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STRESS-CORROSION CRACKING OF COPPER-GOLD SINGLE CRYSTALS

by

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ABSTRACT

The stress-corrosion susceptibility range of the copper-gold system has been measured, using single crystals loaded to give 5 per cent glide strain in 2 per cent ferric chloride. Alloys containing less than about 10 at.% gold fail by the progressive reduction of cross section due to general corrosive attack. Alloys containing between 10 and 29 at.% gold fail by stress corrosion, with the stress-corrosion susceptibility steadily increasing up to 29 at.% gold. Those alloys containing in excess of this gold content are not susceptible to stress-corrosion. The stress-corrosion behavior of Cu_3Au is independent of structure (short-range-order, long-range-order, or domain size) and therefore independent of effects related to structure (yield points, slip line clusters, etc.). The results are discussed in relation to current theories of stress-corrosion, and it is concluded that these are inadequate to account for the observations.

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Introduction

Recent theories of stress-corrosion^{1,2} have emphasized the role of lattice defects in a two-stage electrochemical-mechanical mechanism. For example, Forty¹ discusses the effect of dezincification in promoting local surface embrittlement in alpha-brass, with consequent pinning of dislocations and eventual crack nucleation. The same author proposes that crack propagation is dependent on a reduced dislocation mobility such as would result from short-range-order, although other structural parameters affecting dislocation behavior are considered; in general, the theory regards a yield point phenomenon as an indication of possible stress-corrosion susceptibility. Robertson and Tetelman² consider a low stacking fault energy to be indicative of proneness to stress-corrosion, and envisage the effect of dislocation pile-ups against grain boundaries, Lomer-Cottrell dislocations, etc., in promoting stress concentrations and eventual cracking. Barnartt³ lends support to this latter theory by demonstrating that stress-corrosion-susceptible austenitic stainless steels do in fact appear to contain dislocations essentially in planar distributions of pile-ups, while non-susceptible steels of rather similar composition exhibit a cellular dislocation distribution. Unfortunately, such a theory cannot be easily applied to ordered phases.

Relatively little stress corrosion work using single crystals has been attempted, and the present research was planned to test some aspects of the above theories.

Crystal Preparation

Copper-gold alloys of various compositions up to 50 atomic per cent gold were prepared from metals of 99.999 per cent purity by induction melting in spectroscopically pure graphite boats, the operation being conducted under an atmosphere of argon/5 per cent hydrogen. The alloys were cast into 0.188 in. diameter rods, and swaged to 0.085 in. diameter.

The alloy rods were grown into single crystals by a Bridgman soft-mould method which not only accurately retains the specimen shape and dimensions, but also avoids distortion of the crystal during its removal

from the mould. Pure alumina powder is commonly used for the mould material, but to prevent oxidation of the specimens, powdered graphite was mixed with the alumina. The technique proved highly successful, the as-grown crystals being quite free from oxidation. The above simple method was inadequate for those specimens containing in excess of about 40 at. per cent gold. Specifically, they grossly distorted and cracked during the slow cooling, this being attributed to the internal stresses induced by long-range ordering with the resultant change in structure from face-centered-cubic to body-centered-tetragonal CuAu at temperatures below 426° C. To overcome these difficulties, the single crystals grown from those alloys >40 at. per cent gold were not allowed to cool to the critical temperature, but were quenched directly from the single crystal furnace into cold water.

The crystals, measuring approximately 6 inches in length, were electropolished in a potassium cyanide bath of approximately [#] the composition recommended by Bakish and Robertson,⁴ and checked for single crystallinity and orientation by the usual Laue method. The crystals were then cut into one inch lengths and homogenized in vacuo.

The possibility of segregation in copper-gold single crystals has been noted by Honeycombe,⁵ therefore the compositions of the individual one-inch lengths were determined as follows. Theoretical densities were calculated using lattice parameter data⁶ for different compositions, and a theoretical density versus composition curve was prepared. Actual densities were computed from careful dimensional measurements and weights.

