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CLEANING AND STABILIZATION OF DISPERSION STRENGTHENED MATERIALS

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ABSTRACT

A method for producing stable dispersion strengthened materials from mechanically produced blends of metal plus oxide powders has been demonstrated. The method depends upon the controlled cleaning and densification of partially consolidated thin shapes. It is surmized that the use of thin shapes permits easy access of the cleaning gas to all of the material and the thorough removal of the gaseous impurities and reaction products and prevents agglomeration of the stable oxides.

A fine ball milled blend of nickel plus alumina, with good microstructural parameters was made into coins by either wet or dry compaction. The coins were cleaned at temperatures up to 2000° F and annealed at 2300° and 2600° F in hydrogen. Although some agglomeration was noted, both methods gave products which retained ultrafine oxide particles and showed relatively good stability even after annealing at 2600° F. The dry coins did not sinter as completely as those produced by wet compaction and the particle size increase as a result of annealing was somewhat greater. A nickel plus thoria composite with unusually good microstructural parameters was also produced from a ball milled blend. Furthermore it is believed that the method may have aided in the reduction of chromium oxide in a chromium bearing nickel alloy and possibly eliminated sulfur (which is known to promote oxide agglomeration) in blends of nickel and thoria.

INTRODUCTION

Ever since the production of dispersion-strengthened aluminum by Irmann in 1946 (ref. 1), investigators have been working to achieve similar gains in strength in higher melting point metals. Since matrix oxides of many of the higher melting metals are relatively unstable (compared with Al_2O_3 in aluminum), investigators have tried incorporating stable oxides by means other than surface film formation and extrusion. Improved high temperature strength and stability has been obtained in higher melting point metals than aluminum. Some of the best results to date have been obtained with an internally oxidized copper aluminum system (ref. 2) and a nickel thoria system prepared by a colloidal-chemical approach (ref. 3). Mechanical milling and blending methods have been used with varying degrees of success. Such an approach may offer a number of advantages such as ease and low cost of production and flexibility in terms of application to complex alloys. In principle, there should be no reason why products made by mechanical methods should not be as good as those made by other methods. In view of the urgent needs for dispersion-strengthened superalloys and high melting point materials for such applications as the SST, VTOL, VSTOL and space power systems it was felt that a critical evaluation of problems associated with mechanical production methods of dispersion strengthened materials was warranted.

It is strongly felt that one of the reasons that SAP-analogue materials have not been made by mechanical methods is that impurities have prevented the realization of their full strength potential. Thus, if there were a capability of producing a very fine distribution of oxides in a powder metal matrix, difficulties in cleaning and subsequent consolidation may prevent the retention of the fine blend (ref. 9). Furthermore, even if a material with good

microstructural parameters (fine particle size and interparticle spacing) were
achieved, small quantities of impurities might still cause detrimental reactions
in subsequent processing or use conditions (ref. 5).

Mechanical blending and comminution methods have been developed at the
Lewis Research Center (ref. 6) that show that submicron particles of both metal
and oxide may be obtained by adding materials to the grinding media that tend
to maintain fine particles close to a colloidal state. Other ultrafine particles
are also available from commercial sources. In using ultrafine powders of metals
with large surface areas problems of achieving high purity in a final product
would be expected. While most investigators using the mechanical mixing approach
subject their powders to a reduction type cleaning process, there are a number of
inherent difficulties which tend to limit the efficiency and completeness of the
methods employed. For example, in cleaning fine powders some powder may sinter at
the cleaning temperature and trap reaction products such as water vapor and
carbonaceous gases. Secondly, in cleaning cold compacted billets or deep beds
of powder the cleaning gas may not reach all of the powder at the interior and
reaction products may recombine with clean material before reaching the surface.
Finally, in cleaning partially densified billets or large specimens the surface
may sinter so that the cleaning gases cannot enter or the reaction products
escape. It should also be noted that even well cleaned materials may be re-
contaminated during subsequent processing before they are completely densified
in the final product.

In view of the possible difficulties and problems associated with cleaning
fine powders, it is not too surprising that many of the dispersion strengthened
materials made by mechanical methods have exhibited microstructural instabilities.
Considerations arrived at through experience with many of the problems listed

above suggested that thorough cleaning, sufficient to achieve high temperature

stability may be accomplished by using a partially densified powder with shapes

sufficiently thin to permit easy access of the cleaning gas to the interior of

the product and escape of the reaction products. Furthermore, it was felt that

a slow heating rate would permit elimination of the impurities prior to final and

complete densification. Thus, the objective of the present investigation was to

determine whether by careful control of cleaning and densification rates, shapes

of mechanically blended dispersion materials could be produced that would have

an ultrafine dispersion of a highly stable oxide.

Nickel plus alumina powder blends were wet ball milled, washed, pressed

into coins or balls and heated in hydrogen at a programmed rate to 2000° F or

above. The cleaned and sintered materials were annealed in hydrogen at 2000°

and 2600° F to evaluate the stability of the oxide distribution. The measured

interparticle spacings and particle sizes for oxides in the sintered and annealed

specimens were compared with those of the as-blended structure. A wet ball

milled nickel plus thoria blend and a nickel plus thoria blend contaminated with

sulfur and a nickel alloy containing chromium and tungsten were also evaluated.

