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RESEARCH ON MECHANISMS OF ALLOY STRENGTHENING

- I. Alloy Strengthening by Fine Oxide Particle Dispersion
- II. The Splat Cooling Process for Alloy Development

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I. ALLOY STRENGTHENING BY FINE OXIDE PARTICLE DISPERSIONS

A. Oxide Dispersion Iron - BeO Alloys

The complete processing and extrusion of the five iron - beryllium alloy powders has been completed. The starting powders were produced by atomization of the appropriate liquid melts, in an inert gas atmosphere, using vacuum melted materials. The five alloys are listed in Table I, in weight percent beryllium, atom percent beryllium, and (anticipated) volume percent BeO, assuming complete conversion of the beryllium to BeO.

TABLE I
Composition of Fe-Be Alloys

<u>Alloy No.</u>	<u>Be, wt. %</u>	<u>Be, at. %</u>	<u>BeO, vol. %</u>
1	0.11	0.68	0.8
2	0.43	2.6	3.0
3	0.45	2.7	3.2 (contains 4.65% Ni)
4	0.70	4.2	4.9
5	0.96	5.7	6.7

Two methods of internal oxidation were tried on these five alloys. The results are summarized in Table II. All or part of alloys 1 to 4 were treated as -44 micron powders, and internally oxidized in that condition. As reported in earlier progress reports, the -44 micron powders could be internally oxidized in a satisfactory manner.

TABLE II
Processing of Fe-Be Alloy Powders

<u>Alloy No.</u>	<u>-44 micron powder</u>	<u>-1 micron, attrited</u>
1	x	-
2	x	x, flake
3	x	-
4	x	x, flake
5	-	x, granular

Half of alloys 2 and 4 were comminuted to sub-micron flakes by an attriter technique. The alloys worked down to this fine flake size without undue difficulty. They were subsequently checked by electron transmission techniques and found to be about 0.2 micron thick. All of alloy 5, the highest beryllium content alloy, was converted by attriter techniques into submicron powder. In this case, the material did not flake, but tended to be more granular, presumably because of the brittleness associated with the high beryllium content. Thermodynamic calculations indicated that there was little chance of being able to convert the beryllium to beryllium oxide by internal oxidation through-

out the thickness of a 44 micron powder when the beryllium composition was near 1 weight percent.

Internal oxidation of the -44 micron alloys, as well as of the flake materials, was carried out by exposure to a hydrogen - water vapor atmosphere selected to oxidize beryllium but not iron. The coarser powders were exposed to the H_2O/H_2 atmosphere in carefully spaced, vertically stacked, layers of powder about 1/4-inch thick. Oxidation took place at 820°C for 42 hours at an H_2O/H_2 ratio of 0.3 to 0.4. At this temperature, the H_2O/H_2 ratio to form FeO is about 0.5

The sub-micron, attrited powders were arranged in a muffle furnace so that the gas flow had to pass through the powder mass. The loose powders were supported on porous aluminum oxide discs, with pores of about 5 micron diameter. By careful arrangement of the powders, channeling of the gas stream was avoided. Uniform exposure of the fine powders to the total gas flow was achieved with pressure drops of 3 mm of mercury.

One portion of the sub-micron sized number 5 alloy (.96% Be), was treated in a different way, namely, by means of a modified SAP technique. The natural iron oxide which had formed on the fine powder during attrition was permitted to dissolve into the powder by holding it at 820°C in argon for about 18 hours.

Semi-quantitative analysis of the powders by solution and extraction techniques indicated full internal oxidation of the beryllium, except in the case of the number 5 alloy treated via the SAP technique. In the latter case, about 1/2 of the beryllium was oxidized to BeO.

Because there is fairly abundant evidence that residual base metal oxides in dispersion strengthened alloys adversely affect the high temperature stability of the alloys, every precaution was taken to reduce the presence of iron oxide. Even the thinnest iron oxide films on the sub-micron flake powders are expected to contribute up to 2 weight percent of iron oxide to the alloy.

Accordingly, the preparation procedures which were established considered every possible precaution to prevent exposure or re-exposure of the treated powders to an oxidizing atmosphere. First the powders (-44 micron or -1 micron) were treated in dry hydrogen at about 500°C for periods up to 48 hours to reduce iron oxide. After reduction, the pyrex tube assembly was sealed off in such a way that residual hydrogen was retained. The assembly was transferred to a stopper-sealed steel tube container arrangement, which had previously been evaluated and purged with hydrogen. Powder transfer was accomplished by pouring through a completely closed system, after which the assembly was tightly sealed to provide final protection.