Some later crystals were grown in a horizontal travelling furnace rather than by the vertical method employed earlier. Gravity segregation was avoided, and the density variation along the rod was satisfactorily small. However, the single crystal yield was reduced.

* Phosphoric acid was included in the recommended solution, but this caused it to become brown and clouded within a few minutes. Therefore, it was omitted---with no adverse effects---and the solution life extended to several hours.

Stress-Corrosion Testing

For stress-corrosion testing, the crystals were silver-soldered into stainless steel holders, and mounted in Teflon jigs, Fig.1. All immersed stainless steel parts were coated with a Latex corrosion-resistant paint, so that the actual specimen was the only metal exposed to the electrolyte.

Stress-corrosion tests are usually conducted under loads which represent a definite fraction of the tensile strength, but in the case of single crystals the load may remain relatively constant over a fairly large strain range. Since the plastic strain is likely to be a critical variable, it was decided to test under loads corresponding to a constant glide strain, arbitrarily chosen as 5 per cent. The corresponding specimen extensions, usually about 2.3 per cent, were calculated from the crystal orientations.

The loaded specimens were tested in 2 per cent aqueous ferric chloride.

Behavior of Copper-Rich Susceptible Alloys

The following comments summarize the experimental observations.

<u>Composition</u>	<u>Failure Time</u>	<u>Remarks</u>
10 at % Au	(1) 16 1/2 hours	Large-scale general corrosive attack preceded the final failure which was apparently due to stress-corrosion.
	(2) 20 1/2 hours	Failure due entirely to a large reduction in cross-sectional area associated with general corrosive attack.
11 at % Au	(1) 7 1/2 hours	Failure definitely due to stress-corrosion cracking, but some general attack still clearly visible.
	(2) 9 1/2 hours	Crack took approximately thirty minutes to traverse the specimen.

12 at % Au	(1) 2 hours	At this composition there is very little visible evidence of general corrosive attack.
	(2) 2 1/2 hours	Crack took approximately twelve minutes to traverse the specimen.
13 at. % Au	(1) 74 minutes	No visible general attack.
	(2) 1 hour	Crack took approximately eight minutes to traverse the specimen
16.5 at. % Au	(1) 50 minutes	Crack period reduced to a few seconds.
	(2) 38 minutes	- -
	(3) 75 minutes	- -
18.5 at. % Au	(1) 8 1/2 minutes	- -
	(2) 13 1/2 minutes	- -

Since it is not possible to say with certainty when a crack has just been initiated, the times reported for the crack to traverse the crystal are necessarily approximations. However, the propagation time showed a marked decrease with increase in gold content.

Behavior of Gold-Rich Susceptible Alloys

Initially, the possibility of a relationship between stress-corrosion susceptibility and the ordered structure Cu_3Au was investigated. This phase, α' , ends at a gold content of 37.2 atomic per cent, and so alloys on each side of this limit were tested. None of these alloys was susceptible even when the conditions were intensified by increasing both the applied stress and ferric chloride concentration.

Below are listed the additional high-gold compositions which were stressed to give 5 per cent glide strain in 2 per cent FeCl_3 .

<u>Density (g.cc⁻¹)</u>	<u>Composition (at. % Au)</u>	<u>Failure Time (min.)</u>
12.55	27.5	6
12.69	28.6	7
12.70	28.8	4
12.72	29.0	Did not fail

The 29.0 at. % specimen together with others of 30.2 and 21.0 at. % gold content did fail under very intense (qualitative) conditions of stress and solution concentration. A fourth specimen of 31.6 at. % gold content did not fail under any conditions. In all cases, if the conditions were satisfied failure occurred within a few minutes as with the slightly less noble alloys.

These results suggest that the "end-point" (parting limit) is dependent on the imposed test conditions as well as composition. This is in partial agreement with the results published by Graf ⁽⁷⁾ (Fig. 2), but the susceptible range he reported extended as far as 36 at. % Au.

