

FOREWORD

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ABSTRACT

A study of the mechanical behavior of copper single crystals in solutions containing surface-active agents shows that the weakening effect is associated with the formation and solution of metallic soaps. A large change in the stress-strain characteristics of polycrystalline aluminum alloys was found when the surface of the specimens was removed during plastic deformation. Studies of the effect of size of the specimen on the changes of slopes of Stages I and II by surface removal showed that the change of the slope of Stage I was independent of size with respect to the polishing rate; however, the change in the slope of Stage II with polishing rate increased directly in proportion to surface area or cross section. A surface removal treatment on single crystals eliminated the yield point, whereas the same type of treatment enhanced the yield point drop on aluminum alloys. Measurements of slipband spacing indicate that surface treatment affects the egress of dislocations.

This report has been reviewed and is approved.



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I. INTRODUCTION

In previous reports and papers (Refs. 1 through 4), it was reported that the surface played an important role in the plastic deformation of metals. By removing the surface layers of a crystal of aluminum by electrolytic polishing during tensile deformation, it was found that the slopes of Stages I, II and III were decreased and the extent of Stages I and II were increased when the rate of metal removal was increased. The results of the investigation of surface-active agents showed that changes in the slopes and extents of Stages I and II occurred when single crystals of aluminum were deformed in tension in a bath containing solutions of paraffin oil and stearic acid. The amount of change was a function of the concentration of stearic acid and the maximum effect occurred at a concentration of 0.02 mol/liter.

These results were interpreted in terms of the rate of solution of metal soaps which form as a result of the chemical reaction between the surface-active agent and the metal. According to the mechanism proposed, the rate of solution of the metal soaps is dependent upon the concentration of surface-active agents in the solution. At low concentrations, the number of metal soap molecules formed is low; at high concentrations, the rate of solubility is low because of the degree of saturation of the solution. In a general sense, the type of reaction which occurs when a metal is deformed in a bath containing surface-active agents is similar to that which occurs when a metal is deformed in an electrolytic polishing bath. In both cases, the effect on the mechanical behavior is related to the rate at which the metal is removed. A difference which exists is that an overall removal occurs in the case of electrolytic polishing, whereas for the surface-active agent, the removal seems to be confined mainly to the high energy dislocation sites.

In the present work, the research has been directed toward further studies to obtain more direct evidence on the mechanism by which surface-active agents affect the mechanical properties. Since copper soaps in solution may be analyzed with a sensitivity of 0.02 ppm, single crystals of copper were studied. Studies also were conducted on the effect of surface-removal on the plastic flow characteristics of polycrystalline aluminum (1100-0 and 7075-T6) and gold. The yield point behavior of single crystals of high purity aluminum and gold, and polycrystalline aluminum also was studied.

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II. EXPERIMENTAL PROCEDURE

For those portions of the investigation involving creep and tensile specimens, the single crystals had a nominal 1/8-inch square cross section and were prepared by a modified Bridgman technique using a multiple-cavity graphite mold. The aluminum was 99.997% pure and the copper 99.999%. The aluminum specimens for the size effect studies were prepared through the use of a three-tier mold in which crystals having a cross section of 1/8 inch, 1/4 inch and 1/2 inch were grown from a common seed. The mold design was arranged so that one 1/2-inch crystal, two 1/4-inch crystals and four 1/8-inch crystals of the same orientation could be cast. With this technique, it was possible to obtain only one set of crystals of the same orientation. Because of this limitation, it was not possible to determine both the changes of extent and slope of the various stages since a large number of crystals of the same orientation would have been required. Instead, only the change of slope as a function of the rate of metal removal was studied by abruptly altering the current density of the electrolytic polishing bath at various strains within the regions of Stages I and II.

The experimental techniques used for the tensile studies were essentially the same as those used previously (Refs. 1 through 4). The specimens were deformed in a 200-pound Instron tensile machine, usually at a rate of 10^{-5} sec^{-1} . A methyl alcohol-nitric acid solution was used for the polishing bath. The temperature was maintained constant within $\pm 0.1^\circ \text{C}$ by means of a water bath. The tensile machine was equipped with an automatic recorder with which it was possible to measure elongations to within 3×10^{-5} inch and loads of 0.01 pound.

The creep experiments were conducted under constant stress with the use of an L-shaped loading beam (Ref. 5) which changed the loading moment as the specimen elongated (Fig. 1). In order to accommodate specimens of a wide variety of crystal orientations, the apparatus was designed so that the length of vertical leg of the loading beam could be changed. This was done by providing four sets of let mechanisms which allowed the length of the leg to be adjusted accurately prior to the creep test. The strains were measured by means of a magnetic transducer which was mounted directly above the creep specimen. The electrical output from the transducer was fed to the Y bridge of an X-Y plotter. The time base coordinate was obtained with a synchronous motor-driven variable resistor so arranged that the output voltage from the battery changed linearly with time. The sensitivity of the recording system was such that it was possible to measure elongation to within 10^{-5} inch and time to one second.

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III. EXPERIMENTAL RESULTS

A. SURFACE-ACTIVE AGENTS

1. Copper Single Crystals

In a previous investigation (Refs. 2 and 4) of aluminum crystals in stearic acid-paraffin solutions, because of insufficient sensitivity of the analytical methods for detecting aluminum stearate, only a qualitative relationship was obtained between the amount of metal soap in solution after the tests and the concentration of the stearic acid solution. Since copper soaps may be analyzed quantitatively when present as low as 0.02 ppm, a number of copper single crystals tensile specimens having the same orientation were studied using stearic acid-benzene solutions. Each test was conducted at room temperature and the deformation process was maintained for three hours. The entire solution was then collected and analyzed for copper.

In a manner similar to results obtained on aluminum, the slope and extent of Stages I and II of the tensile curves from the copper crystals changed as a function of the concentration of stearic acid in the benzene solution (Figs. 2 and 3). The slope of Stage I decreased from 3500 psi for the specimens deformed in benzene to approximately 1500 psi for specimens deformed in a solution containing 0.025 mol/liter of stearic acid. Above this concentration, the slope increased and, at a concentration of 0.1 mol/liter, attained a value approximately the same as that obtained in the benzene solution. The extent of Stage I, ϵ_2 , increased from a value of 4% for specimens deformed in benzene to 6% for specimens deformed in the solution containing 0.025 mol/liter of stearic acid. The slope and extent of Stage II followed the same general pattern as those of Stage I. The maximum effect of the stearic acid solution was at a concentration of 0.025 mol/liter. The slope of Stage II, θ_2 , dropped from 19,000 to 13,200 psi and the strain at which Stage II ended, ϵ_3 , increased from 16.5 to 20.5%. At a concentration of 0.1 mol/liter, the values for θ_2 and ϵ_3 are approximately the same as those for specimens deformed without stearic acid in solution.

The square points in Figs. 2 and 3 were obtained from specimens pulled in a 0.05 mol/liter stearic acid-benzene solution which had been saturated with copper stearate. Under this chemical environment, the values for ϵ_2 , ϵ_3 , θ_1 and θ_2 were approximately the same as those obtained from specimens pulled in benzene or in the solution containing 0.1 mol/liter.

The critical resolved shear stress (CRSS) of copper specimens used in this investigation did not change as a function of the concentration of the stearic acid solution (Fig. 4). The CRSS was taken to be the stress at which the stress-strain curve became nonlinear rather than the value of the stress obtained by the intersection of the elastic portion of the stress-strain curve with the extrapolated portion of Stage I. In the latter case, the point of intersection will vary with the slope of Stage I which changes markedly as a function of the concentration of the solution. The value for τ_2 , the stress at which Stage I ends, also appears to be constant. A constant value for τ_2 also was found for aluminum single crystals irrespective of

the rate of metal removal (Refs. 1 and 3). The value of τ_2 was approximately 290 psi. The ratio of τ_2 and CRSS was equal to approximately 2.9 as compared to 2 obtained by Rosi (Ref. 6) and Garstone and Honeycombe (Ref. 7). No complete explanation can be given at this time to resolve this rather large difference other than that it was found in these experiments that the preparation of the surfaces of the specimens before testing exerted a large influence on the extent and slope of Stage I. Prior to testing, the specimens were electrolytically polished, rinsed, dried quickly and immediately placed in the solution. When the specimen was exposed to laboratory atmosphere for a long period of time, the ϵ_2 value was decreased and the θ_1 value was increased.

The value for τ_3 , the stress at which Stage II ends, as a function of concentration of stearic acid appears to have a minimum at 0.025 mol/liter. As will be seen later, the amount of copper found in solution after the tensile tests was a maximum at this concentration. It has been shown (Ref. 3) that for aluminum crystals, τ_3 decreased with increasing rate of removal of the surface layers during deformation.

As mentioned earlier, the stearic acid-benzene solutions were analyzed for copper in solution after testing for 3 hours. These results (given in Fig. 5) show that up to a concentration of approximately 0.025 mol/liter of stearic acid, the copper content in solution increases and then decreases in the more concentrated solution. A comparison of these data with those given in Figs. 2, 3 and 4 shows that the concentration at which the stearic acid exerts the greatest influence on the mechanical behavior is the same as that in which the rate of solution of the copper stearate is the greatest.

2. Polycrystalline Aluminum

A limited investigation of the influence of various surface-active agents on the stress-strain behavior of a commercial polycrystalline aluminum (1100-0) was performed. Initially, the tests were conducted in a medium of paraffin oil containing 0.002 mol/liter of stearic acid; later, solutions of benzene with 0.025 mol/liter of stearic acid and 0.2% oleic acid were used. No effect on the stress-strain characteristics was found. The stress-strain curves were coincident with each other throughout the entire range amounting to a strain of 10%. Aluminum specimens (7075-T6) were also found not affected by these solutions. A chemical analysis of the solutions after each of the tests failed to detect the presence of aluminum soaps.

3. Gold Crystals

A series of gold single crystals was employed to determine if a surface-active agent would affect the mechanical behavior of metals without an oxide film. These specimens were subjected to a creep test and, to avoid variations in creep behavior from specimen to specimen, the composition of the solution was altered during the run. Since Klinkenberg, Lucke and Masing (Ref. 8) had reported that the creep behavior of gold specimens was increased when tested in a 0.2% oleic acid-paraffin oil solution, this medium was tried. Using a resolved shear stress of 600 psi, the tests were conducted at room temperature by allowing the specimen to creep and, while still in the transient creep range, the oleic acid was introduced. Under these conditions, no change in creep rate could be detected. A similar set of experiments

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was conducted in the steady-state creep region but again no change in creep behavior was noticed. Two series of tests also were conducted by adding known quantities of octanoic acid and oleic acid in incremental steps to the paraffin oil while the creep was proceeding. The concentration of the solution was varied in steps of 0.02% to cover a range up to 4%. At no time during the creep tests did the rate change when either octanoic acid or oleic acid was added. Analyses of the solutions after the tests failed to reveal the presence of gold soap.

B. EFFECT OF SURFACE REMOVAL

1. Size Effect

The effect of the rate of metal removal on the change in slope of Stages I and II for aluminum crystals is shown in Table 1 and Fig. 6; the orientation of crystals is given in Fig. 7. As may be seen, the change in θ_1 as a function of the polishing rate is approximately the same regardless of the size of the crystals. However, this does not appear to be the case for θ_2 . The value of $d\theta_2/dR$ is nearly the same for the same size crystals but increases by a factor of 2.2 when the cross section of the specimens is increased from 1/8 inch to 1/4 inch. The measured ratio of the surface area of the 1/8-inch specimen to that of the 1/4-inch specimen was 2.1 for the specimens of crystals 115 and 116.

Within the limits of the data obtained, it appears that when the surface layers are not removed during deformation, the θ_2 values are approximately the same for various size specimens, while θ_1 for the 1/8-inch specimens tends to be lower than that of the larger ones (Table 2).

In agreement with other data (Refs. 9 and 10), the critical resolved shear stress was found to decrease as the size of the specimen increased (Table 3). A plot of these data as a function of S , where S is the surface area per unit length, is given in Fig. 8. If a straight line is drawn through the average of the points, the equation becomes:

$$\sigma_c = 60 (S)^{-0.25} \quad (1)$$

or

$$\sigma_c = 28 \left(\frac{S}{V} \right)^{0.25} \quad (2)$$

and

$$\sigma_c = 44 A^{-0.12},$$

where A is the cross-sectional area. Maddin's (Ref. 9) results indicated an equation

$$\sigma_c = 454 A^{-0.3}$$

2. Gold Crystals

In a previous investigation (Refs. 1 and 3) of aluminum, it was not possible to determine if the change in θ_1 and θ_2 was due to change in thickness of the oxide layer or due to the removal of metal. Therefore, a series of gold crystals having a cross section of 1/8 inch was selected for study since it is believed generally that an oxide layer is not present on the surface. These crystals were deformed in a solution of aqua regia at 3° C at a strain rate of 10^{-5} sec⁻¹. Figure 9 is a typical representation of the changes in slope which occur when the current density is changed during the course of deformation. The change in slope as a function of rate of metal removal is shown in Fig. 10. Similar to the observation on aluminum, the slope of the curve in Stages I and II decreased when the current density was increased. The $d\theta_1/dR$ and $d\theta_2/dR$ are nearly the same as those found on the same size aluminum crystals. In this case, however, a sudden drop in load was not observed when the current density was changed from a low value to a high value.

3. Zinc Single Crystals

It was of interest to determine the effects of surface removal on zinc crystals, since slip occurs on the basal plane and the possibility that slip may occur on the secondary system is eliminated. Figure 11 demonstrates the effect on the slope when the current density was changed during the deformation process. It is apparent that removal of the surface layers during plastic deformation very effectively changes the slope of the stress-strain curve. When the tests were conducted at a strain rate of 10^{-5} sec⁻¹, the effect was so strong that even at a removal rate as low as 4×10^{-4} inch per minute, the slope changes from a positive to a negative value. At this rate of polishing, the change of slope in Stage I for aluminum specimens was much smaller than that of zinc crystals. After the deformation exceeded 5%, the strain rate was increased to 10^{-4} sec⁻¹ and again the current density was changed during the run. Even at this strain rate, the change in slope is large in comparison with the aluminum specimens which display only a very small change under these conditions. A drop in load due to dislocation "pop-out" also was observed at the slower strain rates when the current density was changed from a low value to a high value. This effect was not detected at the high strain rate.

4. Polycrystalline Aluminum

A three-point bend test was employed initially to determine the effects of surface removal on the plastic flow characteristics of commercial aluminum alloys. Figure 12 is a typical result when both sides of the specimen were allowed to be removed by the polishing bath at a rate of 50×10^{-5} inch per minute. Immediately, upon applying the current, a drop in load occurred which was similar to that experienced with single crystals of aluminum. When only the compression side of the specimen was removed, the drop in load did not occur (Fig. 13), whereas it did appear when only the tension side was exposed to the polishing action (Fig. 14). In the first four applications of current, the polishing action was allowed to continue for only one minute and the effect on the slope of the deformation curve is not seen; however, in the last cycle shown it may be seen that the slope of the curve is lowered markedly.

Figure 15 shows the influence of surface removal on the deformation behavior of a fine-grained commercially pure aluminum (1100-0). The data presented as true stress-true strain curve demonstrate clearly that the work-hardening coefficients are modified by the conditions which exist at the surface of the specimen. Similar to the results on single crystals, the slope of the curve decreases as the rate of polishing increases.

When a tensile specimen of aluminum (1100-0) was pulled in the polishing bath with a removal rate, R , of 25×10^{-5} inch per minute (Fig. 16), very early in the plastic range the stress-strain curve departs from that of the specimen pulled at $R = 0$. When the current through the polishing bath is reduced to zero, the slope of the curve is changed and follows that of specimen No. 9.

5. Creep Behavior

The effect of removing the surface during creep of a gold crystal is shown in Fig. 17. The orientation of the crystal is given in Fig. 10. In this experiment, the current through the cell was changed at periodic intervals in an attempt to avoid the problem associated with the large variation in creep rate from specimen to specimen. The secondary creep rate of a gold crystal was found to increase exponentially with the rate of removal (Fig. 18) according to the form $\dot{\epsilon} = 9.5 \times 10^{-4} e^{0.07R}$ where $\dot{\epsilon}$ is the creep rate in percent per minute and R is the rate of change of the cross section in inches per minute.