The powders were mechanically compacted in these cans at a pressure of about 50,000 psi. Prior to the compaction step, the cans were evacuated by inserting a hypodermic needle through the rubber stoppered ends. These same rubber stoppers also serve as seals during the compaction and afterwards. The densities of the compacts

varied from about 70 to 75 percent of theoretical.

The canned compacts were next inserted into larger steel containers, which were then end-welded. This was the final assembly built up to fit the cavity of the extrusion press. The alloys have all been hot extruded. Preliminary examination indicates that the extrusions were all successful.

Over the next several months, the extruded Fe - BeO alloys will be examined for size and distribution of BeO particles, interparticle spacing, and stability with respect to temperature for one hour holding times, up to about 900°C. These preliminary tests are necessary to qualify the material for mechanical tests.

B. Oxide Dispersion Strengthened Copper-Al₂O₃ by the SAP Technique

A series of four alloys were prepared by liquid atomization to produce powders of approximately -44 microns diameter. The compositions are as follows:

1. 99 copper - 1 aluminum
2. 97 copper - 3 aluminum
3. 92.5 copper - 7.5 aluminum
4. 79 copper - 20 nickel - 1 aluminum

All of the materials have now been attrited to a very fine flake powder, the thickness of which is indicated to be about 0.2 micron. Laboriously, ten pounds of powder have been produced for each of these compositions.

As indicated in prior reports, the aim of the program is to produce internally oxidized material by two different techniques. Either of these techniques is far more simple than internal oxidation along conventional routes, which require a low pressure oxygen source generally supplied by the decomposition of copper oxide at the internal oxidation temperature. If coarse powders, thin strip, or wire is to be internally oxidized, there is always the problem of supplying just enough oxygen to penetrate half the cross section to oxidize all of the aluminum to aluminum oxide, without leaving either residual oxygen in the copper, or excess aluminum in the copper. Because copper is readily internally oxidized, the process can be simplified very much by working with exceedingly thin flakes, which would necessitate very short holding times at relatively low temperatures to accomplish internal oxidation.

One half of each alloy powder is undergoing hydrogen reduction as the only treatment. Any copper oxide on the surface of the fine flakes will be reduced back to copper; however, some small amount of oxygen will accomplish shallow internal oxidation. The surface aluminum oxide will be the prime source of the dispersoid. The resultant alloy will be a copper solution containing a small amount of aluminum, with an aluminum oxide

dispersion.

The second half of the powdered alloys is undergoing treatment at about 650°C in an argon atmosphere. The surface copper oxide will be consumed to provide internal oxidation by conversion of aluminum to aluminum oxide. In the more dilute alloys, practically all of the aluminum will be converted to aluminum oxide; however, in the high aluminum oxide alloys there will be some aluminum remaining in solution.

The two sets of alloys will differ significantly, both in the amount of aluminum oxide and in the amount of aluminum remaining in solid solution. In neither case will there be an excess of oxygen or copper oxide.

Depending on the success of the oxidation treatments, at some later date it may be desirable to supply additional oxygen, from whatever source one chooses, to completely convert aluminum to aluminum oxide.

The major source of difficulty in the preparation of these alloys is the tendency for these highly reactive sub-micron powders to be contaminated by oxygen from the atmosphere, and thereby to introduce significant amounts of copper oxide into the alloy. Even small amounts of copper oxide are expected to be detrimental to the properties of the alloys. Accordingly, extreme precautions have been taken to devise equipment and facilities for the handling of these very fine powders to avoid reoxidation after the internal oxidation treatments. Progress has been slow and painstaking, but it appears that success is being achieved in the protection of these powders from the atmosphere. It is anticipated that extrusion of the powders will take place in the next four to eight weeks.

C. Chromium Oxide Control in Oxidation Resistant - Oxide Dispersion Strengthened Alloys

It is the intent of this phase of our program to determine the role played by residual chromium oxide in oxidation resistant alloys of the stainless variety. It is speculated that the presence of the non-refractory, readily decomposable chromium oxide leads to an unstabilization of the otherwise stable thorium oxide dispersoid. Alternatively, it has been proposed that chromium itself may be able to interact with thorium oxide, leading to partial reduction of thorium oxide. Both hypotheses will be checked.