The present results are summarized in Fig. 3; included in this curve are data from a study of Cu₃Au, described in the next section.

Behavior of Cu₃Au under Various Conditions of Order

The mechanical properties and mode of plastic deformation of Cu₃Au can be varied considerably by appropriate heat-treatments, and certain theories suggest that these variations may significantly affect stress-corrosion life. Biggs and Broom, ⁽⁸⁾ following a theoretical prediction by Cottrell, investigated the dependence of yield stress on domain size of long-range ordered polycrystalline Cu₃Au and found that the yield stress reaches a maximum when the domain size approximates 50 Å. The single crystals used in the present research were approximately the same size as the specimens of Biggs and Broom, and so it was decided to emulate their heat-treatments. All crystals were initially disordered by quenching from 580° C, and the subsequent annealing times (at 346° C) and presumed domain sizes (after Biggs and Broom) are listed below.

Annealing Time at 346° C (min.)	0	1	3	10	80	1000
Presumed Domain Size (A)	3	43	48	63	112	250

In addition, a fully ordered specimen was obtained by slowly cooling from 390° C, and the domain size was assumed to be limited only by the size of the crystal. All these crystals were of the same orientation, i.e. cut from the same 6 inch crystal. After electropolishing, they were tested on an Instron hard-beam tensile machine at room temperature, the stress-strain curves being reproduced in Fig. 4. Although the upper yield points were only about one-half the polycrystalline results, the relative values agree well with the polycrystalline data reproduced in the same diagram. Further crystals of Cu_3Au were given identical heat-treatments, and then stress-corrosion tested under the same conditions as in previous tests. The failure times and corresponding domain sizes were:

<u>Time to Failure</u>	<u>Domain Size, A</u>
21 min. 30 sec.	3
4 min. 35 sec.	43
12 min. 40 sec.	48
5 min. 45 sec.	63
15 min. 0 sec.	112
20 min. 30 sec.	250

It was thought that these times were too short to give any real indication of a susceptibility trend, and so the tests were repeated using 2.5 per cent glide strain and 1 per cent a.c. FeCl_3 , with the following results:

<u>Time to Failure(min.)</u>	<u>Domain Size, A</u>
132	3
40	43
70	48
75	63
78	112
41	250
15;49	Unknown, but perhaps approximating to the crystal dimensions since these specimens were slowly cooled from 390° C

There is no indication of any particular trend, and it appears that changes in strength and deformation characteristics, caused by different domain sizes, do not significantly affect stress-corrosion behavior. The results also agree with the findings of Bakish and Robertson⁴ that ordered and disordered Cu_3Au exhibit about the same stress-corrosion susceptibility.

The Role of General Corrosion in Stress Corrosion

The extensive general corrosive attack on the 10, 11, and 12 at. per cent Au alloys has already been noted, and it seemed of interest to examine all alloy compositions in this respect. This was done by determining the weight loss after immersion in concentrated FeCl_3 solution for 24 hours.

The results were:

<u>Composition</u> <u>(at. % Au)</u>	<u>Initial</u> <u>Weight (g.)</u>	<u>Final</u> <u>Weight (g.)</u>	<u>% Weight</u> <u>Loss</u>
16.5	0.9532	0.8635	9.42
20.0	0.9667	0.8768	9.31
28.5	1.1000	1.0979	0.19
30.0	1.2050	1.2046	0.04
31.2	1.2002	1.2002	---

The composition range over which general corrosive attack occurs coincides with the stress-corrosion susceptible range. This is to be expected since there is no question that corrosive attack is a prerequisite for a stress-corrosion failure. The loss in weight of the 28.5% alloy is very much less than that of the 20.0% alloy, but the stress-corrosion susceptibilities are quite comparable; evidently, a slight susceptibility to general corrosion may accompany a high degree of stress-corrosion susceptibility, and in itself is no indication of probable performance under combined stress and corrosive conditions.