An increase in the current through the polishing bath causes a large increase in the creep rate and appears to extend the primary creep region. With a current density of 1.5 amp/in.^2 , transient creep occurred; however, when the current was reduced to zero, the creep rate immediately fell to a value of approximately that for secondary creep.

In the secondary region, whenever the current density was changed from a low value to a high value, a steady-state creep rate was not attained immediately. The creep rate increased gradually with time and only after several minutes had elapsed was the steady-state value reached. The length of time required for the transition period seems to increase with the amount of creep which occurred at the lower polishing rate and the difference in value of the two current densities. For example, at a current density of 1.5 amp/in.^2 , it required one minute for the steady-state creep rate to be reached after a prior strain of 0.006% at zero current and three minutes after the strain at zero current was 0.015% . With a change from zero to 2.2 amp/in.^2 and a prior strain at zero current of 0.01% , it required two minutes to reach a steady-state condition.

A change in current density from a high value to a low value produced an immediate change in the creep rate and no incubation period was found. In the secondary creep region when the load on the specimen was removed, a transient creep region appeared upon reloading at zero current. When the load was applied while a current was passing through the polishing bath, the transient creep rate was increased.

C. YIELD POINT PHENOMENA

It has been shown in previous investigations (Refs. 11 through 14) that a yield drop occurs when a metal having a face-centered cubic structure is re-loaded after a given amount of prior plastic strain. Similar yield point experiments were carried out on gold and aluminum single crystals. For these crystals, a yield point was found as a result of an unloading-loading cycle without a surface treatment. If, however, the surface was removed after the specimen was unloaded, the yield point failed to appear. Polishing the aluminum during plastic deformation always caused a decrease in the applied load; however in no case did a yield point appear when the load was returned by reducing the cell current to zero. In several cases of both gold and aluminum crystals, the specimen was subjected to a consecutive series of unloading and loading cycles. When a yield point occurred after a sufficient amount of plastic strain had been reached, a subsequent unloading and loading cycle reproduced a yield point. Figure 19 shows the type of yield point obtained from a single crystal of gold which had been strained to 6.5% and given a stress cycle. Upon recycling at a strain of 8.5%, the yield point appeared. If a specimen was polished after the yield point appeared, it failed to appear on the next stress cycle and the flow stress was lower than that before unloading (Fig. 20). In all of these tests with single crystals, about 0.001 inch was removed from the cross section and no attempt was made to study the decrease of the yield point drop as a function of the amount of metal removed.

A typical example of the yield point behavior for an aluminum alloy (7075-T6) is given in Fig. 21. A yield drop of approximately 50 psi occurred after the specimen had been strained 8.8% and reloaded. When the applied stress was decreased by only 750 psi, no yield point appeared upon reloading (Fig. 22); however, it was found that when the tensile tests were conducted in an electrolytic polishing bath and a current was allowed to pass through the cell for a short period of time, a yield drop occurred with the same amount of unloading (Fig. 23). In this case, the stress was dropped about 1000 psi, the machine stopped and the specimen polished; upon reloading, a yield drop of 80 psi was found. The same phenomenon may be shown by the effects of the surface removal alone (Fig. 24). At a strain of 5.4%, a drop in stress of 350 psi occurred when a current of 10 amperes was passed through the polishing bath ($R = 8 \times 10^{-4}$ in./min) while the tensile machine was still running. When the current was reduced to zero, the load returned but a yield point did not appear. At higher strains ($\epsilon = 6.8\%$ and 8.7%), a decrease in applied load by the polishing action produced a yield drop of 125 psi. Figure 25 shows the yield point phenomenon under two different conditions of metal removal during the deformation process. In Curve A, the specimen was strained to 6.3% and then the applied stress was reduced by 3000 psi and polished to remove 8×10^{-4} inch from the cross section. Upon reapplication of the load, a yield drop of 125 psi occurred. In Curve B, during the process of plastic deformation, the surface of the specimen was removed by chemical etching just before the unloading portion of the cycle. After unloading and removing the solution, a yield drop of 125 psi occurred when the loading cycle was resumed.

These experiments show that the yield drop produced by a chemical etch or by electrolytic polishing is significantly larger than that produced by loading and unloading without any surface removal. In addition, it was found that the strain

rate must be relatively slow to show the yield point. If $\dot{\epsilon}$ exceeded $2 \times 10^{-4} \text{ sec}^{-1}$, no yield drop was observed regardless of the surface treatment of the specimen.

D. LAUE' SPOT AND SLIP BAND OBSERVATIONS

A limited study was made of the comparison of the width and spacing of slip bands in aluminum crystals with and without surface removal during deformation at 3° C. The results of this study are given in Table 4. Two specimens with the same orientation were strained first to within the Stage I region and then to strains within Stage II. Slip band measurements and Laue' back reflection patterns were obtained after each deformation. It is quite apparent that in both stages of deformation, the slip band spacing is larger for the specimens pulled in the polishing bath. Microscopic examination disclosed that the slip bands of the specimens deformed without polishing were narrower than those of specimens pulled while the surface was being removed.

The Laue' back reflection X-ray patterns revealed several interesting features. In Stage I the spots were sharp although those from the polished specimens showed some breakup. In Stage II, the spots from the specimens pulled in water became elongated and continuously streaked, whereas those from the polished specimens were broken up into small discontinuous regions.

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IV. DISCUSSION

The results obtained on the effect of surface-active agents on the deformation characteristics, coupled with those previously reported (Refs. 2 and 4) on aluminum, show that the change in mechanical behavior as a function of the concentration of the surface-active agent in solution is associated with the rate of desorption of the metal soaps which are formed. This conclusion is supported by two sets of observations. In the experiments on copper crystals, it was found that the average rate of solution of copper as copper stearate reached a maximum value at the same concentration as that which produced the maximum effect on the mechanical behavior. In experiments on both aluminum (Refs. 2 and 4) and copper, it was found that the addition of the metallic soaps to the solutions containing the surface-active acids eliminated the "weakening" effect of the surfactants.

According to the proposed mechanism, at low concentrations of the surface-active agent, the rate of solution of the metal soaps is limited by the rate of formation of the soaps; at high concentrations, the rate of solution is limited by the degree of saturation of the solution.

The fact that no effect was found when gold crystals were used in the presence of octanoic acid and oleic acid may be explained in terms of the free energy change (ΔF) for the reaction. It is known that the ΔF value for the reaction between gold and fatty acids is highly positive and that the reaction will not occur. Smith (Ref. 15) suggested that plastic deformation may promote the reaction between a clean metal surface and a surface-active agent. Apparently, the soap did not form with gold and oleic acid or octanoic acid under the conditions of the creep experiments since gold soap was not found in solution.

In many respects, the copper crystals behaved in a manner similar to aluminum crystal when tested in a solution containing polar molecules. The CRSS and the stress at which Stage I ends did not change with the concentration of the solution. There appears to be a decrease in the value of τ_3 , the stress at which Stage II ends, at the concentration where the weakening effect is a maximum. In this respect, the effect is similar to the decrease in τ_3 when the surface is removed by electrolytic polishing (Refs. 1 and 3).

The study of surface removal on the plastic deformation of various sizes of aluminum crystals did not reveal a size effect in Stage I. The change in θ_1 as a function of the rate of removal was a constant regardless of the size of the crystal. In previous papers (Refs. 1 and 3), evidence was presented which could be interpreted to show that, as a result of plastic deformation in a tensile test, a higher density of dislocations existed in the surface region than in the interior. This region appears to extend deeper into the crystals as the plastic strain is increased. Since, in Stage I, internal obstacles do not seem to contribute greatly to θ_1 , a large percentage of the dislocations generated move easily to the surface region. The slope, θ_1 , increases with the size of the crystal, indicating that the density of dislocations in the surface region is greater for the large specimens. If the slope of Stage I is governed predominantly by the density of dislocations in the surface region, then a constant value of $d\theta_1/dR$ for various size crystals

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implies that the percentage of dislocations escaping from the crystal is constant for a given rate of removal of the metal.

In Stage II, a size effect was found. The value of $d\theta_2/dR$ was directly proportional to the surface area of the crystal and to the cross-sectional dimension since square section crystals were used. From the experimental data, it appears most likely that θ_2 is independent of size when the surface is not removed during the testing.

The experimental results are consistent with the following model: In Stage I, it has been shown that the slope is determined mainly by the dislocations in the surface region rather than by the internal obstacles. In Stage II, both internal obstacles and surface barriers are important. Of all the dislocations that reach the surface region, a given percentage will escape as a function of the polishing rate. In Stage I, since practically all the dislocations contributing to plastic deformation move to the surface region, a constant percentage decrease in the number of dislocations by the surface removal will result in a constant $d\theta_1/dR$.

However, in Stage II, not all of the dislocations contributing to plastic deformation reach the surface because of the interference of internal obstacles. Apparently, a great percentage of these dislocations reach the surface region for the larger specimens. Therefore, with a constant percentage decrease of the dislocations by surface removal, the greater will be the decrease in the total number of dislocations as compared to the smaller specimen; $d\theta_2/dR$ will increase with the size of the specimen.

The experimental results on the effect of removing the surface of gold crystals show that the changes in θ_1 and θ_2 in other metals are not due only to the removal of an oxide film but are associated also with the rate of formation of a "debris" layer extending from the surface into the body of the crystal. The lack of a dislocation "pop-out" on gold shows that in other metals, the sudden release of dislocations by polishing is due to an oxide coating. The pop-out dislocation was found only in those metals which readily form oxide coating. The presence of this debris affects the creep behavior as well as the stress-strain characteristics. It appears that the rate of creep in both the primary and secondary regions is influenced by the thickness of the debris layer. In the early portion of the primary region when the current through the cell was increased, the creep rate increased. In the secondary creep region, it required from two to four minutes before the new steady-state creep rate was attained when the polishing rate was changed from a low to a high value. This elapsed time may be associated with the time required to reduce the thickness of the debris layer. Further, it appears that the activation energy for creep at 3° C is controlled mainly by surface barriers and not by the Peierls force as suggested by Lytton (Ref. 16). The secondary creep rate was shown to increase by a factor of 30 when the rate of removal of the metal was changed from zero to 50×10^{-5} inch per minute.

The change in the work-hardening coefficient of polycrystalline aluminum by removing the surface during the course of deformation shows that surface effects are important even though strong internal obstacles such as grain boundaries are present. This effect may be viewed as a relief or a decrease of the back stress on the dislocation sources which allows them to operate more freely.

Conclusions

In an interior grain, a number of dislocations may be stopped against the grain boundary and produce a back stress which slows down or stops the generation of dislocations. If the grain boundaries are not completely opaque, the back stress on the source will be a function of the number of dislocations piled up within the grain and the number of dislocations from the neighboring grain pressing against its boundary. In the case of a surface grain and its interior neighboring grains, it is seen that if the number of piled-up dislocations in the surface grain is reduced by a surface treatment, the back stress against the neighboring grains is reduced and both dislocation sources are able to operate more freely at a given stress level. This back stress reaction will extend to every grain in the system.

The enhancement of the yield point in the aluminum alloy (7075-T6) by electrolytic polishing or by chemical etching appears to be associated with the precipitation of impurities rather than with the polycrystalline nature of the material. A large increase in the yield point was found when a 7075-T6 alloy was used; however, practically no effect was noted with 1100-0. It is possible that during the chemical attack, vacancies may be introduced into the surface layers of the specimen. These vacancies may interact with impurity atoms in solution and cause them to precipitate on slowly moving or stationary dislocations. The interaction between the dislocations and the vacancy precipitated impurity atoms will impede the motion of dislocations when the stress is reapplied and a higher stress will be required to start the dislocation moving. After the dislocations break away, a lower stress will be sufficient to keep them moving.

The introduction of vacancies into the metal by the chemical attack seems reasonable since, in the process of removing the aluminum from the surface, the aluminum ions must diffuse outward through the vacancies in the oxide layer. Under this condition, it is unlikely that only one layer of atoms will be removed at a time and surface vacancies will be created. Since the vacancy concentration in the oxide is highest at the surface, the concentration gradient for the diffusion of the surface vacancies requires that they diffuse into the metal. Evidence for the formation of vacancies by oxidation has been reported by Dunnington, Beck and Fontana (Ref. 17). These investigators show that the most likely explanation for the oxidation of iron may be based on the diffusion of lattice vacancies.

The precipitation of impurities does not appear to be the only mechanism which causes a yield point. The results of investigations of high purity single crystals of gold and aluminum show that removing the surface between the unloading and reloading cycle eliminates the yield point. From this observation it is clear that the yield point phenomenon is associated with dislocation barriers in the surface regions and not with interior Lomer-Cottrell locks. When the load is relaxed sufficiently, the moving dislocations are slowed or stopped. Perhaps, through a rearrangement of the dislocation debris, a larger stress would be required to make the dislocations move again than would be necessary only to keep them moving.

It has never been entirely clear whether surface effects are a result of altering surface dislocation sources or the egress of dislocations from the interior sources. The nature and spacing of the slip bands of specimens deformed with and without removing the surface should help to resolve this question. If surface sources are the dominating factor, it is expected that the slip bands of the specimen deformed during polishing would be more closely spaced and narrower because new surface sources would be generated continuously. When a

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source stops operating because of the back stress imposed upon it, more sources are made available by the removal of the surface layers. On the other hand, if the egress of dislocations is altered, the opposite results would be expected. The slip bands of specimens deformed during a surface removal treatment would be more widely spaced and broader than those of specimens pulled without surface removal. In this case, the internal dislocations cannot be affected directly by the polishing and a source will stop operating when the number of dislocations piled up against surface barriers become sufficiently high. If the dislocations in the surface region are allowed to move out easily, the internal source may operate for a longer time before it is stopped and a fewer number of such sources are required to produce the same strain. The experimental data show that the slip bands are more widely spaced and broader for the specimens pulled with surface removal than those without; this indicates that the egress of dislocations is being affected.

Although only a limited study was conducted, it is quite clear that large changes in the slope of the stress-strain curve of zinc crystals may be affected by removing the surface during the deformation process. At the temperature used, zinc will slip only on the basal planes and, therefore, the changes in slope cannot be associated with slip on secondary slip systems which may have become activated by bending of the specimen.

V. CONCLUSIONS

The extent and slope of Stages I and II of copper crystals deformed in a benzene solution containing stearic acid changed as a function of the concentration. A correlation between the rate of solution of copper soaps and the change in mechanical behavior confirms previous conclusions that the weakening effect of a surface-active agent is associated with the rate of removal of the surface. Surface-active agents in solutions of paraffin oil did not affect the creep behavior of gold crystals, presumably because gold soaps were not formed.

A large effect on the plastic strain characteristics of polycrystalline aluminum alloys was found when the surface of the specimens was removed during the deformation process. This demonstrates that grain boundaries do not control completely the movement or generation of dislocations in these materials. At large strains, a yield point appeared when specimens were unloaded and reloaded; however, the yield point drop was enhanced if the specimen was subjected to a surface removal treatment either before or after the unloading portion of the cycle. In contrast, a surface removal treatment on high purity single crystals eliminated the yield point. It was considered that two mechanisms could be responsible for the yield point. One may be due to a precipitation of impurities and the other to the temporary blocking of dislocations by the surface debris.

The change in θ_1 as a function of R was found to be independent of specimen size; however, $d\theta_2/dR$ increased with specimen size. In Stage I, it appears that the percentage of dislocations escaping from the crystal is constant for a given rate of metal removal; in Stage II, the percentage of escaping dislocations increases directly with the size of the crystal.

The critical resolved shear stress decreased with the size of the specimen.

The creep behavior of single crystals also was found to be affected by the removal of the metal during the deformation process. Further evidence for a debris layer at the surface regions was indicated by observations that the new steady-state creep rate was not attained immediately when the rate of metal removal was changed from a low value to a high value. It appears that the activation energy for creep may be due largely to surface barriers.

Observations of the slip band spacing indicate that changes in mechanical behavior with polishing are due to the change in the rate of egress of the dislocations and not to the surface sources. The slip band spacing for the specimens deformed while the surface was being removed is much wider than that for specimens deformed without removing the surface.

