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DISPERSION STRENGTHENED SYSTEMS

This report covers a five-month period from about 16 September 1965 to February, 1966.

Research programs during this period were the following:

1. Structure Control on the Strength and Ductility of Fe-BeO Alloys

2. Mechanisms of Deformation and Fracture in Oxide Dispersion Strengthened Alloys

3. Oxide Dispersion Strengthened Alloys by Surface and Internal Oxidation Processes

4. Regarding Internal Oxidation Processes

5. Control of Chromium Oxide Content in Oxidation Resistant, Oxide Dispersion Strengthened Alloys

Publication activities were the following:

1. "Dispersion Strengthening" (Chapter) by N. J. Grant. Due to appear shortly in Proceedings of the Sagamore Army Materials Research Conference: Strengthening Mechanisms in Metals; presented in August, 1965.

2. "Aluminide-Ductile Binder Composite Alloys" by J. S. Benjamin and N. J. Grant. Accepted for publication by AIME Met. Society; will appear in early 1966.

3. "Titanium Carbide Dispersion Strengthened Nickel" by R. J. Murphy and N. J. Grant. Submitted to AIME for publication.

Several other publications are in rough draft form.

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1. Structure Control on the Strength and Ductility of Fe-BeO Alloys

As indicated in previous discussions, iron base alloys will always carry the brunt of all constructional requirements whether the assignment calls for aircraft, nuclear power generation, steam and gas turbines, intermediate temperature pressure vessels, etc. Further, too little work has been done with the oxide dispersion strengthened body-centered-cubic metals to see how they behave relative to the close-packed metals. Finally, oxide dispersion strengthened iron alloys have been produced, with extremely good properties up to 650 to 700°C, well in excess of the strength values shown by conventional stainless steels, both ferritic and austenitic. The results indicated merit considerable additional research and development.

Because some of the earlier work was based on unstable or meta-stable oxide dispersoids (for example, transformations in gamma Al_2O_3, water pick-up by fine MgO or ThO_2, rapid coarsening tendencies by SiO_2 and spinel formation by alpha Al_2O_3), BeO appeared to be an attractive choice for additional, refined studies.

The apparatus for controlled oxidation of the iron-beryllium alloy powders has been constructed, and the procedural details for trouble-free operation have now been established, on the basis of a large number of trial experiments. Briefly, the process is as follows: the loose Fe-Be powder is placed in copper cups to a depth of about 1/4-inch. The cups are arranged in well spaced tiers inside a holder-frame which is placed vertically in a verticle tube furnace. Pre-selected ratios of argon and hydrogen gas are passed through water at a particular temperature to establish a furnace atmosphere of argon + H_2 +H_2O at any desired H_2 H_2O ratio. The argon is used to attain a greater efficiency of water vapor transport and more sensitive control of H_2/H_2O ratios by sharply minimizing

thermal separation of the mixed gases. A special arrangement of copper screening in the muffle acts as an efficient baffle to maintain a well mixed, constant gas composition throughout the hot zone. Post-examination of the exposed alloy powders indicates no significant copper contamination and a homogeneous exposure of the powder to the gaseous atmosphere.

In order to determine the best method to obtain a fine, well dispersed beryllium oxide in the iron a series of runs has been made on an Fe-Be alloy with a beryllium content of 1.3 percent by weight. This would provide a beryllium oxide content of about 9 percent by volume. Lack of data regarding the diffusion and reaction kinetics in the Fe-Be-O system made it necessary to investigate the system over a wide range of exposure conditions.

Three basic mechanisms of forming an oxide dispersion are in process:

1) internal oxidation of the beryllium

2) formation of beryllium oxide only at the surface of thin flakes

3) total oxidation of the solid solution alloys with subsequent selective reduction of iron oxide.

Both bulk samples and -325 mesh powders have been treated under the following conditions:

a) Internal oxidation: conditions are controlled at H_2/H_2O ratios which will not oxidize iron, but will readily oxidize beryllium, working at the maximum permitted oxidizing potential. This should prove to be much more satisfactory than using decomposition of oxides of copper or nickel or iron, etc.

b) Fully oxidizing atmosphere: that is, ratios of H_2/H_2O low enough to form iron oxides as well as BeO. Oxidation was performed at 650°, 850°, and 1000°C at gas flow rates of 1 to 2.5 cfh (total). Complete

oxidation of the -325 mesh powders was accomplished in times of 4 to 6 hours at all temperatures. Internal oxidation of beryllium was done for times of 6 hours and 24 to 30 hours at each of the same temperature.