Effect of FeCl_3 Concentration on Stress Corrosion Susceptibility of 8, 8.8, and 9.9 at. % Au Alloys

The results described in the previous sections suggested that the failure times of low-gold alloys in quite dilute FeCl_3 might be informative. Accordingly, single crystals containing 8, 8.8, and 9.9 at. % Au were tested

in 0.1 % FeCl_3 solution (5 per cent glide strain). It was reasoned that a dilute electrolyte solution might reduce general corrosive damage sufficiently to allow a stress-corrosion crack to nucleate. As expected, the surface was slightly attacked, but cracking did not occur, at least within an imposed time limit of two weeks. These alloys were subsequently tested in 0.5% FeCl_3 solution after their long immersion in the 0.1% solution, and definite stress-corrosion failures now occurred. For example, the 8.8% and 9.9% alloys failed in about 50 and 10 hours respectively, broadly in agreement with the earlier results. The main feature of the failure of the 8.8% at. % Au specimen was that the crack took over 24 hours to traverse the specimen.

It seems reasonable to conclude from this investigation that,

- 1) Too weak a corrosive solution cannot stimulate sufficient electrochemical attack, and too strong a solution removes the surface too rapidly for crack nucleation to occur,
- 2) There is no definite lower limit to the susceptible range.

Discussion

The diagram of stress-corrosion susceptibility for the copper-gold system, Fig. 3, shows several features by which it differs from that determined by Graf, Fig. 2. The determination of the range of general corrosion lends support to the idea that there is some definite composition limit beyond which stress-corrosion cannot occur; this limit is indicated by a vertical line in Fig. 3. The solid line represents the limit for the selected experimental conditions, and the broken line the ultimate limit which seems to be independent of glide strain (or applied stress) and Fe^{+++} . The measured failure times indicate a continuous increase in susceptibility with increasing gold content, maximum susceptibility coinciding with the limit of susceptibility. Of course, it must be realized that Graf's polycrystalline alloys failed by intercrystalline cracking, and it is proposed that composition differences at grain boundaries might account for the more complex behavior displayed by the polycrystals.

If the susceptibility does increase with increasing gold content up to a composition limit imposed by electrochemical behavior, it seems possible that this increase is associated with the accompanying increase in alloy

hardening. This does not explain how a brittle crack can propagate through an otherwise ductile material, but it seems not unreasonable to suppose that the brittle effect is enhanced by an increase in hardness. On the other hand, the variation in hardness (yield strength) of Cu_3Au with domain size is quite marked, while the stress-corrosion behavior apparently remains unaffected. Also, disordered (short-range-ordered) Cu_3Au is much harder than the long-range-ordered alloy, but the stress-corrosion behavior is similar; this latter fact merely confirms the earlier observation by Bakish and Robertson⁹.

It is suggested that the marked reduction in susceptibility at the copper-rich end of the range is due to the effect of large-scale general attack in impairing the nucleation of cracks. It is hard to see why stress-corrosion should ever occur if such an attack were to prevent crack nucleation entirely, and it is therefore proposed that nucleation is achieved on a statistical basis, with the average number of available sites falling off as the amount of general attack increases.

Most recent ideas on stress-corrosion envisage a two-stage periodic electrochemical-mechanical mechanism, with the mechanical fracture step influenced by structural details. For example, Forty¹ describes a model in which restricted dislocation mobility causes susceptibility to stress-corrosion cracking. Such restricted slip might be associated with difficult cross slip and a low stacking fault energy,^{2,3} although Forty discusses restricted slip in susceptible alloys in terms of yield points which might be due, although not necessarily, to short range order. Neither of these possibilities appears to completely fit the copper-gold stress-corrosion data. Thus, as shown in Fig. 4, long-range-ordered Cu_3Au does not show a yield point but it is quite as susceptible to stress-corrosion as the short-range-ordered alloy, which displays marked yielding. Swann and Nutting¹⁰ have observed enhanced chemical activity at stacking faults in copper alloys, which might be taken as an indication of the possible significance of a low stacking fault energy. However, (a) the stacking fault energy of short-range-ordered Cu_3Au may not be particularly low¹¹ (about 85 ergs. cm^{-2}), and (b) a different type of active site must be sought in long-range-ordered