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APPENDIX

TABLES AND ILLUSTRATIONS

TABLE 1

The Change of Slope of Stages I and II as a Function of Rate of
Metal Removal, R, for Various Size Crystals

Aluminum crystals 115, 116, 117; Temperature 3° C; $\dot{\epsilon} = 10^{-5} \text{ sec}^{-1}$

Nominal Cross Section (in.)	$\frac{d\theta_1}{dR} \times 10^4$			$\frac{d\theta_2}{dR} \times 10^4$	
	1/8	1/4	1/2	1/8	1/4
Crystal					
115	850	860	860	900	2000
116	1100	1200	--	870	2000
117	1000	1100	950		

TABLE 2

The Relationship of θ_1 and θ_2 with Size of Crystal

Aluminum crystals 115, 116, 117; Temperature 3° C; $\dot{\epsilon} = 10^{-5} \text{ sec}^{-1}$

Nominal Cross Section (in.)	θ_1 (1000 psi)			θ_2 (1000 psi)	
	1/8	1/4	1/2	1/8	1/4
Crystal					
115	9.4	11.7	10	14.0	17.0
116	8.4	7.4	--	16.0	16.0
117	6.4	8.3	9		

TABLE 3

Critical Resolved Shear Stress as a Function of Crystal Size

Aluminum crystals 115, 116, 117; Temperature 3° C; $\dot{\epsilon} = 10^{-5} \text{ sec}^{-1}$

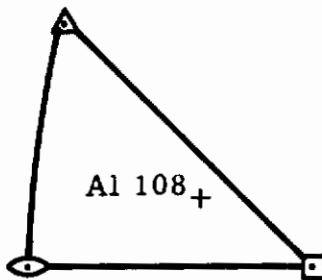
Nominal Size (in.)	CRSS (psi)		
	1/8	1/4	1/2
Crystal			
115	74.0	65.9	48.1
116	69.7	56.3	49.6
117	<u>85.5</u>	<u>68.3</u>	<u>56.5</u>
Average	76.4	63.5	51.4

TABLE 4

**Comparison of Slip Band Spacing of Aluminum Specimens with
and Without Surface Removal During Deformation**

Temperature 3° C; $\dot{\epsilon} = 10^{-5} \text{ sec}^{-1}$; R = $35 \times 10^{-5} \text{ in./min}$

Surface Removed			Surface Not Removed		
Stage	Shear Strain (%)	Bands/cm	Stage	Shear Strain (%)	Bands/cm
I	1.37	50	I	0.58	104
II	2.0	100	II	1.73	608
II	3.4	340			



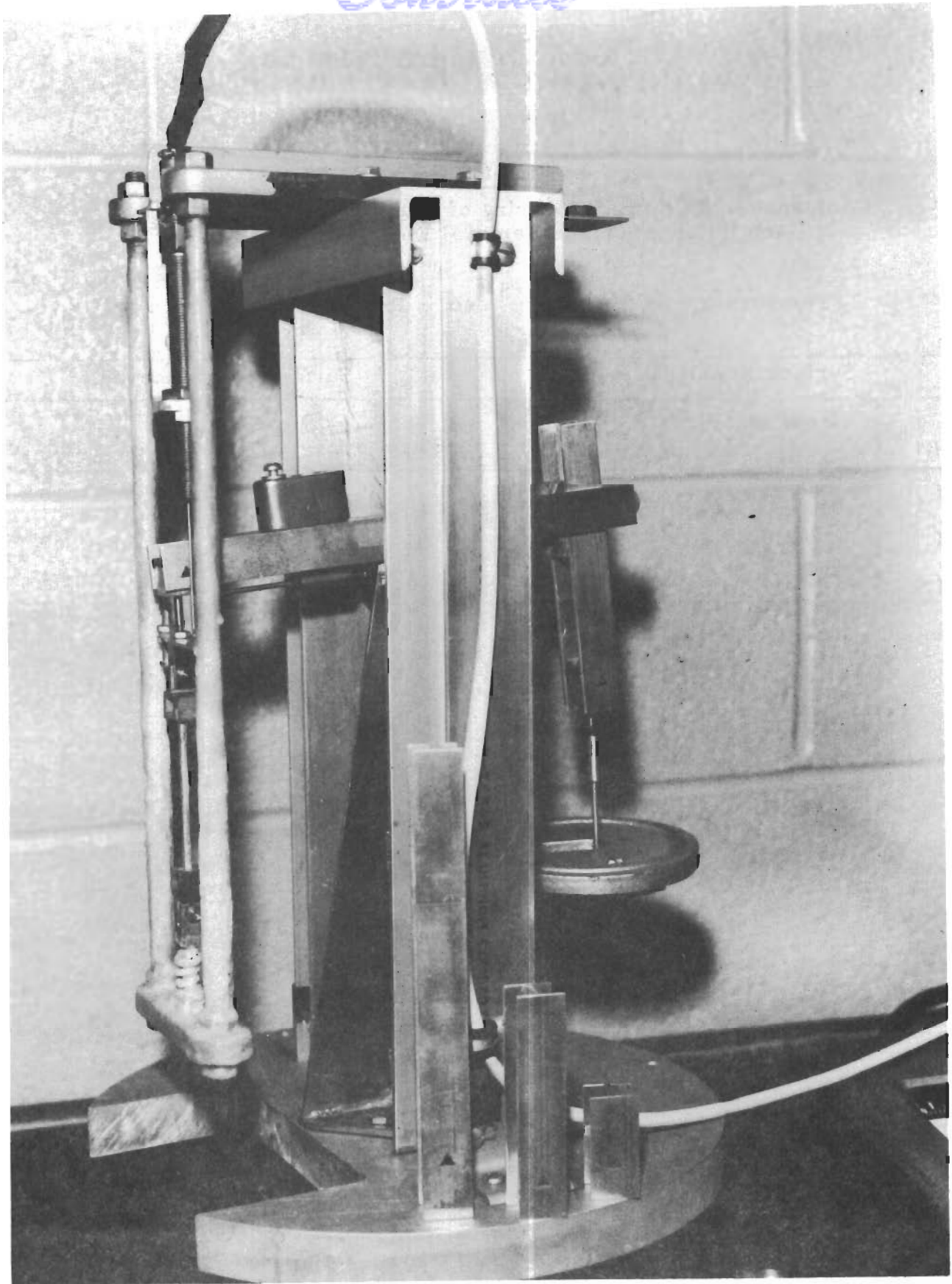


Fig. 1. Creep Apparatus

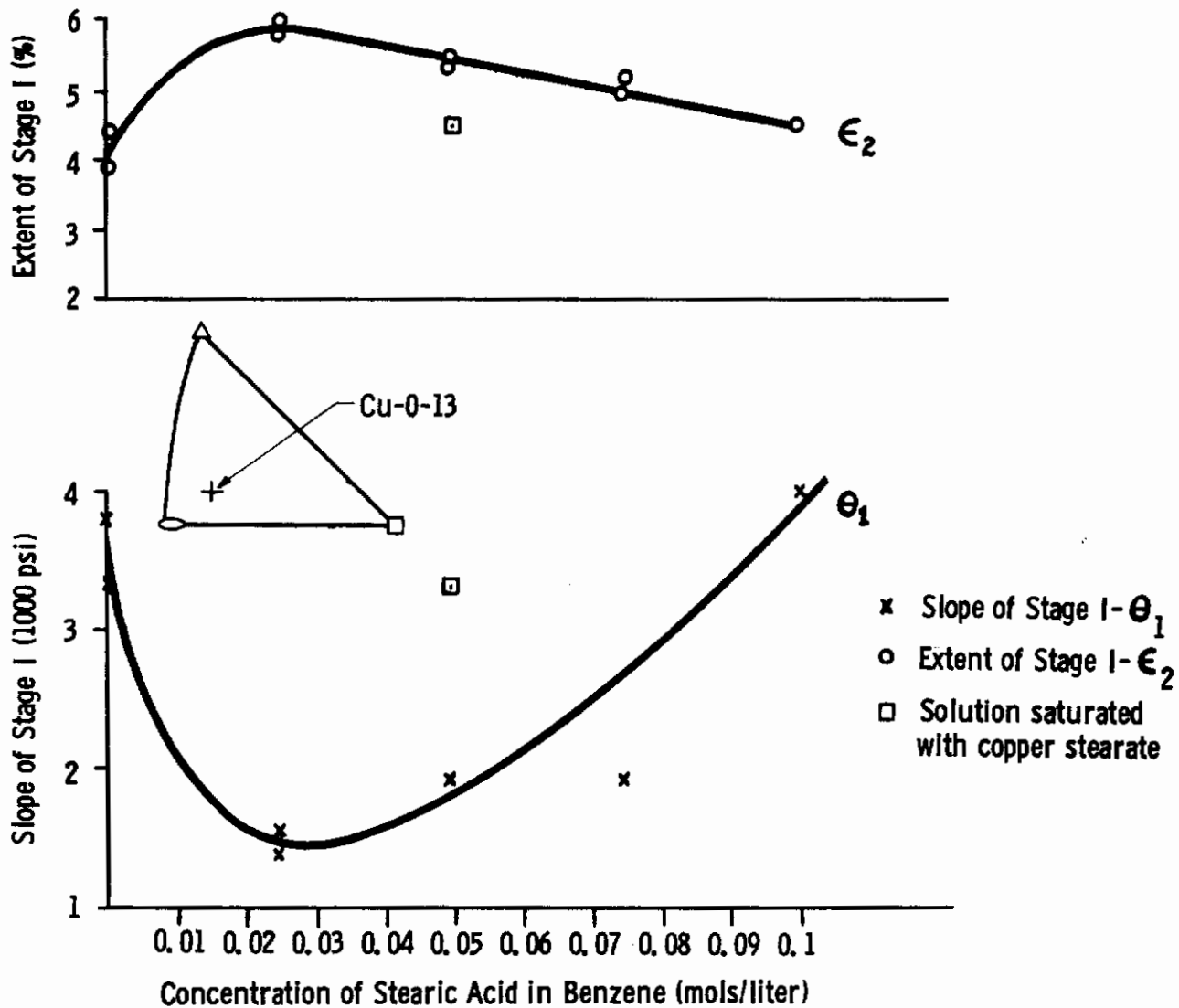


Fig. 2. Change in Slope and Extent of Stage I as a Function of Stearic Acid Concentration in Benzene for Copper Crystals 0 - 13

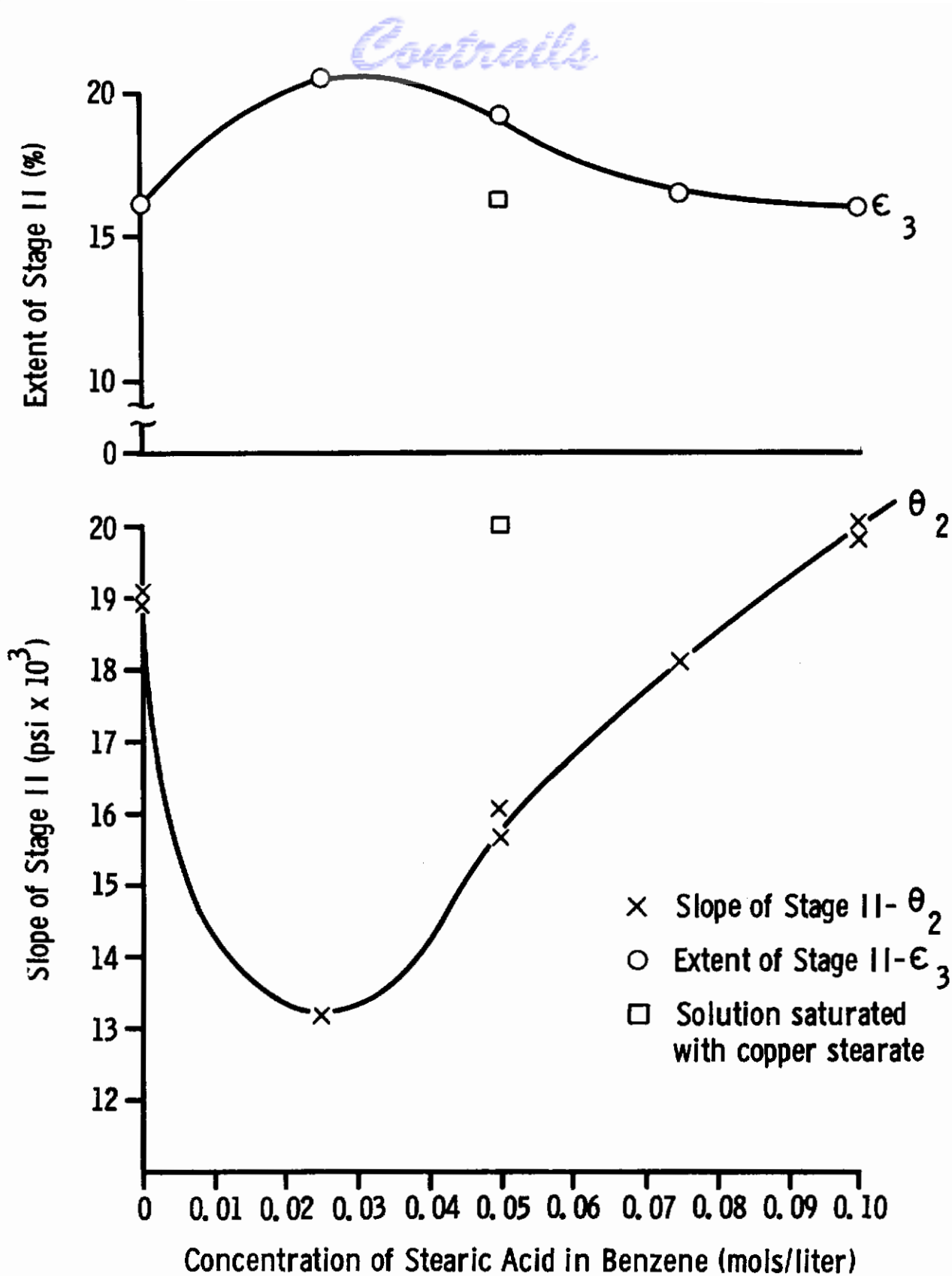


Fig. 3. Change in Slope and Extent of Stage II as a Function of Acid Concentration in Benzene for Copper Crystals 0 - 13

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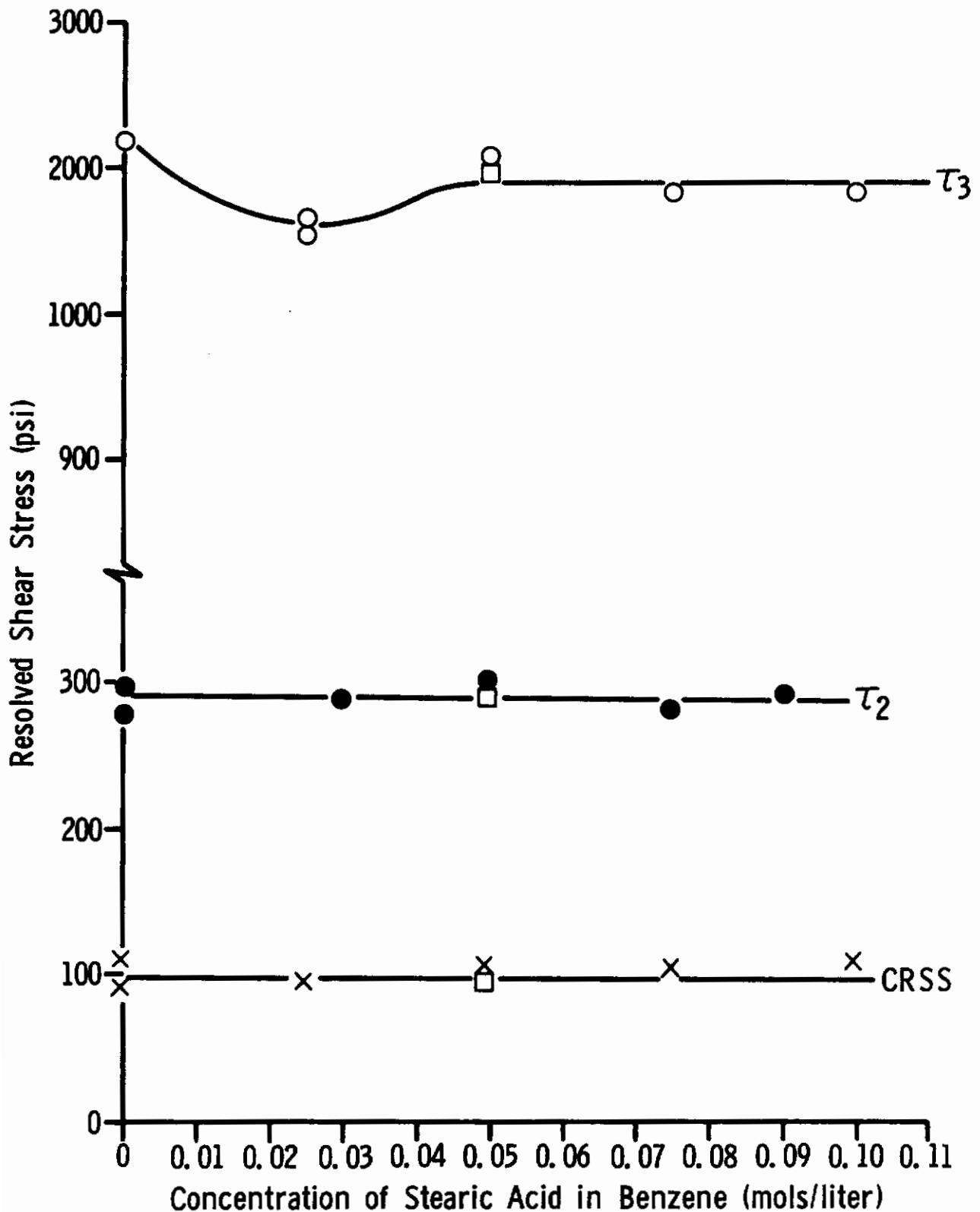