After lack of success with diffusion couples involving stainless materials containing reactive elements in contact with thoria-dispersion-strengthened stainless steels, it was decided that more intimate mixtures of chromium oxide and thoria in stainless steel would have to be produced.

Available to the program were a number of stainless alloys in powder form, of an average powder size of 10 microns. These stainless materials had been analyzed and generally showed about 5 weight percent chromium oxide, due entirely to the large surface

area of these powders.

To study the effect of chromium oxide content, these stainless steel powders will be subjected to hydrogen reduction aimed at leaving a series of smaller residual chromium oxide contents in the matrix. These stainless steels, containing about 5% thoria, will then be canned and extruded to provide the final samples for evaluation of alloy stability.

Difficulties have been encountered in balancing the reduction cycle against sintering effects. If lower temperatures and longer times are utilized for the reduction, excessive sintering takes place, leading to entrapped pores and entrapped chromium oxide particles which can no longer be contacted by the hydrogen. Short-time, high temperature reduction will be attempted.

Further, as in the case with the copper alloys, the reduced material must not be re-exposed to the atmosphere, because this will lead to reoxidation of the material.

A new furnace and reduction system has been built which will permit treatment of the powders and subsequent canning without re-exposure to the atmosphere. Heating to temperature, probably 1200°C, will be done at high rates, so that short reduction times can be utilized. This will minimize the amount of sintering, and may permit production of compacts free of chromium oxide.

The entire furnace and reduction system are undergoing trial with conventional, coarse stainless steels, to establish the efficiency of the system.

D. Internal Oxidation of Thin Nickel-Aluminum Foils

In the past, it has been extremely difficult to produce suitable oxide dispersions by internal oxidation of dilute nickel alloys. Inevitably, the oxide dispersion is relatively coarse (500 - 1000 Å vs. about 100 Å in copper-base alloys), and resultant properties are relatively poor.

Based on recent internal oxidation studies of larger cross sections (1/2 mm or thicker), it was observed that a much finer oxide dispersion exists in a thin outer layer of the specimen. On this basis, it may be possible to produce oxide particles in nickel, through internal oxidation, which may be as fine as 50 - 100 Å. If this could be done, dispersion strengthened nickel base alloys would be expected to show vastly higher high temperature strength values than those achieved currently by TD nickel, or similar alloys. For this reason, thin nickel - aluminum foils are being studied to establish the minimum oxide particle size which can be produced.

Evidence also exists that there are small but important elastic strain fields around the oxide particles, even though coherency may not exist. These strain fields should be a significant factor in the ultimate strength of the alloy itself.

The nickel - aluminum foils have been reduced to 15 - 20 microns thickness; these foils will be internally oxidized at 550, 600, 650, and 700°C. These temperatures are considerably lower than those which have been used in the past to internally oxidize nickel - aluminum powders, which were generally -44 microns in size.

Electron transmission microscopy will be the prime method of studying the size and distribution of the oxides in the foil. For the moment, mechanical testing of these foils is not planned; plans for mechanical testing are deferred until such time as the desired structures can be produced.

The work on nickel-aluminum and nickel-beryllium alloys has been completed, and a technical report is being prepared. This work was concerned with relatively thick sections, in which one of the items of interest was the change in size and distribution of the oxide with depth of penetration. A much wider temperature range was utilized in this program than those listed above, primarily in order to decrease the internal oxidation times necessary to achieve the rather large depths which were sought.

E. Modes of Deformation and Fracture in Oxide Dispersed Metal Systems

After considerable preliminary experimentation, an oxidation treatment was selected for the internal oxidation of the 1/8 inch thick cold rolled, dilute copper - aluminum alloys. A temperature of 650°C was selected; the oxygen source was copper oxide decomposing at the same temperature; the time at temperature was about 400 hours. Metallographic studies indicated that a relatively fine dispersoid was present, however, the shape of the particles tended to be spherical rather than geometrical, raising suspicions as to the adequacy of the internal oxidation treatment.

After fairly extensive stress rupture testing at 650°C, it was observed that the strength values of the as-internally oxidized material were relatively poor. Cold working of the 1/8 inch thick strips at room temperature, after internal oxidation, did not, unfortunately, increase the strength values significantly.