Cu_3Au , possibly the antiphase domain between the superlattice dislocations. If indeed different active sites exist in the S.R.O. and L.R.O. alloys, then bearing in mind the quite different modes of plastic deformation in these alloys (yield points, work hardening rates, etc.,) it becomes very difficult to account for the similarity in their stress-corrosion behavior in terms of a mechanical model. Again, Kear and Yildorf¹² observed that after about 3 percent strain, dislocations in disordered Cu_3Au are arranged in packets as against a more random distribution in the ordered alloy. The present research confirmed this fact, additionally noting that a pronounced yield point accompanied a particularly high clustering of slip lines. Intuitively, and from an electrochemical standpoint, it seems logical to anticipate a severer attack on these disordered alloys, but this is not the case.

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FIGURE 1
Teflon/Nylon Jig For Stress-corrosion Testing Single Crystals.

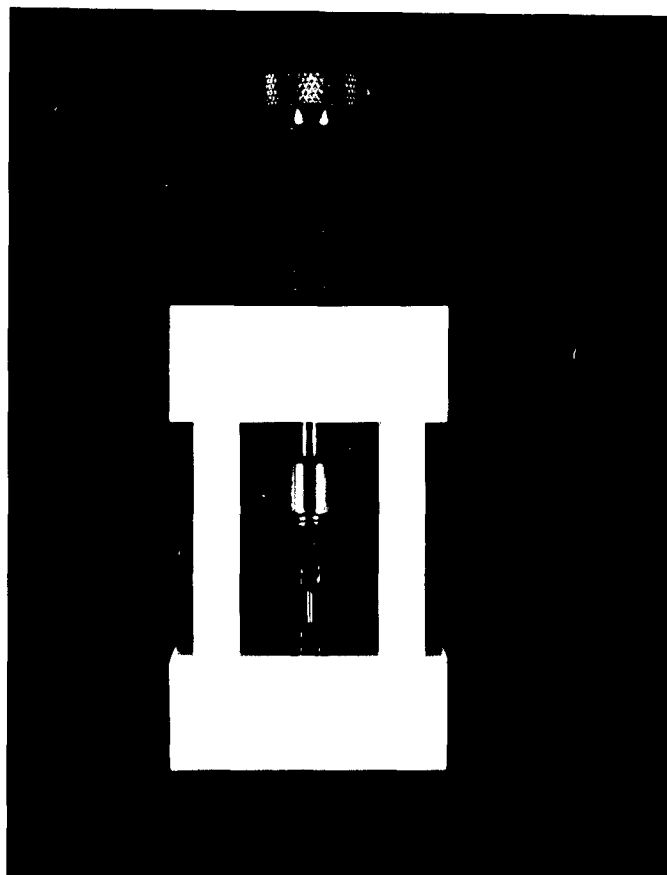


FIGURE 2

LIFETIME OF COPPER-GOLD POLY-CRYSTALS IN 2% FERRIC CHLORIDE (AFTER GRAF)

———— Applied Stress 80% of U.T.S.
- - - - - Applied Stress 20% of U.T.S.

