cu(II) concentrations between $\sim 5 \times 10^{-5}N$ and $10^{-2}N$.

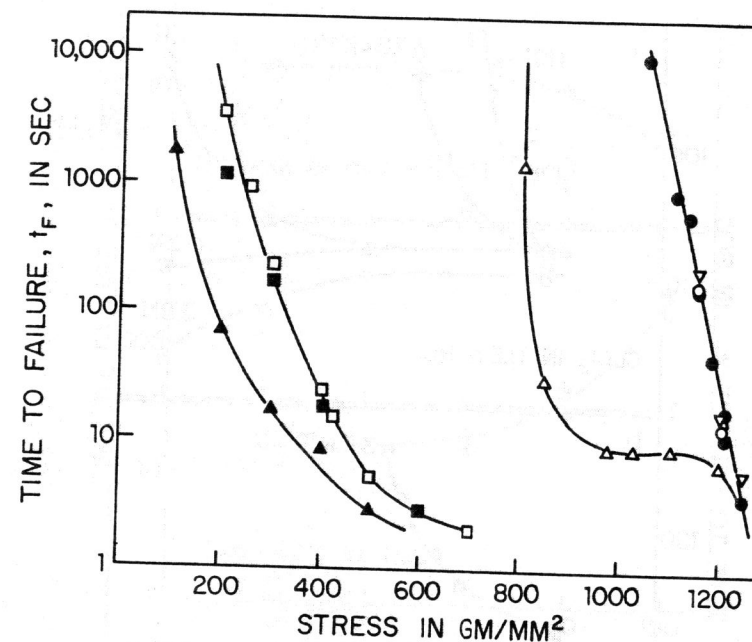


Fig. 5.- Variation of t_f with applied stress and type of copper complex predominating in the environment: ● Air; □ 7.6 x 10⁻¹N Cu(II) 11.8N HCl; ▲ 7.6 x 10⁻¹N Cu(II) 5.9N HCl; ○ 7.6 x 10⁻¹N Cu(II) 1N HCl; ▼ 7.6 x 10⁻¹N Cu(II)H₂O; ▲ 7.6 x 10⁻¹N Cu(I) 11.8N HCl; ■ 3.7 x 10⁻¹N Cu(I) 11.8N HCl.

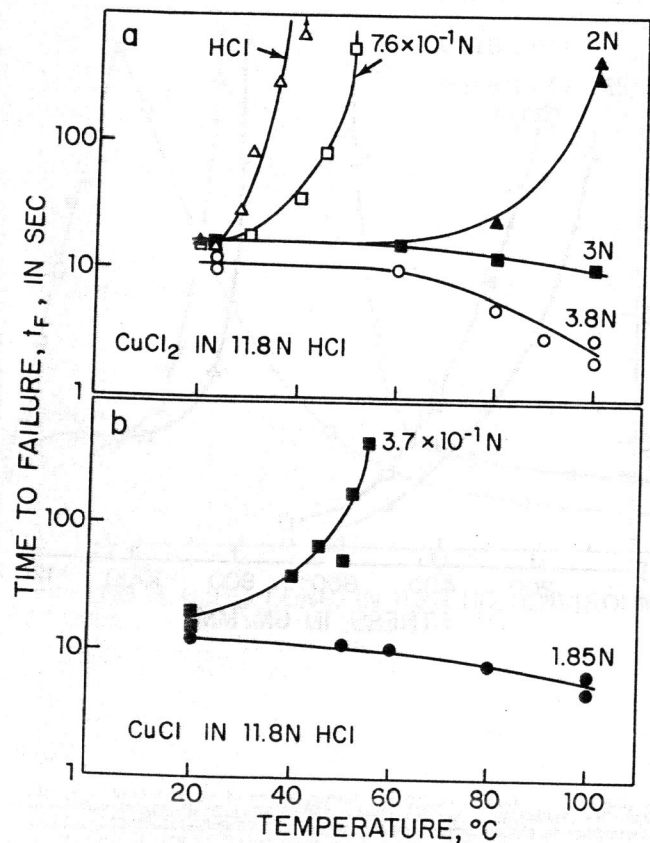


Fig. 6.- Effect of temperature of environment on t_F at a given stress. (a) Cu(II) in 11.8N HCl: \circ 3.8N Cu(II), at 350 gm/mm^2 ; \blacksquare 3N Cu(II), at 400 gm/mm^2 ; \blacktriangle 2N Cu(II), at 350 gm/mm^2 ; \square 7.6×10^{-1} N Cu(II), at 420 gm/mm^2 ; \triangle 11.8N HCl presaturated with AgCl_4^{3-} , at 740 gm/mm^2 . (b) Cu(I) in 11.8N HCl: \bullet 1.85N Cu(I), at 310 gm/mm^2 ; \blacksquare 3.7×10^{-1} N Cu(I), at 400 gm/mm^2 .