Only the samples completely oxidized at 1000°C exhibited significant signs of sintering. Internal oxidation at 1000°C for 24 hours resulted in only slight caking. All other samples were perfectly friable and non-agglomerated.

Selective reduction of iron oxide from the resultant iron oxide - BeO mixture was accomplished at temperatures of 450° and 660°F in H_2 flowing at 1.5 to 2 cfh. Complete reduction, as determined by weight loss, was attained in 5 to 7 hours.

Weight change values and preliminary metallographic observations indicate that significant amounts of BeO formed only in those internally oxidized samples that were exposed for 24 to 30 hours at 850° and 1000°C. The appearance of these samples under the optical microscope at 1000X indicates that internal oxidation took place to a satisfactory depth in the alloys. There appeared to be a discernable but unresolvable precipitate structure, observed under the light microscope at 1000X. However, additional and more detailed examination, particularly by electron micro-scopy, is currently under way to determine particle size, shape, etc. The constitution of the precipitated phase and the surface composition of the samples have not been identified as yet.

The microstructures of the bulk samples (2 to 5 mm linear dimensions) which were treated along with the powders showed progressive inward pene-tration of a precipitate zone with increased time and temperature of treatment. Although grain boundary precipitation was heavier and somewhat more advanced, the grain interiors did not appear deficient. Again, however, a more detailed analysis is under way. As soon as more definitive

examination is finished, it is intended to confirm, extend, and optimize the process for obtaining the oxide dispersion in an alloy composition of 0.5 percent beryllium by weight which corresponds to about 3.5 percent BeO by volume.

The material being used for the processing optimization is from cast pig which was ball-milled to powder form; however, for the investigation of the dispersion hardened properties and characteristics of this alloy system, a high purity, homogeneous series of compositions has been produced by atomization from the melt under an inert atmosphere. So far, -325 mesh powders with 0.11 percent, 0.43 percent, and 0.70 percent beryllium by weight have been made. The 0.43 percent composition contains 4.67 percent nickel and should provide information with respect to a solid solution alloying benefits as well as oxide dispersion strengthening. One additional composition, with between 1.1 percent and 1.4 percent beryllium will also be investigated for BeO contributions from surface oxidation via fine flake Fe-Be powders. The former beryllium compositions correspond to about 0.8 percent, 3.1 percent, and 5 percent by volume of BeO. The highest composition Fe-Be alloy will also be considered for possible investigation of a dispersion strengthened alloy with a Fe-Be solid solution matrix which does not undergo the $\alpha \leftrightarrow \gamma$ transformation by the iron matrix (alpha stabilized).

2. Mechanisms of Deformation and Fracture in Oxide Dispersion Strengthened Alloys

Additional understanding of the deformation and fracture mechanisms in oxide dispersion strengthened alloys is a necessary adjunct in support of proposed mechanisms of strengthening for such materials; this is a particularly timely study, and little is being done anywhere in the country on the subject. As of yet, there has been no evidence of conventional or fine slip in these alloys (though fine slip must exist); grain boundary sliding and migration have not been observed or recorded; folds and kinking

have not been reported. Obviously then, it is too early to speculate on the deformation mechanisms; it is equally too early to discuss the fracture modes. In particular, it is important to ascertain whether fracture is transgranular or intergranular, and whether the substructure plays an important role, regardless which fracture mechanism prevails.

After considerable re-examination of available prior structures prepared by many techniques, coupled with fairly extensive additional experiments, the decision was made to utilize internally oxidized copper-aluminum alloys to achieve the desired structures. The kinetics of internal oxidation in this system are fairly straightforward and well understood; and sufficient prior work has been done to permit the generation of alloys containing various oxides contents, various interparticle spacings, and varying particle sizes. One of the most interesting features about this system is that fairly heavy sections (up to 0.125 inch) of sheet and strip can be internally oxidized with little or no loss in the integrity of the structure. Large depths of penetration are possible because of the relatively high solubility for oxygen, and the high rates of diffusion of oxygen.

A number of vacuum melted copper-aluminum alloys were prepared. Some of these alloys have been converted into finely machined chips and then ball-milled into near micron powders, primarily in flake shapes. These will be used to produce alloys with large contents of aluminum oxide.