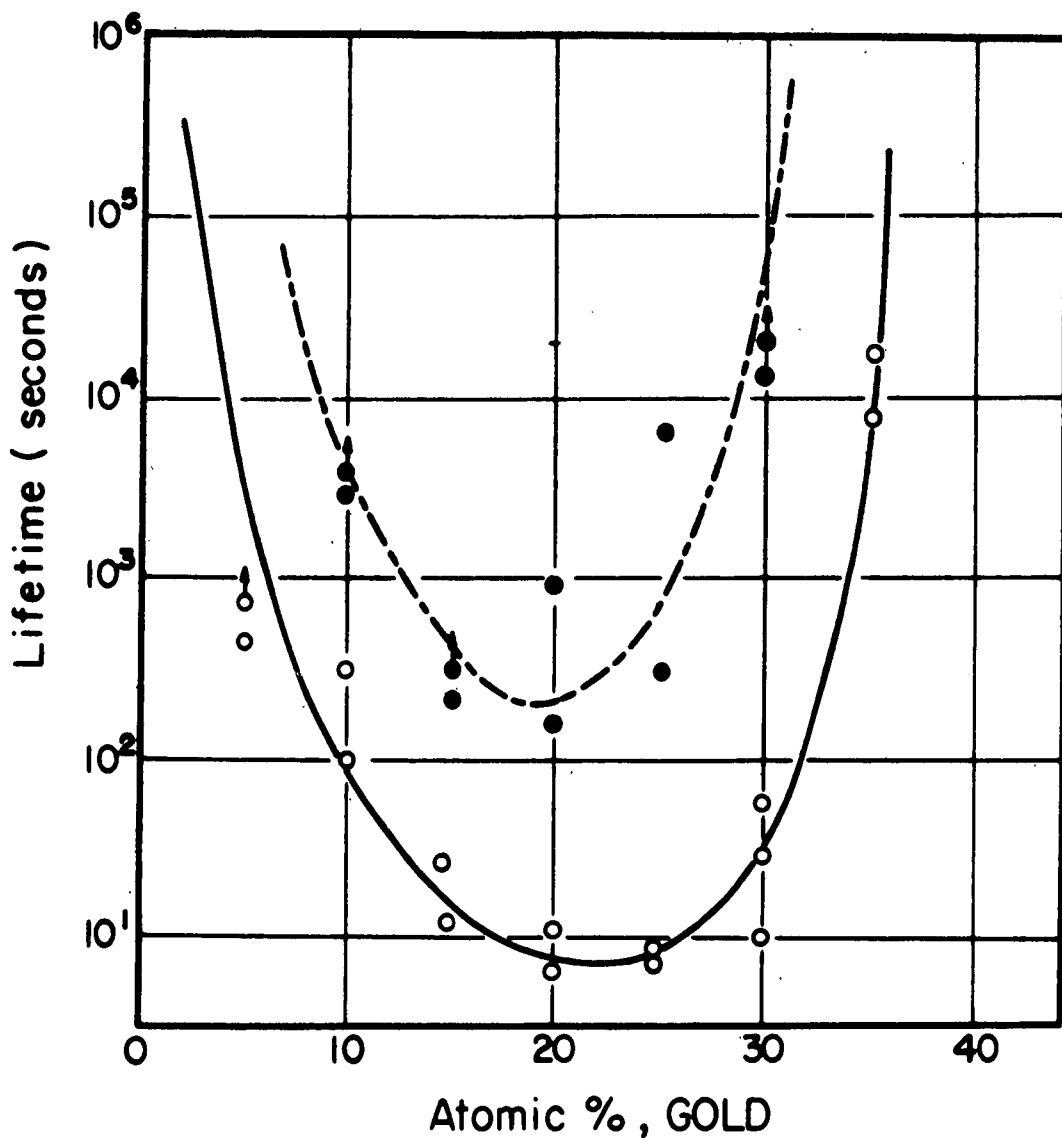


FIGURE 3

LIFETIME OF COPPER-GOLD SINGLE CRYSTALS
SUBJECTED TO 5% GLIDE STRAIN IN 2% aq.
FeCl₃.