Subsequently, test specimens of a 50% cold worked structure were exposed for periods of one hour at increasing temperatures, using a 50% cold worked pure copper sample as a reference; both materials recrystallized at about 300°C. It was evident from these results that something had gone wrong in the processing and oxidation of the Cu-Al sheet materials. After considerable double-checking, it now appears that the alloys were over-oxidized. By waiting too long for oxygen to penetrate to the center of these relatively thick sections to accomplish total internal oxidation of the aluminum, it appears that a residual of oxygen was left in the alloy at 650°C, leading to precipitation of copper oxide on cooling to room temperature. The presence of this significant amount of copper oxide has led to an unstabilization of the aluminum oxide dispersion, leading to poor mechanical properties at 650°C.

New Lots of material are being processed to avoid the over-oxidation of the body so that copper oxide will be avoided. The first samples have now been completed, and the results look satisfactory. Hardness tests at room temperature after exposure of these materials to progressively higher temperatures are currently under way to establish the stability of the alloy and its resistance to recrystallization.

Figure 1 shows the stress rupture test at 650°C for the earlier copper - aluminum alloys, both in the as-internally oxidized condition and after various amounts of cold work. It is evident that the strength values in the internally oxidized condition are only fair; cold working has improved them a little.

Current and Future Activities

During the year 1967, extensive mechanical testing and evaluation will be taking place in three of the programs. Considerable time has been spent in preparing the materials for the test. Precautions were taken, probably beyond normal, to avoid recontamination of the various alloy systems after reducing the matrix metal oxides, which are always non-refractory. It is clear that these precautions are necessary if one is to avoid extraneous effects on mechanical behavior, alloy stability, etc. Progress will remain slow on the program to control chromium oxide in the oxide dispersion strengthened stainless steels. Many preliminary tests would be required to strike the proper balance between our ability to reduce the chromium oxide, and yet avoid sintering so that reduction can be quite complete.

II. THE SPLAT COOLING PROCESS FOR ALLOY DEVELOPMENT

A. Development of Continuously Operating Atomization Units for Larger Scale Powder Production

The continuous shock wave generator described in the previous report has been undergoing further testing; a series of low melting alloys has been atomized and the powder characterized. The particles were collected either after solidification in flight or after solidification on a rapidly rotating quench plate. Both the quantities atomized and the particle size values clearly indicate the potential for pound-lot production.

In addition to this unit, two new approaches are under investigation. One method pulverizes molten metal in a resonance chamber. A high speed gas stream in the chamber creates a local pressure drop in front of a nozzle and continuously aspirates molten metal for atomization. The liquid metal is broken up into fine particles by the high frequency gas pulses in the resonance chamber; during this process, the particles remain liquid, as is desired. The resonance frequency is controllable and defines the size of the molten metal particles which are generated. Fast quenching and collection

of the particles are similar to the arrangements used with the continuous shock wave generator, i.e., the molten droplets are delivered either to the quench plate for rapid liquid quenching (splat cooling) or after solidification in flight. A prototype model of the unit has been built and is being operated experimentally to establish operating conditions and controls. In the second apparatus, molten metal is forced out under high pressure (5-10,000 psi) through a small diameter orifice. The orifice is vibrated mechanically in a lateral direction at high frequencies. This vibration breaks up the high velocity metal stream into small particles which are collected as described for the case of the other two processes. A unit of this type is presently under design. It is hoped to produce powders in the next month or two.

B. Alloy Studies

1. Decomposition of Supersaturated Al-Si Alloys

The electron microscopic study of the precipitation of Si from supersaturated aluminum alloys (up to 11 atomic percent Si) reported previously has been concluded. An independent check of the precipitation kinetics in bulk specimens by X-ray diffraction is presently being conducted. The latter is regarded as of special interest because an earlier study of the precipitation of Si from Al-Si alloys showed an increase of the lattice parameter of aluminum over that of the equilibrium value at a certain early stage of precipitation, indicating that residual, unrecovered lattice strains were present. By obtaining precise kinetic data in the present study, it will be possible to separate the strain contribution to the previous lattice parameter measurements and to evaluate the residual strains quantitatively.

2. Dendritic Spacing in Splat Cooled Aluminum Alloys

In studies of splat cooled Al-Si alloys, the existence of a dendritic structure was observed in the thicker sections of the foils. This structure appears in the form of dendritic rods, or plates with a thickness of 1000-1500 Å, or as small cells of the same diameter. The walls of the plates and cells are delineated by many small precipitated silicon particles due to the slower cooling at such points. Parallel X-ray measurements indicate that on average no more than 1 - 2 atomic percent Si (out of 11 percent in the melt) precipitated due to the slightly slower quench. Experiments made with other aluminum alloys (Al-Fe, Al-Cu, Al-Pd) show the same rod and cell dendritic structures. The dendrite spacings for all these splat cooled alloys are within the same order of magnitude. The effect of solute concentration could not be determined, but the literature indicates that the effect should be quite small.