A second group of these same alloys, in ingot form, has been homogenized at about 950°C for long periods of time, and then cold rolled into 1/8" thick sheet; these materials will be directly internally oxidized. Studies have been directed during the past several months primarily to permit control of the structure, avoiding heavy grain boundary precipitation or a change in oxide particle size with depth of penetration. In preparing samples for this study, the major danger lies in introducing an excess

of oxygen into the rolled strip. Such excess oxygen would ultimately reside near grain boundaries and toward the center line of the strip, leading to embrittlement by ultimate precipitation of copper oxide on cooling. Internal oxidation in all cases is being accomplished by utilizing the oxygen pressure from the decomposition of copper oxide in a copper - copper oxide mixture. A small flow of argon is utilized to attain better transport and distribution of the oxygen in the closed system. These samples have been examined thoroughly to establish the depth of penetration as a function of time, temperature, and composition, with the aim of producing just the right depth of penetration. It is important to stop the introduction of oxygen at a point early enough in the process to permit the consumption of the then dissolved oxygen in the alloy to form Al_2O_3 with no excess of dissolved oxygen.

Sheet of 1/8" thickness was selected for this work, even though it would have been preferred to use considerably thinner material to idealize the internal oxidation, in order to provide a sufficiently thick starting material so that increasing amounts of cold work would be introduced after internal oxidation. Both unidirectional and cross rolling techniques will be utilized after internal oxidation in an effort to introduce or avoid a textured structure, as the occasion demands.

Thus far progress has been good, though slow. It is felt that suitable specimens can be prepared, avoiding the pitfalls of much of the prior work of internal oxidation whereby excess oxygen was always in evidence.

The design of a sheet test specimen has been fixed, specimen holders and other auxiliary equipment has been put together so that room temperature and elevated temperature creep rupture tests can be initiated immediately. Electron microscopic studies have been under way. Techniques for suitable surface replication and transmission electron-microscopy are

being studied. Difficulties are arising, as would be expected, in the thinning of these relatively heavy sections to produce suitable sections for transmission; however, results are quite encouraging.

3. Oxide Dispersion Strengthened Alloys by Surface and Internal Oxidation Processes

One of the least expensive, most straightforward approaches to oxide dispersion strengthened alloys is the SAP method, namely, the process whereby submicron flake powders of suitable composition are permitted to oxidize. In the case of SAP, the pure aluminum or aluminum alloy forms Al_2O_3, avoiding separation and segregation of the oxide. Oxide content is controlled by the surface area of the powder, coupled with any thermal or chemical treatments which would tend to thicken the oxide.

While it appeared that aluminum was uniquely suited for this method, the development of efficient grinding (attritor) processes now makes it possible to produce submicron flake powders of almost any metal or alloy. By proper selection of compositions, such that a particular solute element will oxidize much more readily than the solvent matrix, one can also control the amount and size and thickness of the refractory oxide thus formed.

If, in addition, the solvent can be utilized to diffuse oxygen through it, additional oxidation of the solute can be achieved by internal oxidation.

To this purpose, we have selected the Cu-Al system. The following alloys have been received, atomized by gaseous nitrogen, as -325 mesh powders (in weight percent):

1. 99 Cu - 1 Al

2. 97 Cu - 3 Al

3. 92.5 Cu - 7.5 Al

4. 79 Cu - 20 Ni - 1 Al

Extensive comminution studies have been made, utilizing the 99 Cu - 1 Al alloy (attritor process: Union Process Model 1-5). Stainless steel balls of 3/16" diameter were utilized and it was found that the pick-up of Fe, Ni, and Cr is extremely small. About 2000 grams of the alloy were attrited in a period of 6 hours using ethanol alcohol as a grinding aide. Checks by several techniques are being made to establish flake thickness; the aim is to produce material smaller than 1 micron thick, with an average thickness between 0.2 and 0.5 micron.

As soon as final measurements are made of particle thickness and the grinding time necessary to achieve this thickness, the remaining alloys will be processed.

A portion of the alloys will be extruded such that the amount of Al_2O_3 formed on the surface will be the final oxide content (surface copper oxide will be hydrogen reduced). A second portion will be processed so that the surface copper oxide sill be utilized to internally oxidize some of the aluminum left in solution, thereby increasing the total Al_2O_3 content.

Obviously the proportions of Al_2O_3 contributed by each process will differ according to the composition.

Use of such thin flakes will call for extremely short diffusion times to produce Al_2O_3 internally.

Powders will be isostatically pressed and hot extruded.