(The Solid Vertical Line represents the Limit
of Susceptibility Under the Chosen Experimental
Conditions; The Broken Vertical Line Re-
presents the Limit of Susceptibility Under
the Severest Possible Conditions of Stress
and Corrosive Environment)

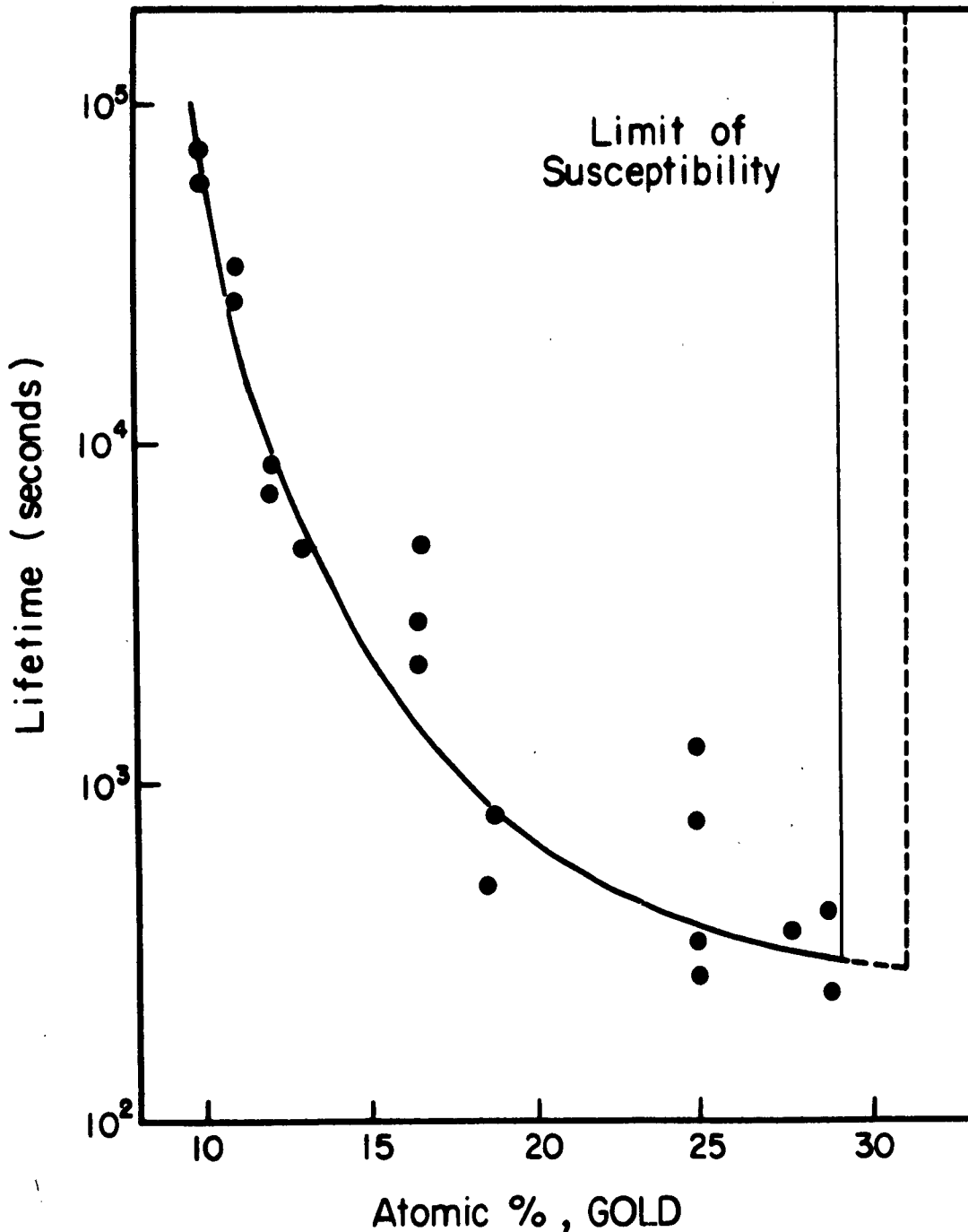


FIGURE 4

STRESS-STRAIN CURVES FOR Cu_3Au AS A FUNCTION OF DOMAIN SIZE, THE NUMBERS BESIDE EACH CURVE INDICATE THE DEDUCED DOMAIN SIZE IN ANGSTROMS.