It is known that the spacing of dendrites is some function of the degree of supercooling; since the extent of supercooling depends on the rate of cooling, one can expect a relationship between dendritic spacing and cooling rates. The relationship is a straight line when plotted on log-log coordinates, and has been reported in the literature for cooling rates up to about 10^3 or 10^4 °C/sec. Assuming cooling rates of $10^7 - 10^8$ °C/sec, based on direct measurements and calculations, we find that our values fall on the extrapolated curve based on the lower cooling rates. There is a small scatter of the dendrite spacing values, corresponding to small variations in cooling rates in different specimens and within the same splat owing the differences in thickness and the quality of thermal contact between splat and substrate. Based on these data, dendrite spacing can be used to measure cooling rates, which would be a very desirable result; complicated physical measurements can then be circumvented.

3. Al-Cu, Al-Ni, and Other Binary Systems

The X-ray determination of the metastable solubility limits of Cu, Ni, Mn, Fe, Co, Pd, and Ag in aluminum has been continued. Both lattice parameters shifts and the appearance of an X-ray pattern of the second phase are being used to determine the solubility limit.

In the aluminum - nickel system a maximum solubility of 5 atomic percent Ni has been observed, but is not consistently reproducible. The cause of this inconsistency has not been determined; it could be due to inhomogeneity of the alloys used in making the splats, different cooling rates in different splat foils, or to some contamination of the specimens. Five percent solubility represents an increase over the maximum equilibrium solubility by a factor of 150.

Similar problems also appear in the aluminum - iron system. The best solubility recorded so far is 3 atomic percent iron in aluminum. The previously reported maximum solubility, with extremely high cooling rates, was approximately 0.4 atomic percent iron. The maximum equilibrium solubility reported was approximately 0.1 atomic percent iron at 655°C. Hence, the splat technique has resulted in an increase over the previous maximum solubility by a factor of 7.5 and an increase over the equilibrium solubility by a factor of 30.

In the aluminum - magnesium system, the X-ray patterns indicate that the maximum metastable solubility lies between 6 and 8 atomic percent Mn. Other investigators have reported a maximum solubility of 4.7 atomic percent or 6.7 times the maximum equilibrium solubility of 0.7 atomic percent Mn.

The maximum solubility of Pd in aluminum appears to lie between 7 and 10 atomic percent Pd. Previous investigators reported that the equilibrium solubility of Pd in aluminum was too small to be measured by the relatively insensitive techniques of X-ray analysis. Investigation of this system is hampered by the rapid oxidation of the alloy

while molten in the splat machine furnace due to the high melting temperatures.

The solubility of Co achieved in aluminum is at, or above, 3 atomic percent Co. The equilibrium solubility reported for Co in aluminum is approximately 0.04 atomic percent at 657°C, yielding a solubility increase by a factor of 75. The melting points of Al-Co alloys in the region of interest increase steeply with increasing Co concentration. Alloys with still higher percentages of Co require a furnace with a higher temperature capacity than is currently available.

In the Al-Ag system, it has not yet been possible to produce a single phase splat with more than 23.8 atomic percent Ag (which is the reported maximal solubility of Ag in Al at 566°C). Most alloys appear inhomogeneous. This possibly may account for the failure to observe any increase in the solubility in this system.

Together with the work on the metastable solubilities in the Al-Cu system described in the previous report, this work shows solubility increases by factors of 4 to 150, and makes further work on the precipitation processes in some of these systems extremely interesting. In particular, in the Al-Ni system, the possibility exists of developing age-hardening, analogous to that in Al-Cu system; ternary Al-Cu-Ni alloys will also be considered.

4. Copper-base Alloy Systems

The reported investigation of the copper-rich regions of the Cu-Si and Cu-Be systems by splat-cooling has been concluded. One main conclusion is that the intermediate phase β (Cu-Be) can be extended metastably to much higher copper concentrations, and may show interesting strength properties after suitable heat treatments; it is planned to produce larger quantities of alloy for such tests. Another item of interest, of more theoretical stature, is to determine the degree of ordering which occurs in the lower beryllium-copper alloys.