Fig. 4. Influence of Concentration of Stearic Acid-Benzene Solution on the Critical Resolved Shear Stress (CRSS) and the Stress at Which Stages I and II End, τ_2 and τ_3 , Respectively, for Copper Crystals 0 - 13

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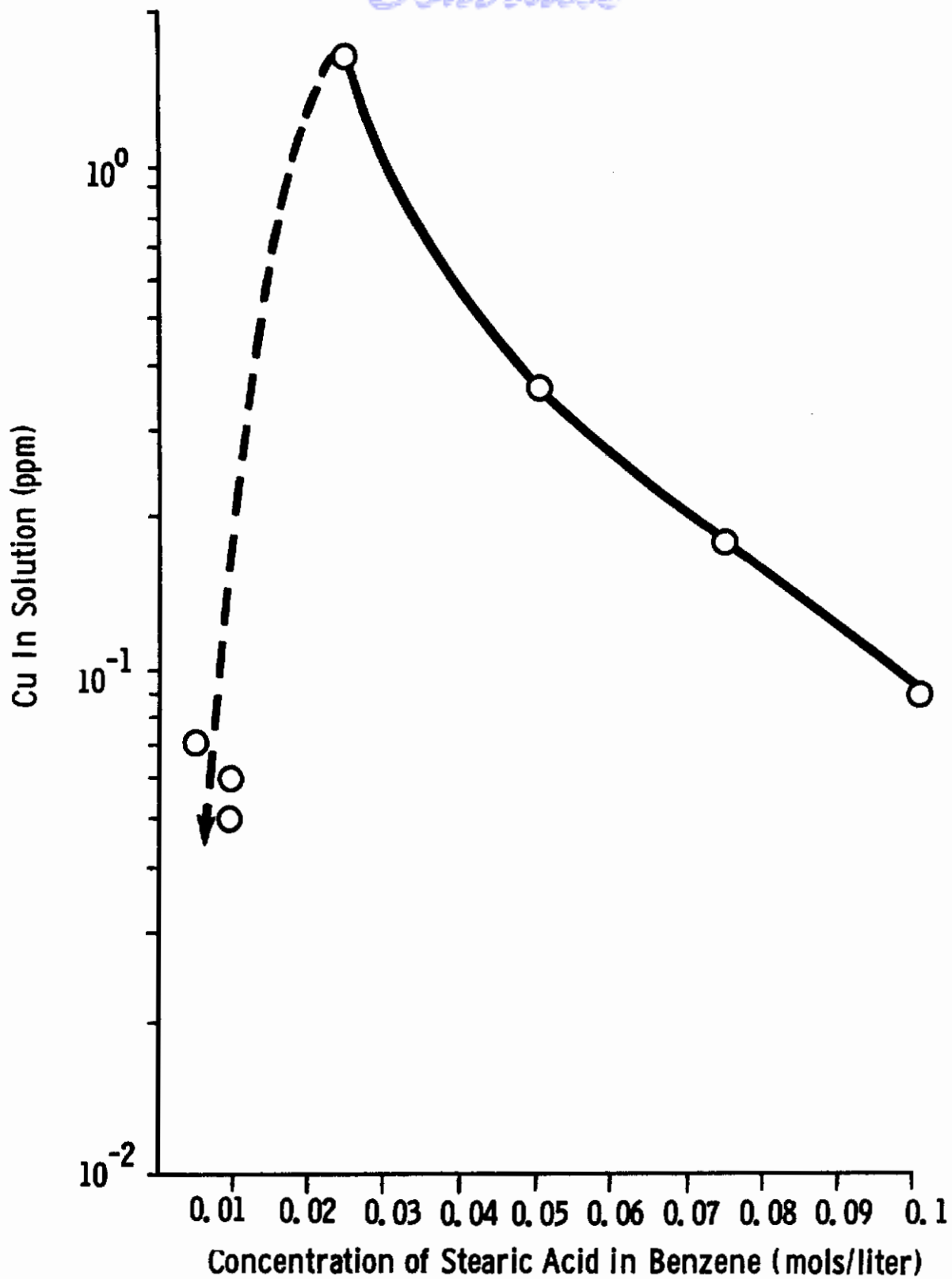


Fig. 5. Relationship Between the Amount of Copper in Solution After a Three-Hour Immersion in Stearic Acid-Benzene Solutions of Various Concentrations

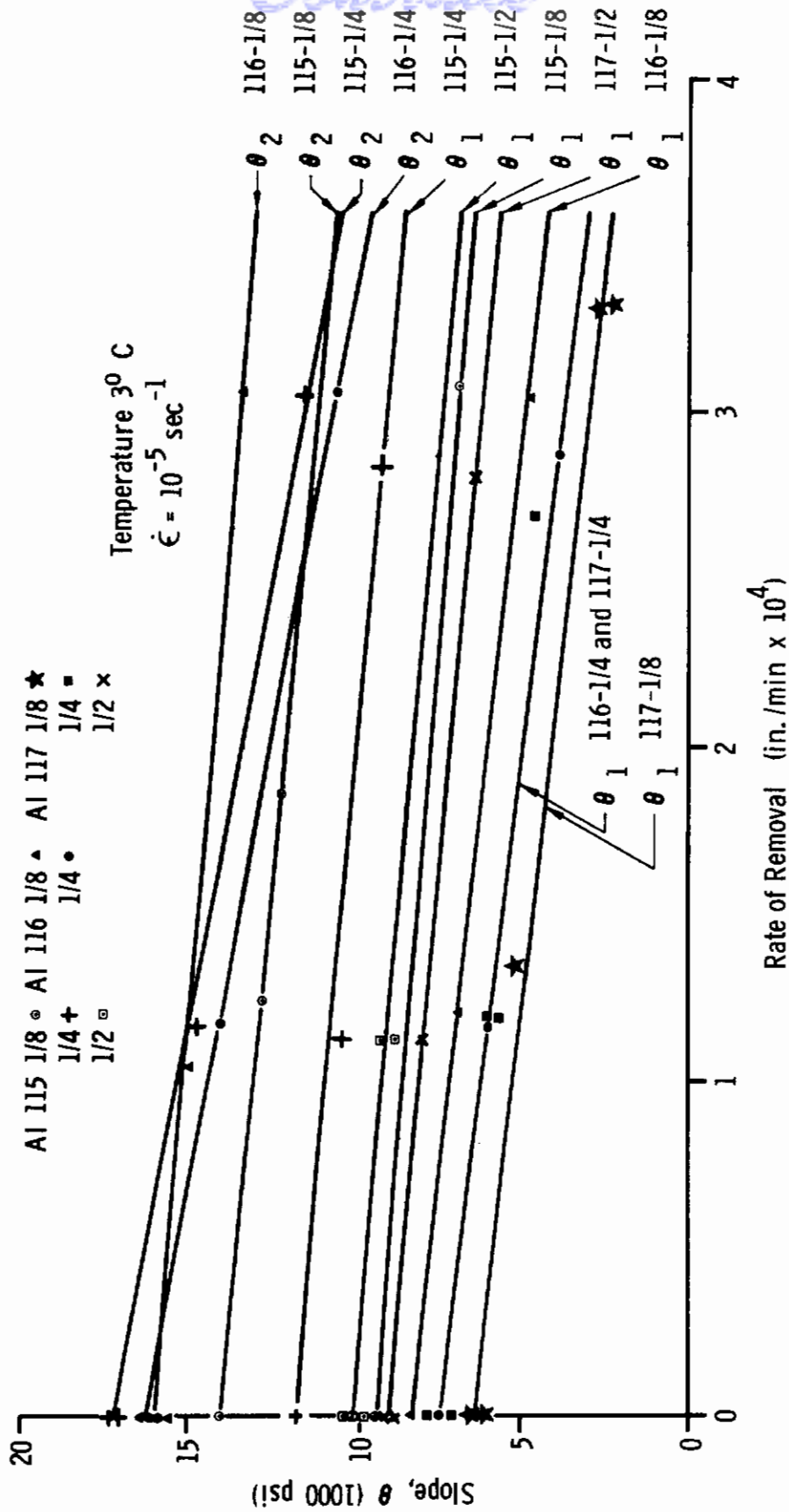


Fig. 6. The Effect of Rate of Metal Removal on the Change of Slope of Stages I and II for Various Size Crystals

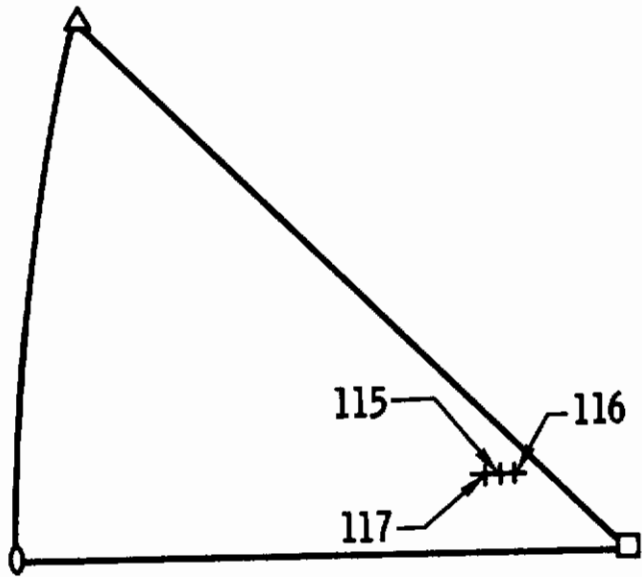


Fig. 7. Orientation of Aluminum Crystals Used in Size Effect Studies

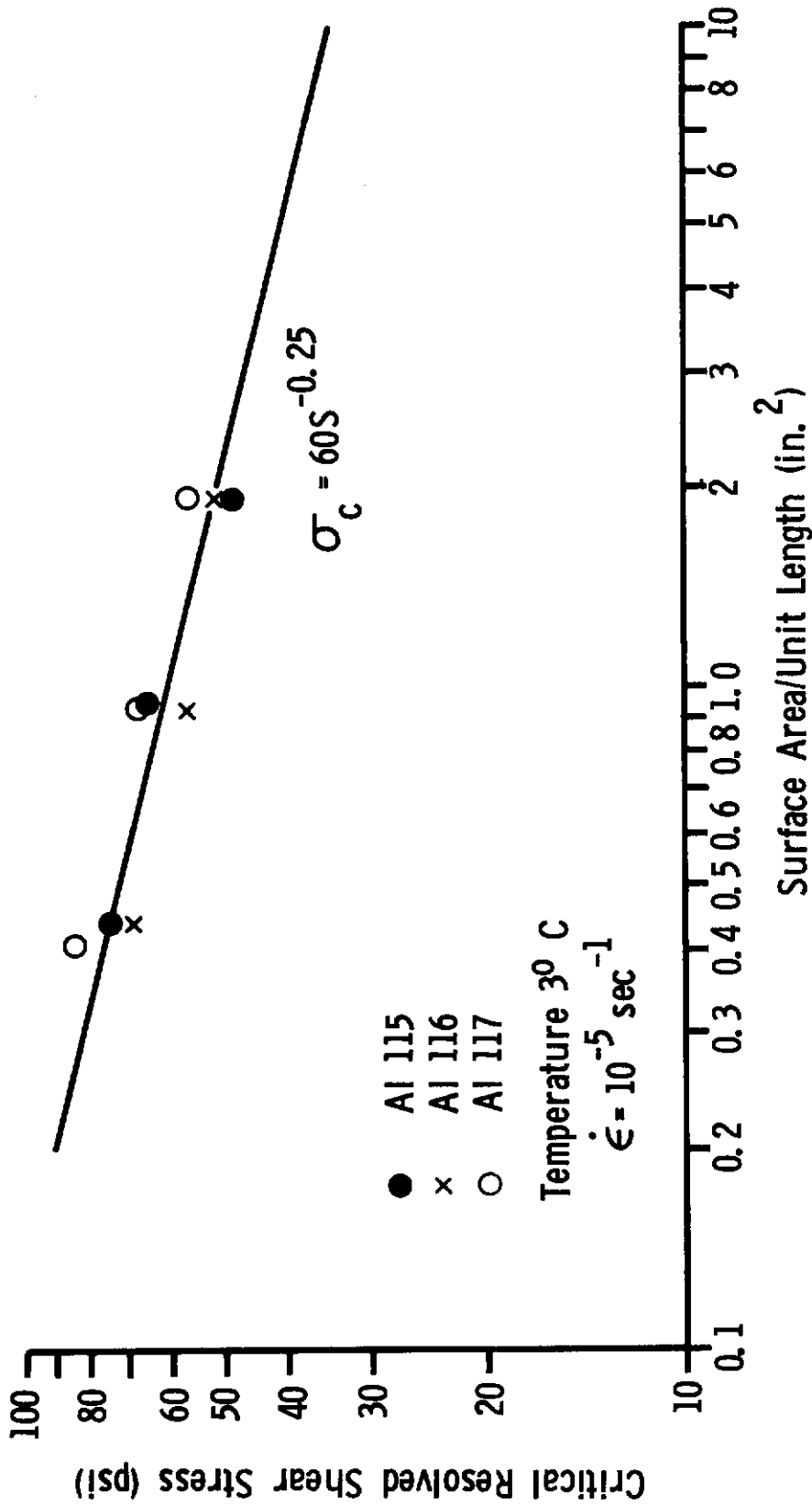


Fig. 8. Relationship of Critical Resolved Shear Stress and Surface Area

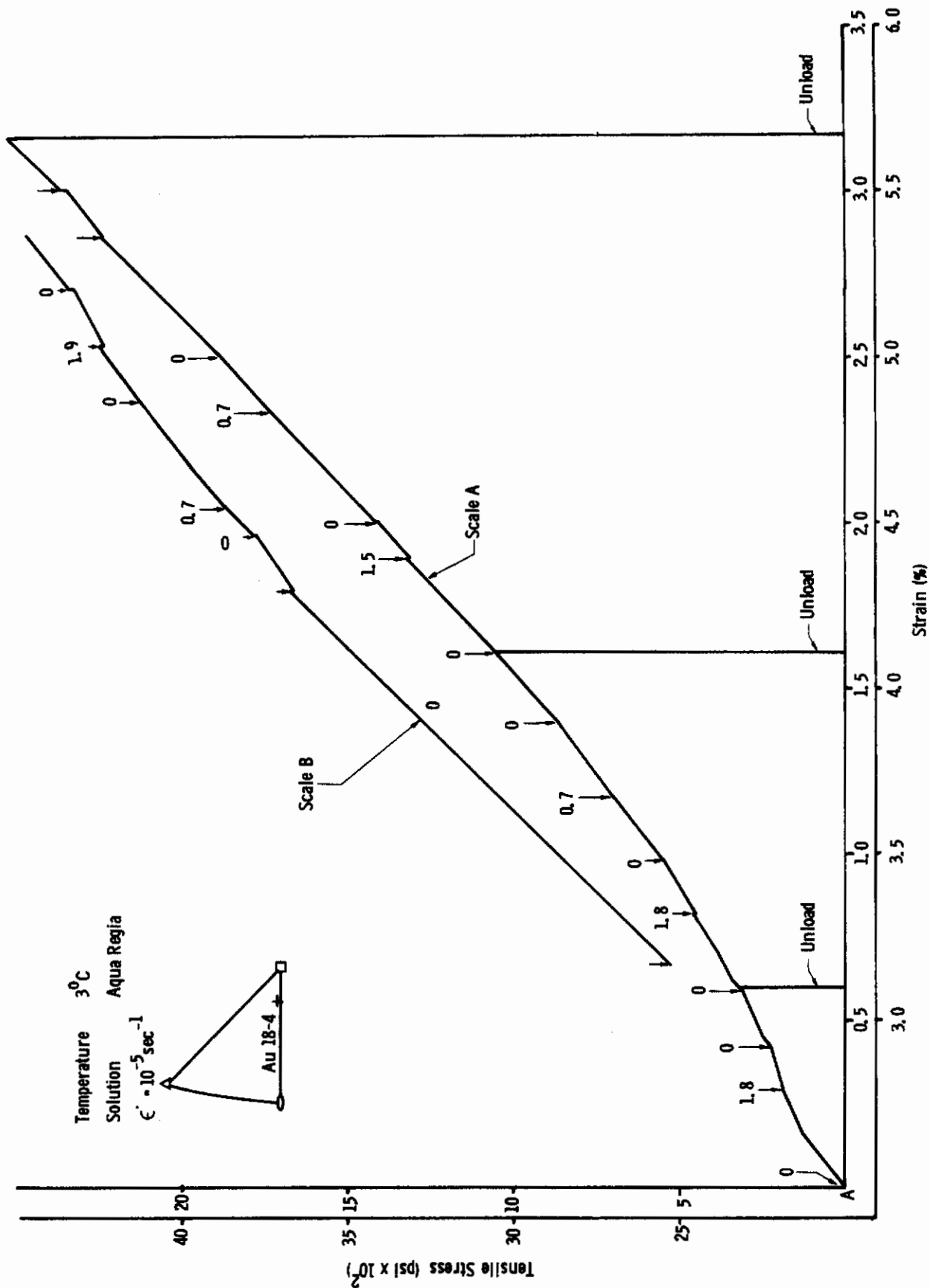


Fig. 9. Effect of Surface Removal on the Stress-Strain Characteristic of a Gold Crystal