4. Regarding Internal Oxidation Processes

Since internal oxidation will always remain one of the most useful methods for dispersion strengthening, it is to our advantage to know as much about the process as possible, and to try to achieve refinements in the method. It is to be recalled that the best M-MO alloy ever produced was by internal oxidation of a Cu - 0.77 percent Al alloy to

produce a Cu - 3.5 v/o Al_2O_3 alloy. On a homologous temperature scale, the results for this alloy were the best reported to date for any metal-metal oxide alloy; further, this copper alloy is by far the strongest high temperature copper-base material ever reported.

The return of a former Research Associate who did considerable work on internal oxidation in the past has made it possible to complete this interesting program. The program included a series of alloys based on nickel and containing up to several percent of beryllium, aluminum, chromium, or titanium. Measurements had been made of depth of internal oxidation as a function of time, temperature, and composition, along with identification of the precipitating phase. Particle size and shape were estimated for a number of the alloys in the series, however the program was far from complete. The current extension of that work, now nearly complete, has concentrated on several of the nickel-aluminum and nickel-beryllium solid solutions. Measurements are being made of oxide particle size, shape, and crystallography, relating the changes that occur as a function of the depth of penetration of the oxide. For several of the alloys there had been observed a major change in the precipitation of the oxide, from discrete fine particles near the surface to needle or rod-shaped particles beyond about 15 microns. In particular, the change in mode of formation was particularly noticeable in the nickel-Al_2O_3 alloys. Extractions have been made of the oxide at various depths, and measurements and identification are being completed. This should give us one of the most complete and detailed studies of its type on internally oxidized structures.

5. Control of Chromium Oxide Content in Oxidation Resistant-Oxide Dispersion Strengthened Alloys

It is becoming increasingly evident that there are problems associated with the presence of chromium oxide in oxidation dispersion strengthened

alloys. It may be that chromium itself may be interacting with the stable dispersoid at the high temperatures, leading to rapid corasening of the refractory oxide.

If this is the situation, there may be unexpected difficulties in producing stable, oxide dispersion strengthened oxidation resistant alloys.

Chromium and chromium oxide both develop fairly high pressures at temperatures of 1000°C and higher. Both the metal and its oxide also have relatively low boiling points. Chromium has a relatively high free energy of formation of its oxide, about 85,000 calories per gram atom of oxygen.

Much of the above is the basis of the speculation that chromium-containing alloys are unstable, as dispersion strengthened materials, at elevated temperatures. The supporting evidence for these claims is all too clear in some instances, and not at all clear in other instances.

Fairly extensive work over the past four or five years, at the New England Materials Laboratory, demonstrated that the presence of 4 to 10 percent of chromium oxide, as an impurity, led to an increase in strength properties from room temperature to about 800°C, but led to rapid weakening above 1000°C. The work at the New England Materials Laboratory utilized fine alloyed stainless steel and Nichrome powders on to which thorium nitrate salts were decomposed to produce thoria. The fine metallic powders oxidized to produce the observed chromium oxide. By a totally different method of alloy preparation, duPont has also observed the unexpected weakening at higher temperatures in alloys containing chromium. The duPont process, if used in this instance, calls for the reduction of chromium oxide to produce the oxidation resistant alloy. Alternatively, they may have used fine chromium powders which would also introduce chromium oxide. In any event, the duPont oxidation resistant, oxide dispersion strengthened alloys show similar high temperature

weakening.

Accordingly, it seemed desirable to examine more carefully the basis of the observed high temperature weakening in oxide dispersion strengthened alloys containing chromium or chromium oxide. There has been initiated, accordingly, a program to produce oxidation resistant materials which would be essentially free of chromium oxide contamination, in an effort to see whether more stable alloys would thereby be produced. At the same time a series of diffusion couples are being studied at temperatures above 1000°C in which reactions between thoria and chromium, thoria and chromium oxide, and thoria and a variety of other active metallic solute elements will be examined. It is hoped that in this way it may be possible to determine whether chromium in solution is capable of partially reducing thoria, or whether the damage comes from the presence of chromium oxide.

Both hydrogen reduction and vacuum carbon reduction of chromium oxide will be utilized to produce chromium oxide free materials. For this purpose we have available several types of oxidation resistant fine alloy powders which will be processed and checked for residual oxygen and chromium oxide content after treatment. If promising results are achieved, a number of alloys will be prepared to establish the level of strength values for oxidation resistant, oxide dispersion strengthened materials.