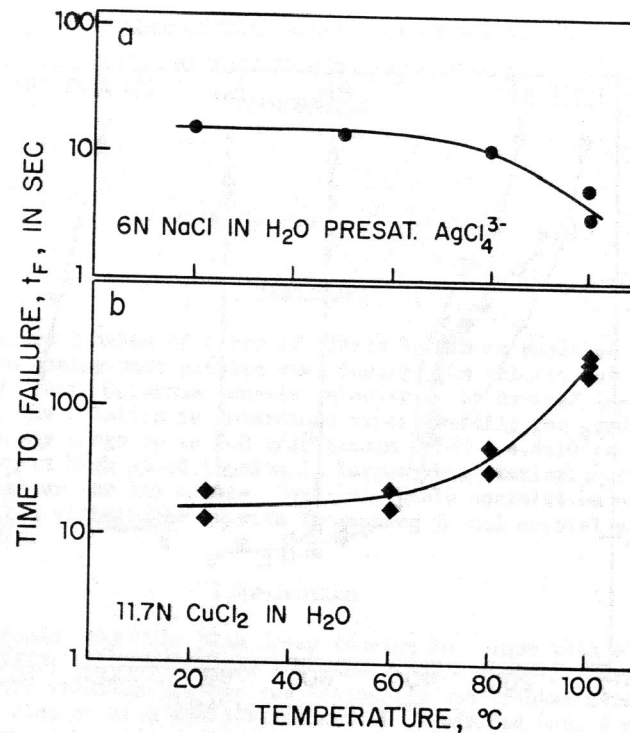


Fig. 7.- Effect of temperature of environment on t_F at given stress. (a) aq. 6N NaCl presaturated with AgCl_4^{3-} , at 500 gm/mm^2 . (b) aq. 11.7N CuCl_2 , at 500 gm/mm^2 .

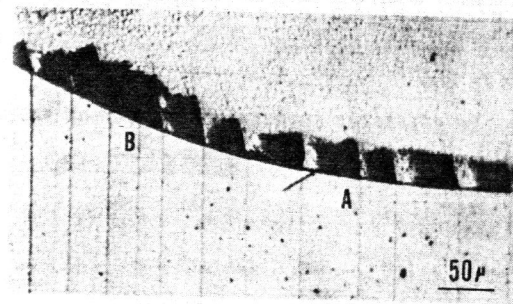


Fig. 8.- Polycrystalline AgCl stressed at 300 gm/mm^2 in 3.8N Cu(II) 11.8N HCl containing copper chlorocomplexes; demonstrating that cracks are initiated where slip bands are arrested at a grain boundary, as at A, and propagate in a brittle, intercrystalline manner, as at B. Transmitted light.

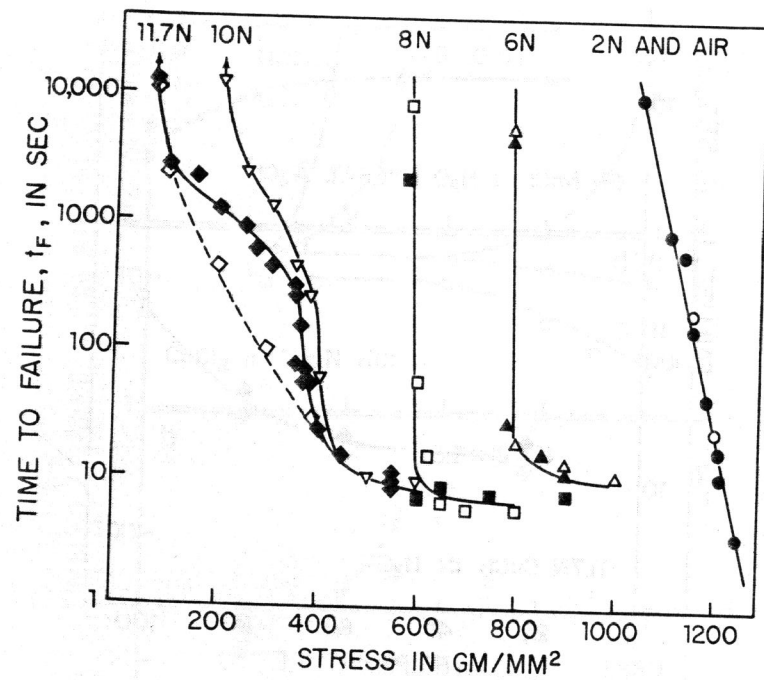


Fig. 9.- Variation of t_F with applied stress and concentration of aqueous CuCl_2 environments: ● Air; ○ 2N CuCl_2 ; ▲ 6N CuCl_2 ; ▲ 6N CuCl_2 presaturated with AgCl ; □ 8N CuCl_2 ; ■ 8N CuCl_2 presaturated with AgCl ; ▼ 10N CuCl_2 ; ◆ 11.7N CuCl_2 ; ◇ 11.7N CuCl_2 , coarse grained specimens.