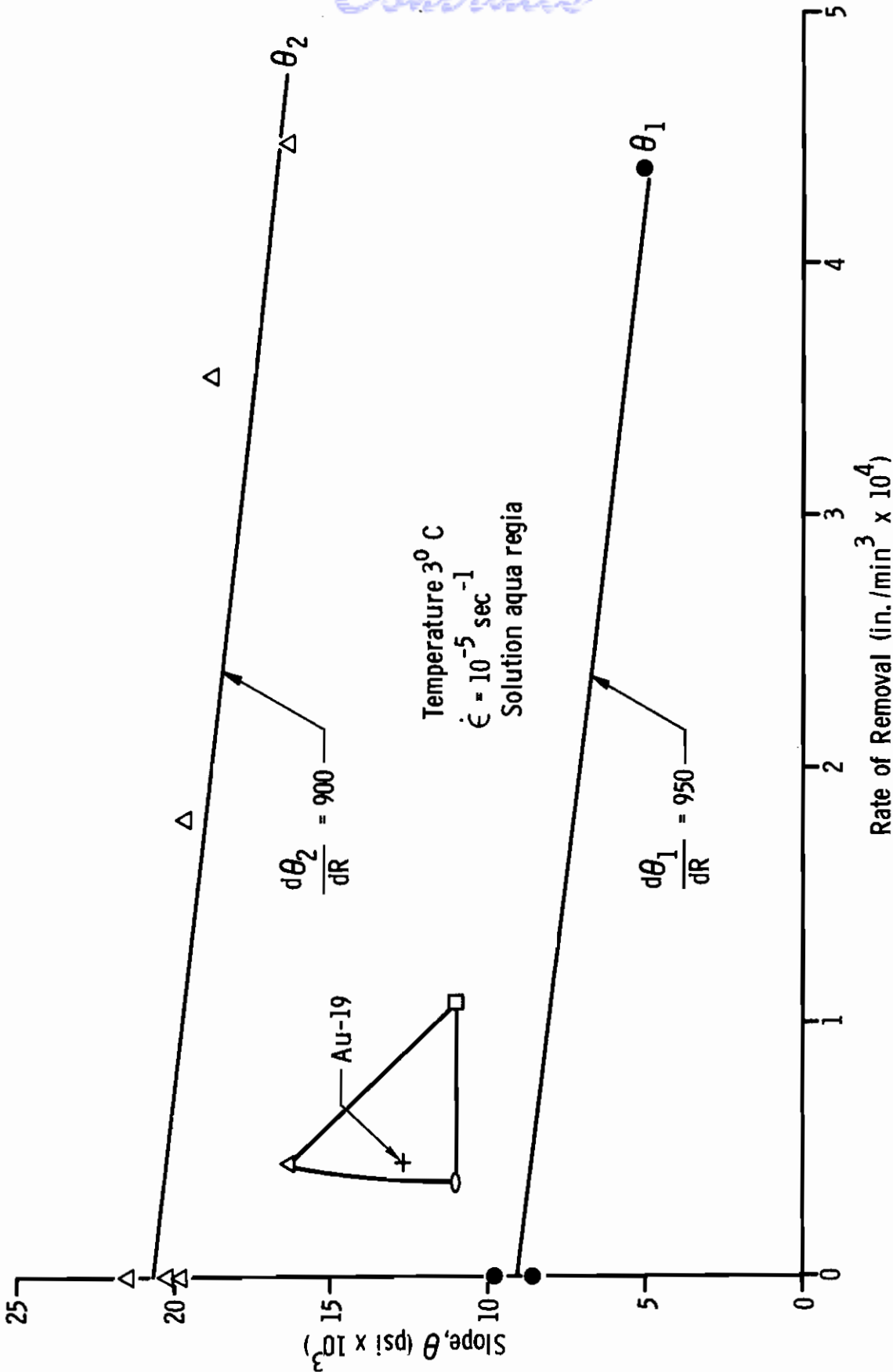


Fig. 10. Relationship Between Rate of Removal and θ_1 and θ_2 for a Gold Crystal

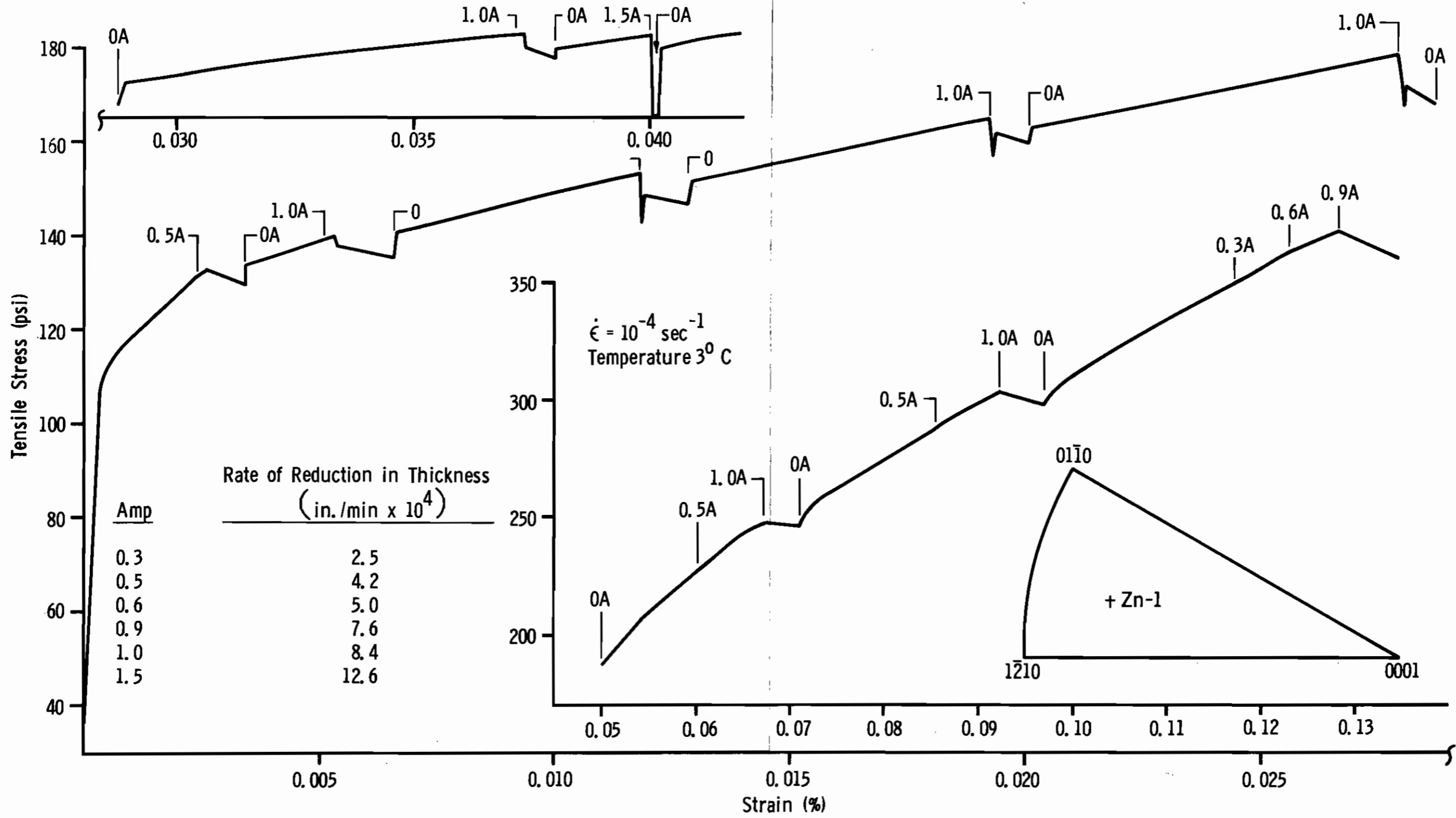


Fig. 11. The Effect of Rate of Metal Removal on the Stress-Strain Behavior of a Zinc Single Crystal

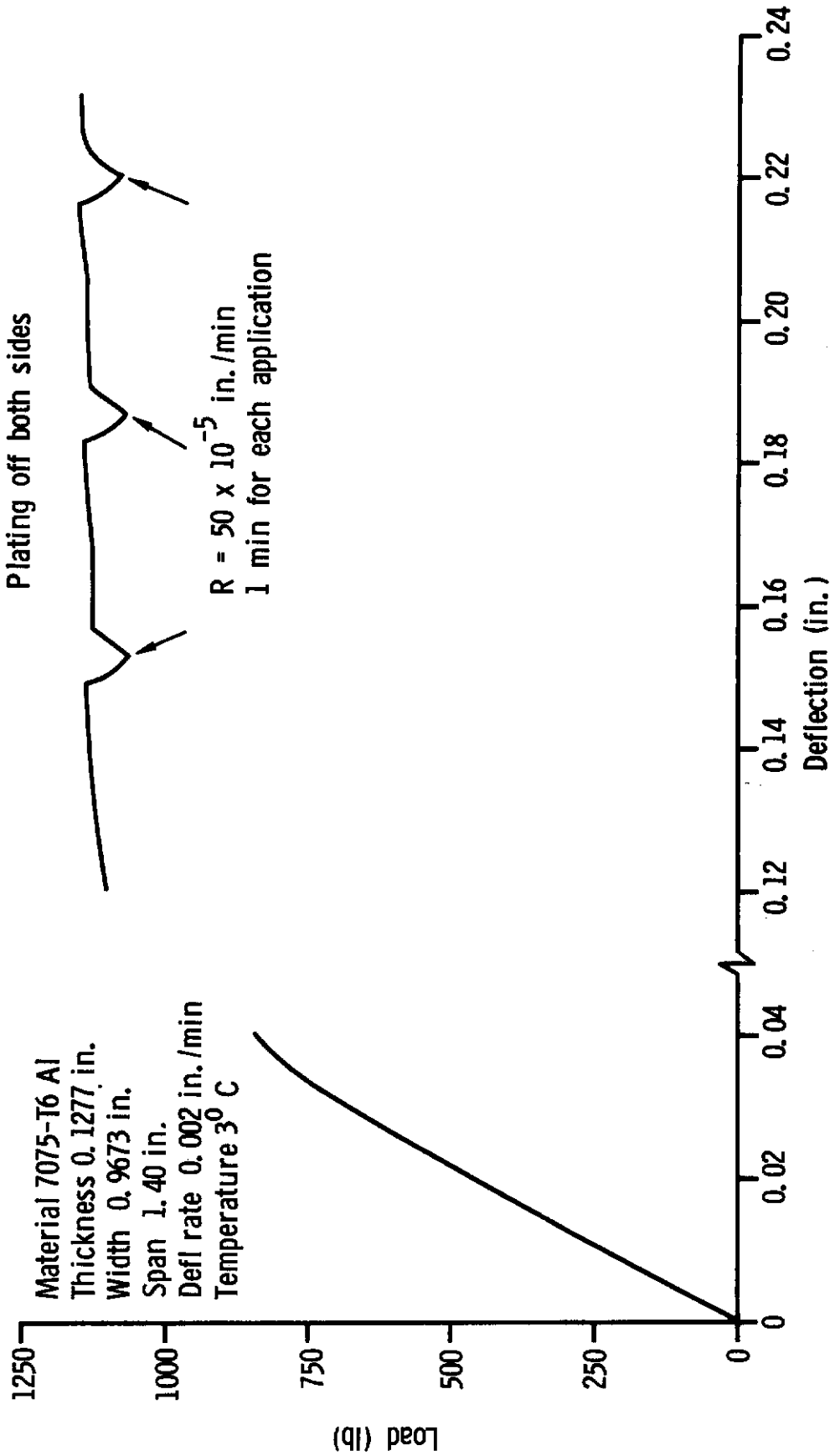


Fig. 12. Effect of Surface Removal on the Mechanical Behavior of an Aluminum Alloy (7075-T6) in Bending (both sides of the specimen exposed)

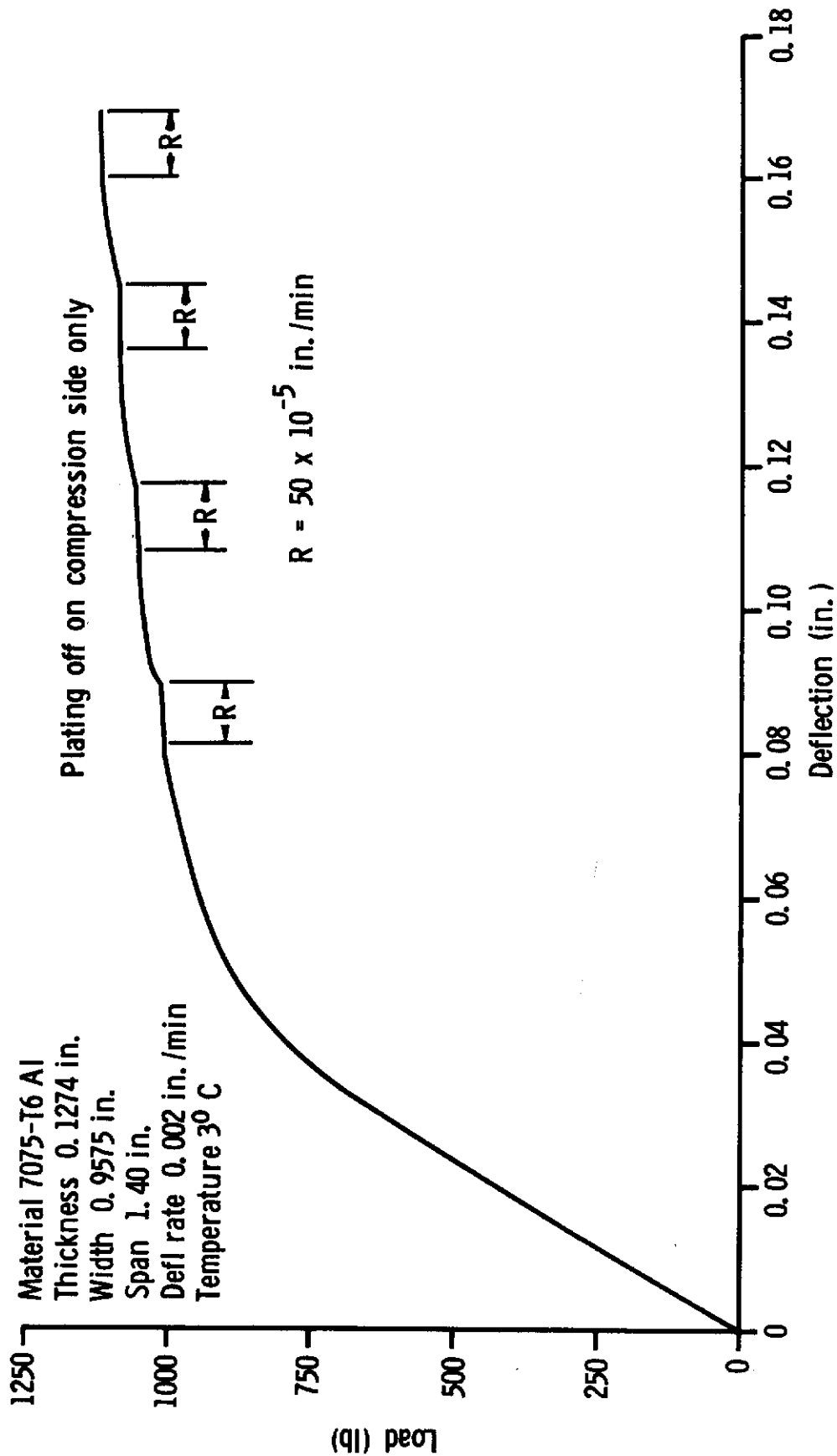


Fig. 13. Effect of Surface Removal on the Mechanical Behavior of an Aluminum Alloy (7075-T6) in Bending (compression face exposed)