Future Work

At least two of the atomization methods appear to work adequately well to permit production of powdered materials. Cooling methods will now be developed to achieve the desired quench rates to control structure, solubility, dispersion, etc.; heat treatments to modify the quenched structures; and consolidation techniques to produce bar and sheet or strip test specimens. A number of the alloys show unusual potential for dispersion hardening or age-hardening, and will be examined in detail.

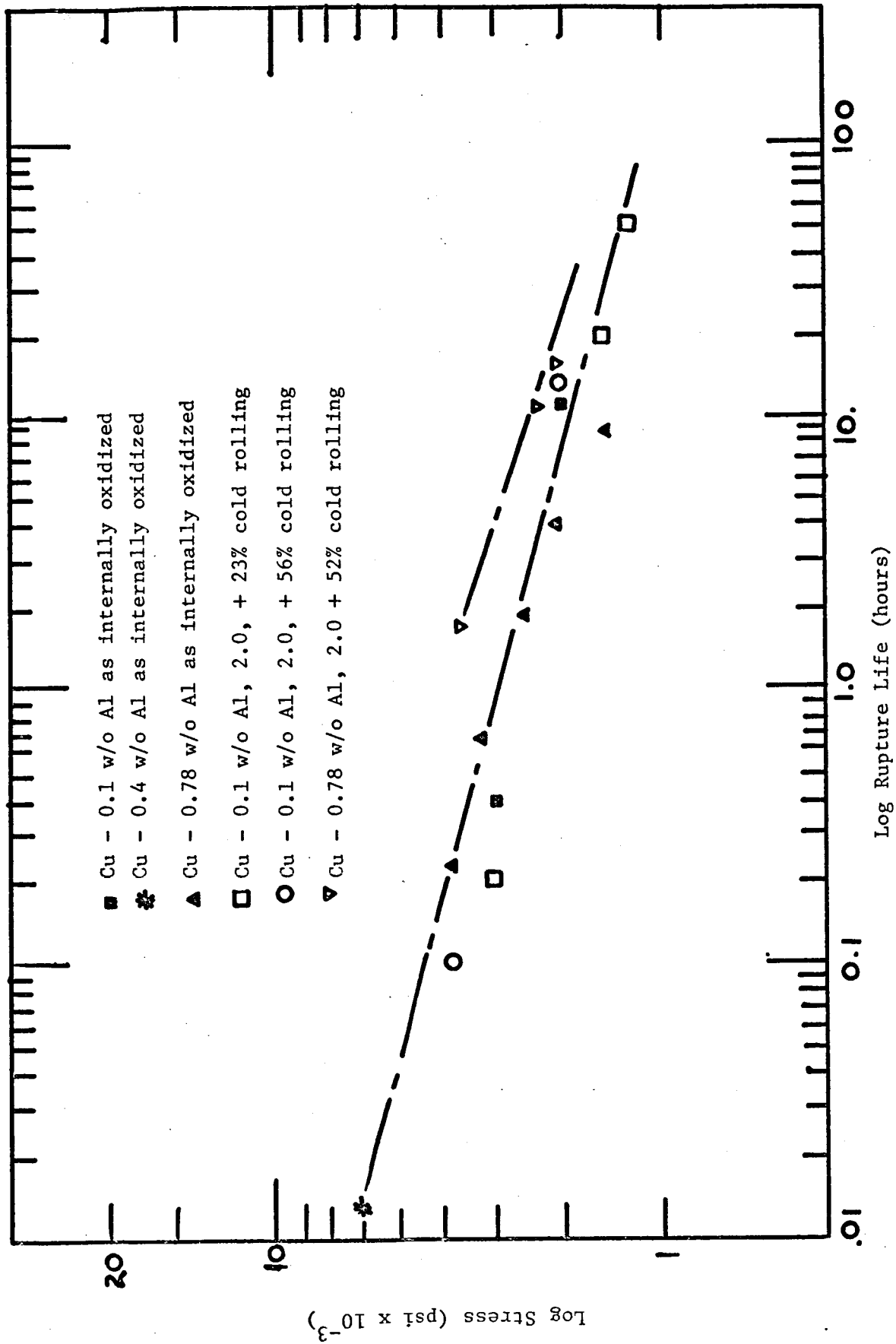


Figure 1. Stress vs. rupture time for Cu - Al₂O₃ alloys in the internally oxidized condition and after internal oxidation plus cold work. Tests in air at 650°C.