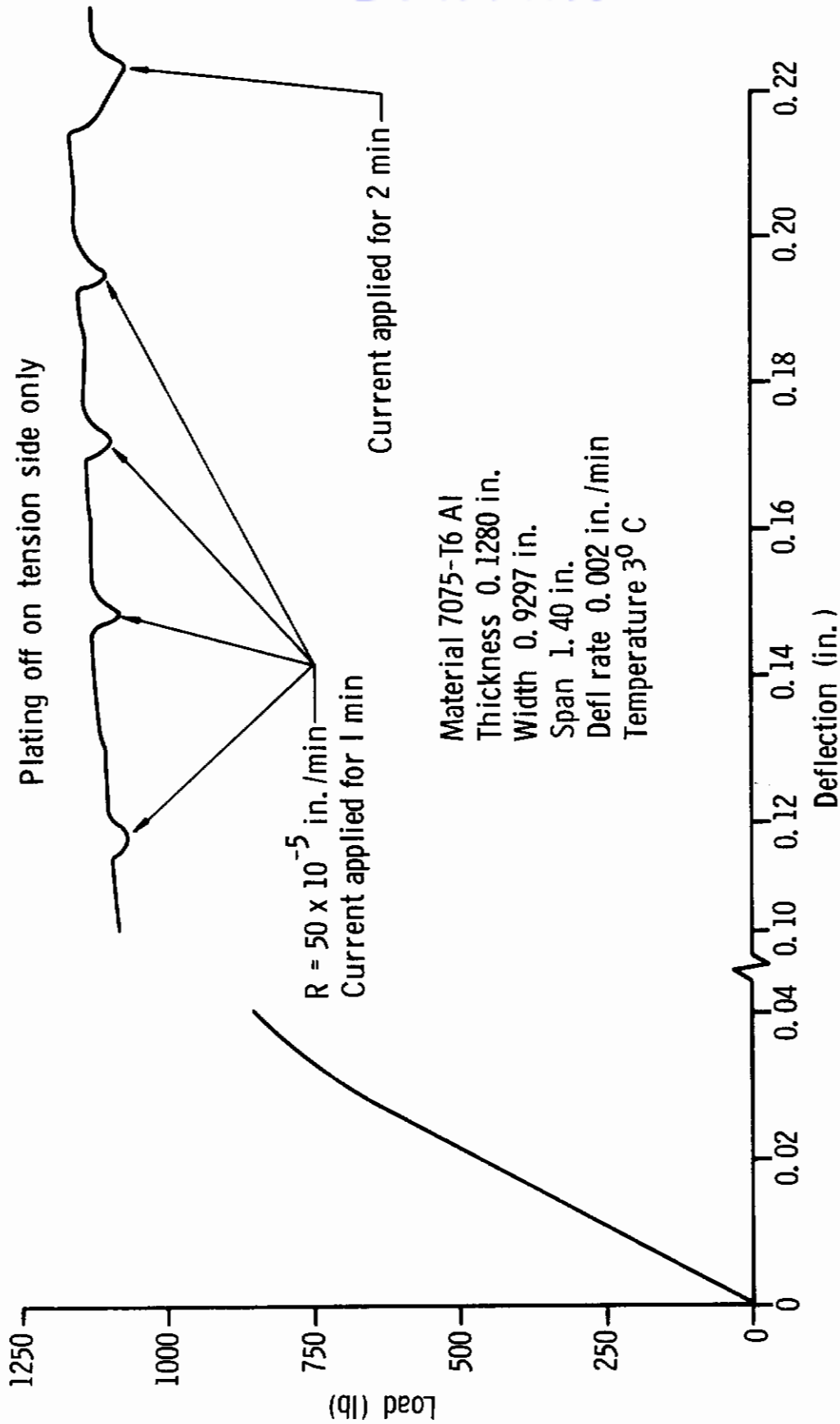


Fig. 14. Effect of Surface Removal on the Mechanical Behavior of an Aluminum Alloy (7075-T6) in Bending (tension face exposed)

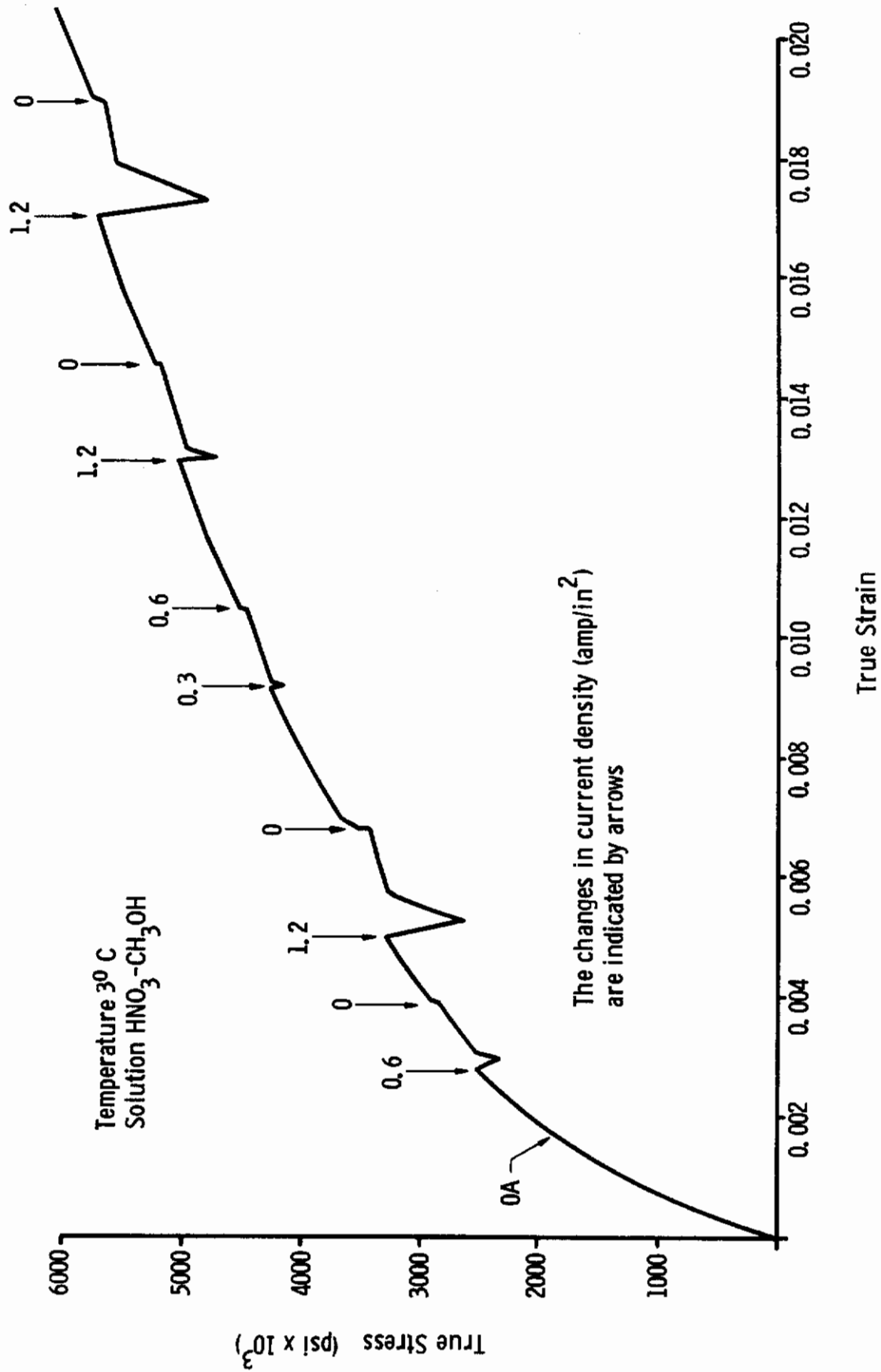


Fig. 15. Effect of Surface Removal on the Stress-Strain Characteristics of a Commercial Aluminum Alloy (1100-0)

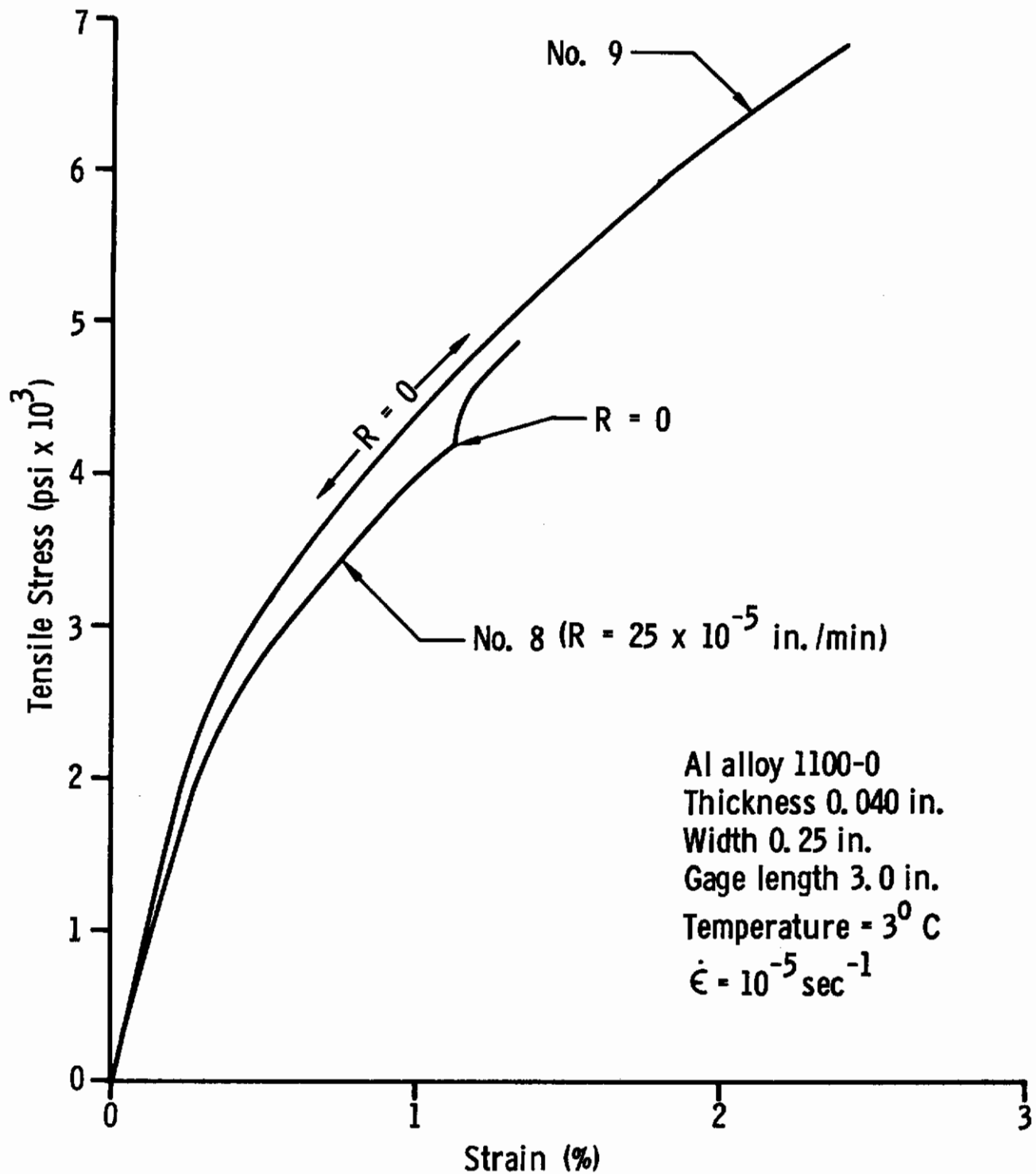


Fig. 16. Stress-Strain Curve for a Commercially Pure Aluminum (1100-0) Deformed While the Surface Was Removed at a Rate of 25×10^{-5} in./min

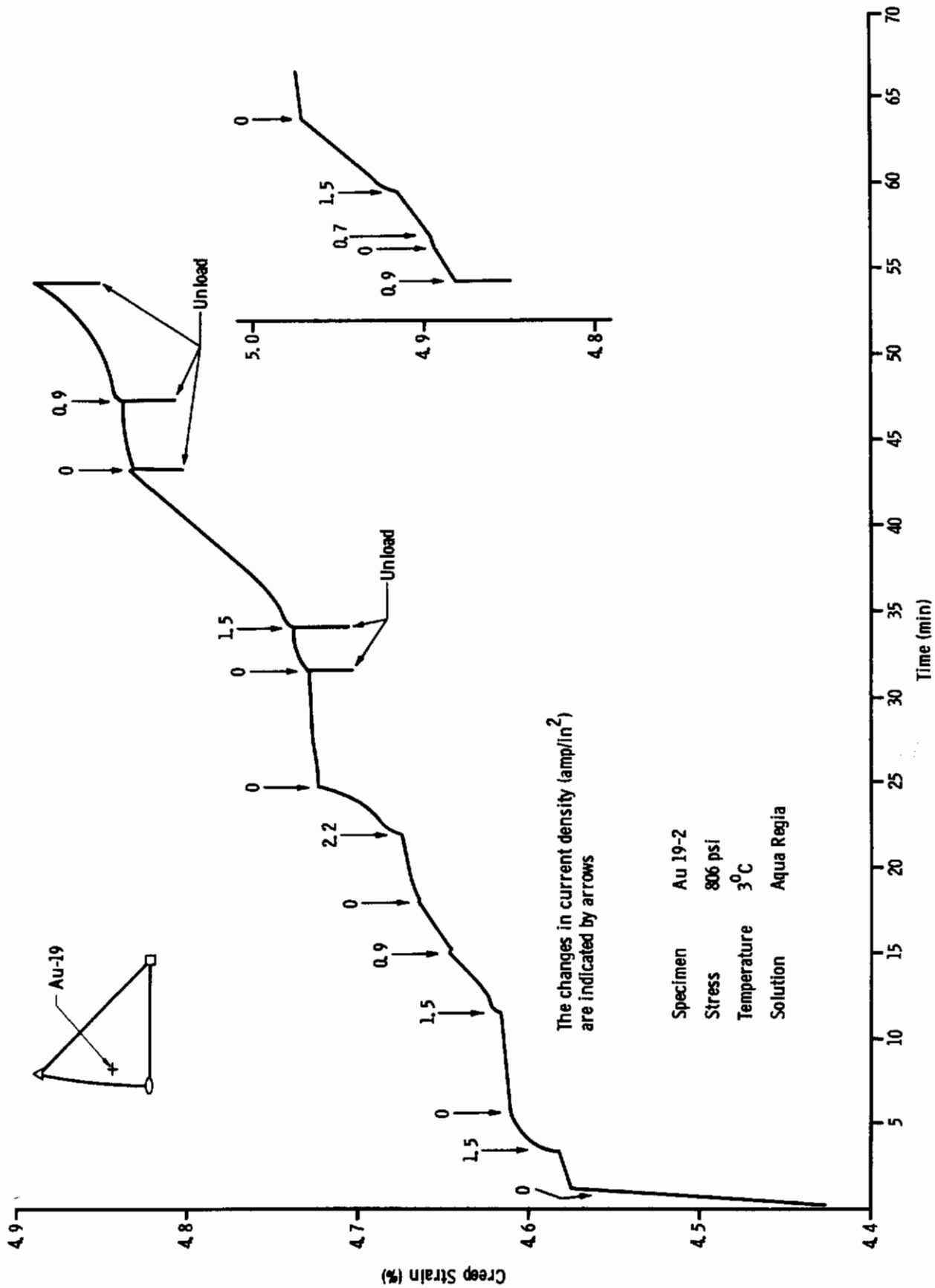


Fig. 17. Effect of Surface Removal on the Creep Behavior of a Gold Crystal

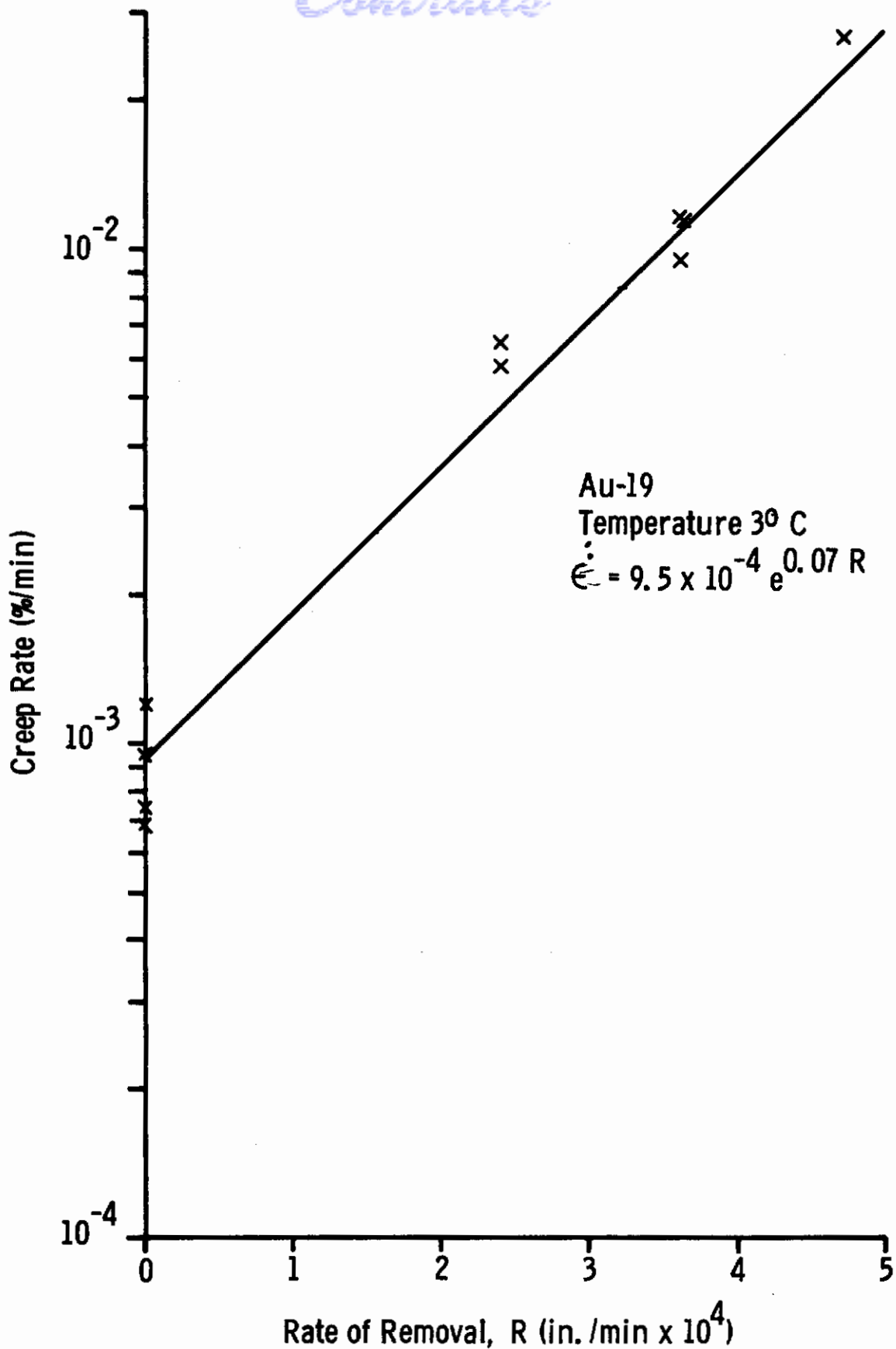


Fig. 18. Relationship Between the Secondary Creep Rate and Rate of Metal Removal

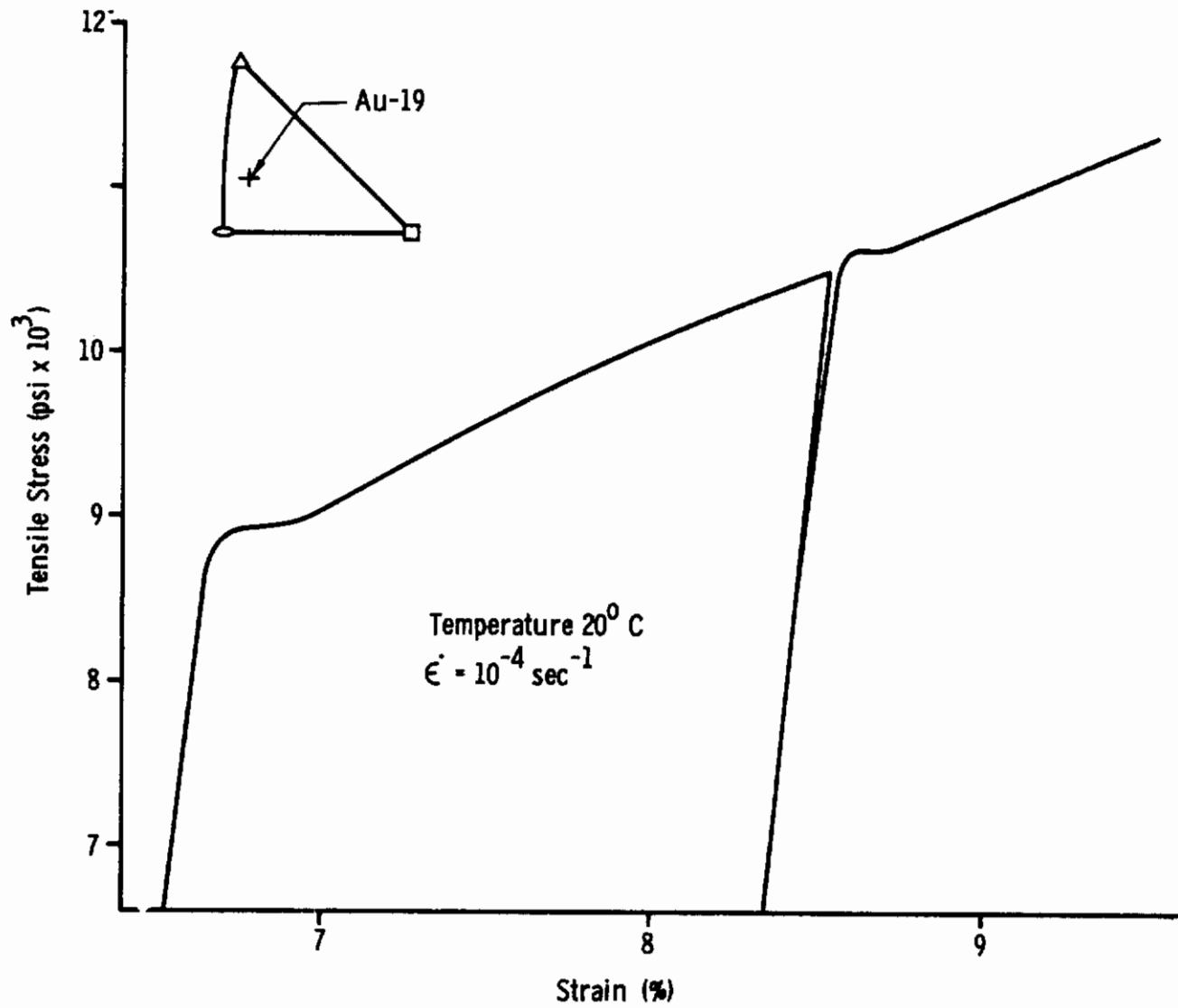


Fig. 19. Yield Point in Gold Single Crystals After Unloading and Reloading

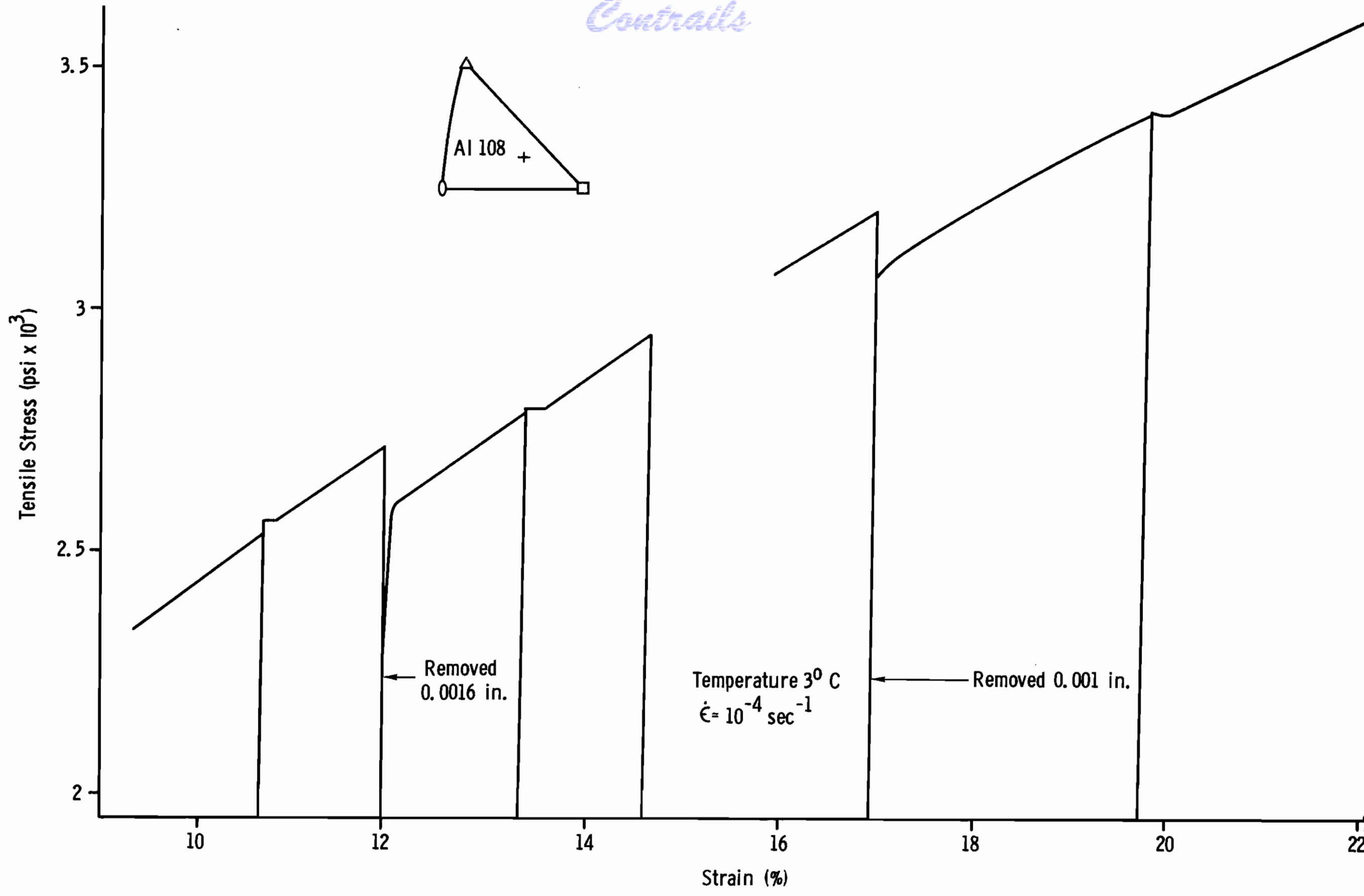


Fig. 20. Effect of Surface Removal on the Elimination of the Yield Point

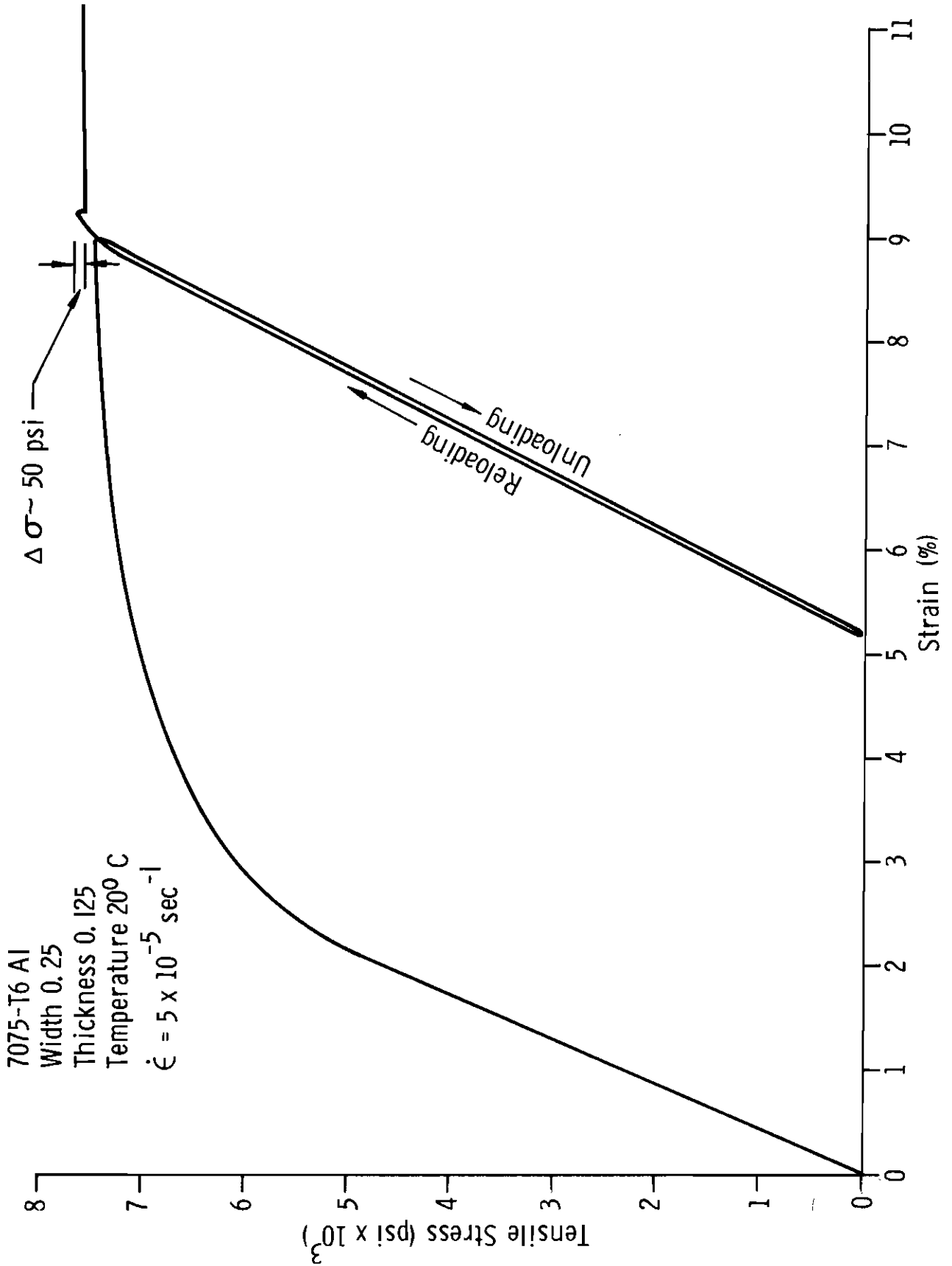


Fig. 21. Yield Point in Aluminum Alloy (7075-T6)

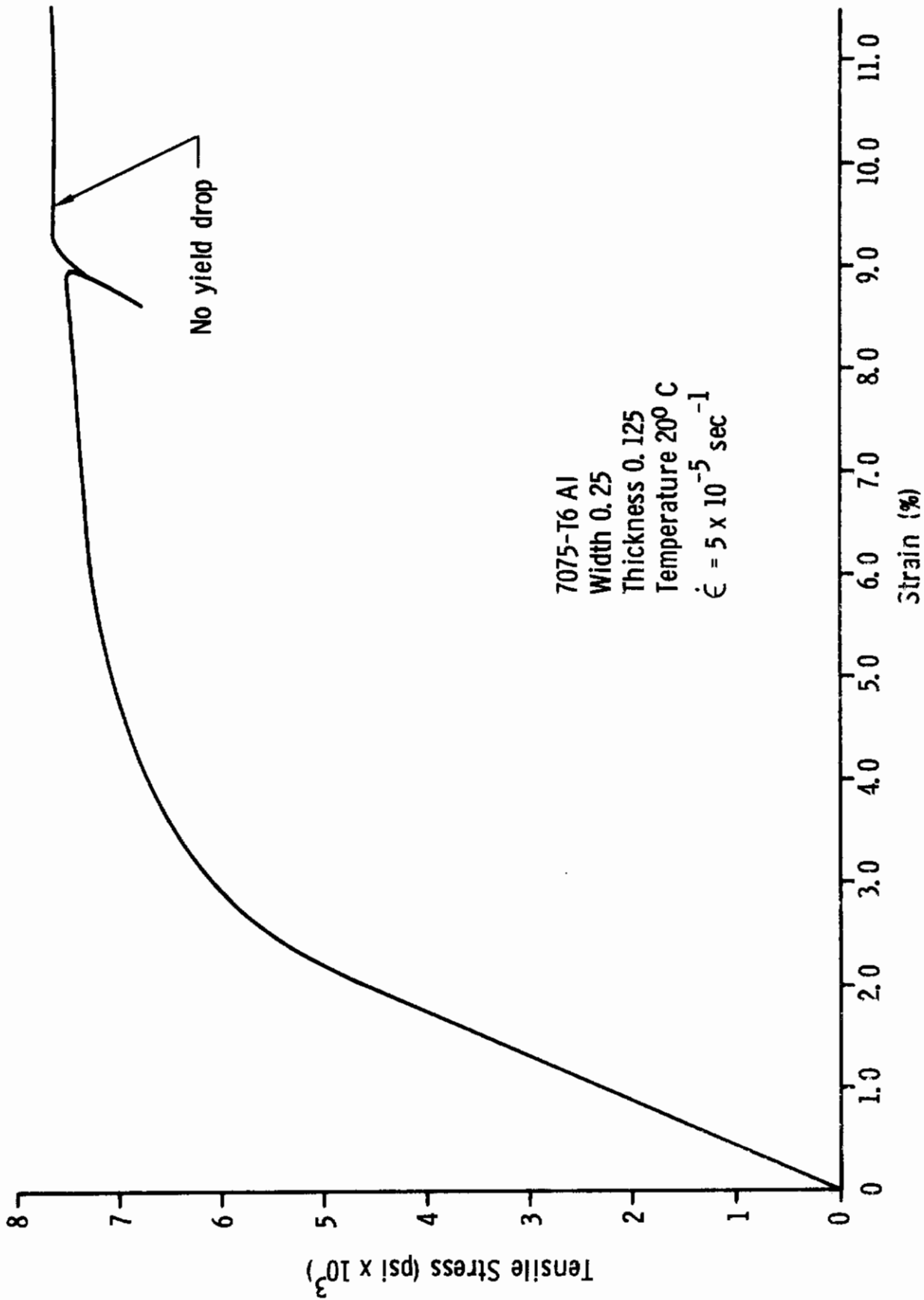


Fig. 22 Stress-Strain Curve for Aluminum Alloy (7075-T6)

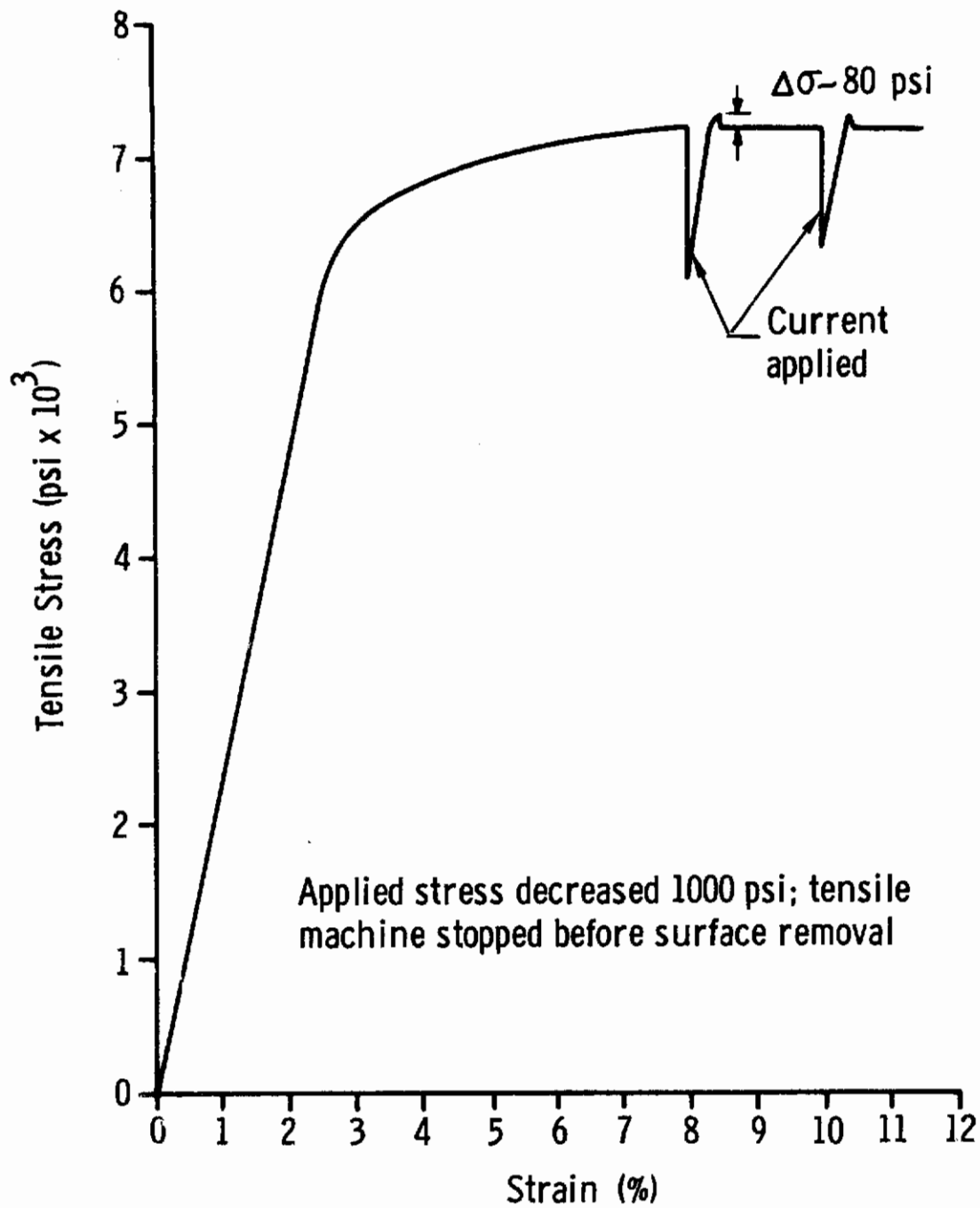


Fig. 23. Yield Point Effect for Aluminum Specimen (7075-T6)

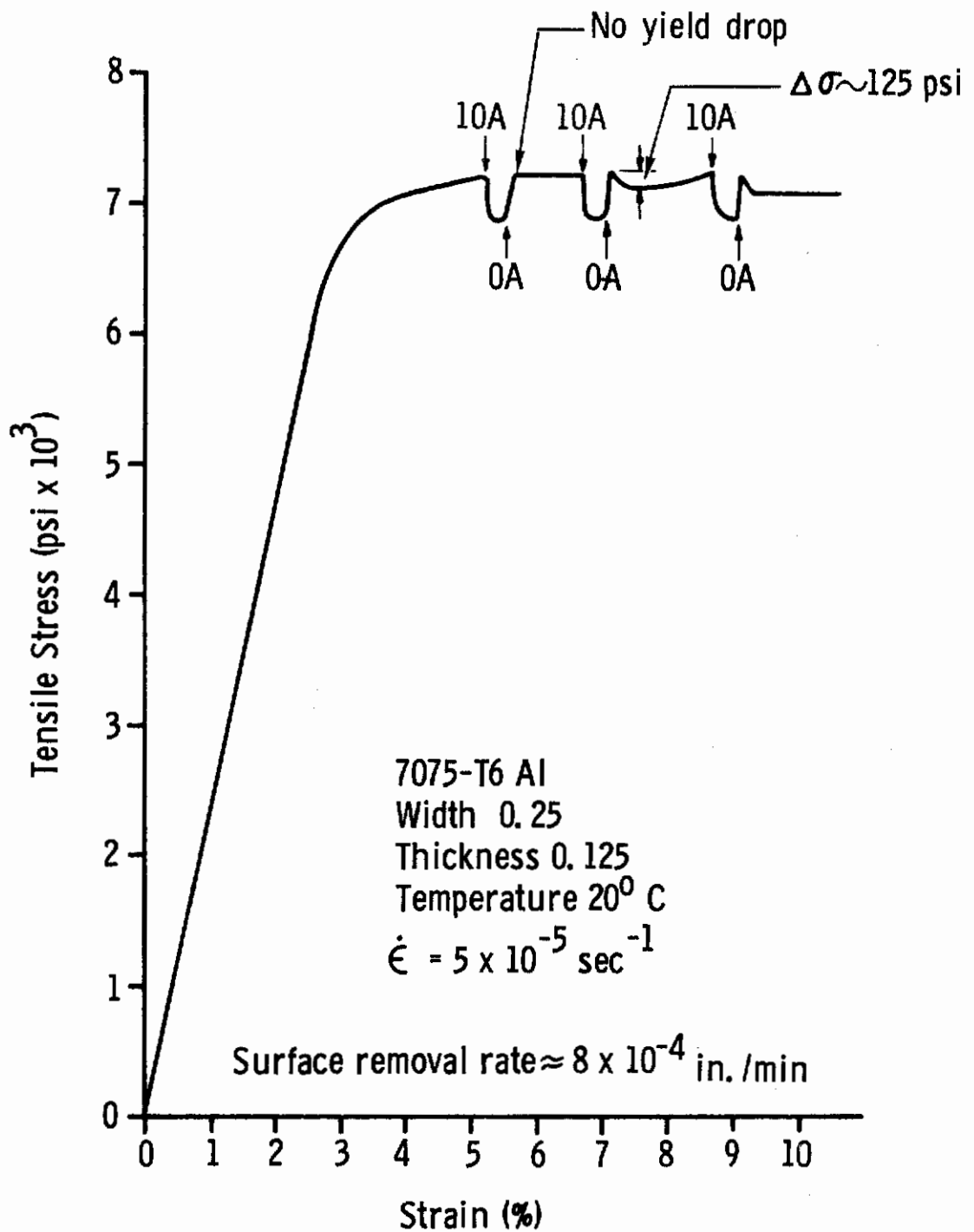


Fig. 24. Yield Point Effect When Aluminum Specimen (7075-T6) Is Unloaded by the Polishing Action

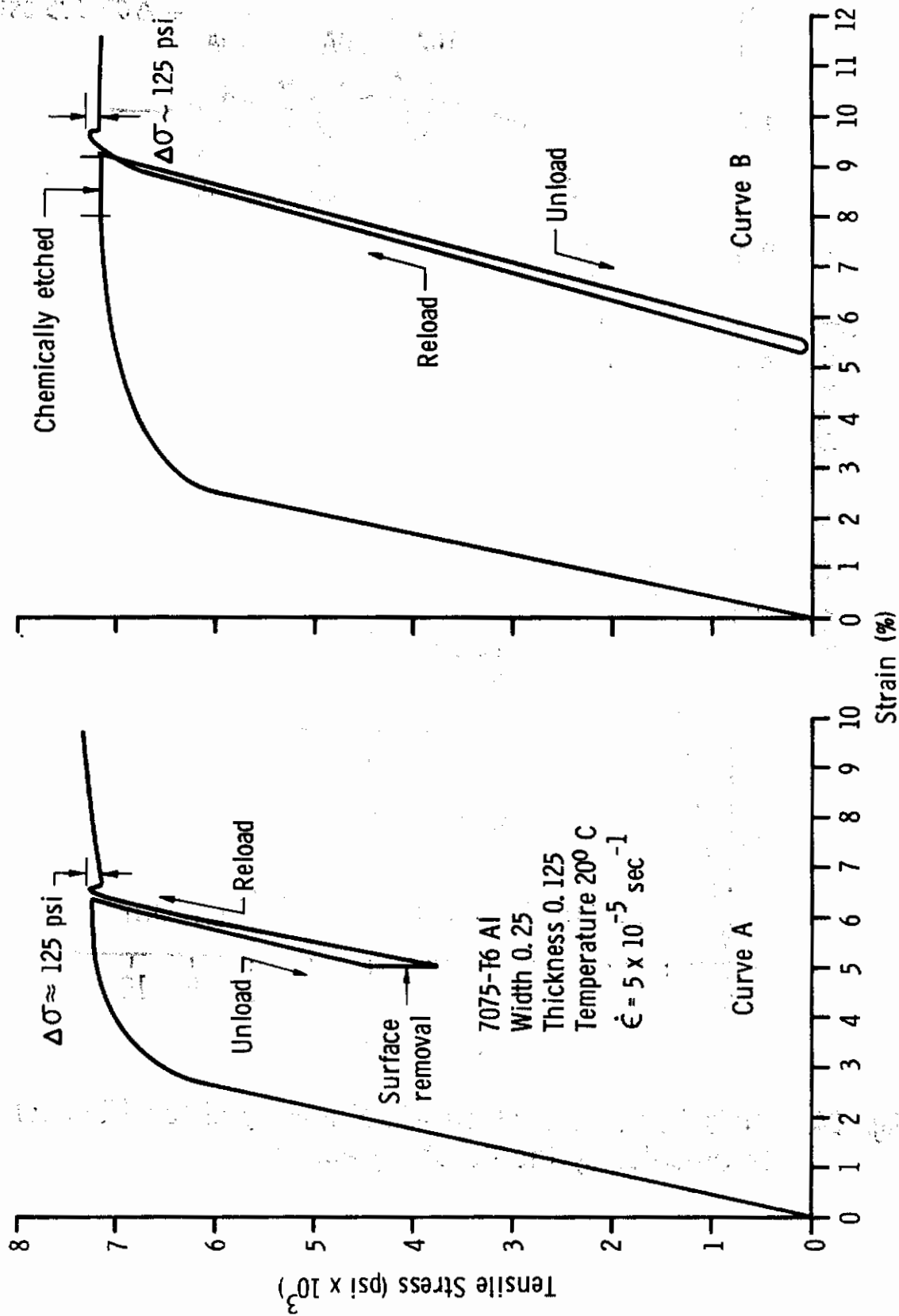


Fig. 25. Yield Point Effect When Aluminum Specimen (7075-T6) Is Partially Unloaded and Polished (Curve A) and Polished Just Prior to Unloading (Curve B)