MATERIALS APPARATUS AND PROCEDURES

Preparation of Ni-Al$_2$O$_3$ Materials

Inco B nickel (2.5 micron in size) was ground to an average size of 0.02

to 0.05 micron in a Szegvari Attritor (fig. 1) with 5 volume percent of Cabot 0.03

micron Alon C alumina. The composite was then washed and the powder pressed into

wafers in both a wet and dry condition. The coins were then subjected to a

series of heat treatments designed to clean and densify the powder. Finally,

the coins were annealed at temperatures above 85 percent of the matrix melting

point to check the stability of the oxide distribution. The measured inter-

particle spacings of the sintered and annealed specimens were compared with the

"as-blended" structure obtained from a cold cartridge actuated compaction pressed specimen (ref. 4) which had been annealed for one hour at 1600° F in vacuum.

The Inco B nickel powder and Alon C alumina were ground for 72 hours in heptane under an argon blanket using balls, stirrers and a mill container, all of which were made of Ni, to avoid contamination. As the grinding proceeded, gradual additions of oleic acid were made to the blend so that the total at the end of the grinding was 20 percent by weight of the powder. The ground material was then washed 10 times with heptane and 2 times with acetone by decantation in an air atmosphere using a centrifuge to speed the settling of the powder. The average particle size of the ground material was 0.02 to 0.05 micron.

Fabrication, Cleaning and Densification of Dry Compacted Ni-Al$_2$O$_3$ Coins

One half of the slurry was dried in air and the powder transferred to a cleaning tube. The powder was first maintained at a reduced pressure (about 25 torr) and 600° F for one day and then cooled to room temperature. The temperature was then brought up slowly to 1000° F while maintaining a flow of 10 cubic feet of hydrogen per hour through the powder. The hydrogen was purified in a palladium diffuser apparatus. The moisture level of the effluent hydrogen was monitored with a phosphorous-pentoxide-electrochemical moisture meter. The increase in temperature was controlled so that the moisture evolution was maintained below 1000 ppm. The temperature and flow of hydrogen was maintained until the moisture reading in the effluent gas fell below 10 ppm, which took three days. The powder was then pressed into 2-inch diameter by 1/8-inch thick coins in air using a 20,000-pound load. The coins were then placed on porous zirconia discs which in turn were mounted on a rack (fig. 2). The entire rack was then placed in the hydrogen tower and the coins recleaned using the same

schedule as for the powder. The rack with the coins was then sealed in plastic under argon and transferred to a sintering furnace. After removing the plastic under an argon blanket, the coins were heated slowly in hydrogen (at less than 200° F per hour) to 2000° F. A two-hour hold at 800° F and two-hour hold at 2000° F in hydrogen was followed by sic hours in vacuum at 2000° F.

Prior to selecting a thickness of 1/8-inch, coins ranging in thickness from 1/32 to 1/4 inches were produced. The thinnest coins were found to warp on processing while the thicker coins were not completely cleaned and densified at the center. The 1/8 inch coins, however, retained their shape, were readily and uniformly cleaned and densified and contained a good distribution of fine particles of the added oxide.

Cleaning and Densification of Wet Compacted $Ni-Al_2O_3$ Coins

The remaining half of the powder slurry was washed with alcohol followed by water to eliminate the organic solvent. Using a ram with a porous pressing surface and a die with a porous bottom to help eliminate excess liquid, the wet powder was pressed directly into coins two inches in diameter and 1/32 to 1/4 inch thick (most were 1/8 inch thick) using a 20,000-pound load (fig. 3). The coins were then placed on porous zirconia discs, stacked on a rack and transferred to a sintering furnace. They were then heated slowly and held successively for 2 hours in vacuum at 600° F, 2 hours in purified hydrogen at 800° F, 2 hours in hydrogen at 2000° F and 6 hours in vacuum at 2000° F. The hydrogen was purified with a palladium diffuser. The moisture content of the H_2 coming out of the purifier was measured to be 2-3 ppm. The rate of heating was controlled by either the outgassing or moisture evolution and did not exceed 200° F per hour.

Cartridge Actuated Compaction Pressing of Pellets

Small pellets 1/2-inch in diameter and 1/8-inch thick were made at room temperature by explosive compaction in a specially constructed die using a 45-caliber cartridge. The pellets were annealed for one hour at 1600° F in vacuum (10^{-4} torr) in order to eliminate the worked background and improve the detail of the oxide particles in the electron micrographs. Powder used for the pellets was cleaned in hydrogen at 800° F prior to compaction. The particle sizes and interparticle spacings of the compacted and annealed pellets were known to be close to that of the initial blend (ref. 4).

Stability Anneals of Ni-Al$_2$O$_3$ Coins

The standard stability anneals of the cleaned and densified coins were conducted in hydrogen and were as follows: (1) 24 hours at 2300° F and (2) 11 hours at 2300° F followed by 11 hours at 2600° F. Other annealing treatments used are noted in the figures. Stability was judged by comparing the microstructures for particle size growth, interparticle spacing, and porosity with specimens of the initial blends prepared as described above.

Additional Experiments

In order to determine whether the cleaning methods with the Ni-Al$_2$O$_3$ blends could be used with other materials, several additional experiments were conducted. These were as follows:

1. Cleaning of Ni-ThO$_2$ coins made from sulfur contaminated Ni (nickel contained 0.25 percent sulfur). A coin was made from a blend of Ni-ThO$_2$ materials, previously known to agglomerate during processing. Blending was accomplished in a homogenizer-type apparatus using a heptane-oleic acid medium. Coins prepared by the wet and dry compaction methods were heated slowly in hydrogen to 2300° F with two-hour holds at 800° and 2300° F. They were then

annealed an additional time of 24 hours in a hydrogen atmosphere at 2300° F.

2. Cleaning and annealing of Ni-ThO$_2$ coins produced using ultrafine ThO$_2$ particles (50 - 150 A$^{\circ}$). The coin was dry compacted in a single actuated die and subsequently cleaned at 800° F for 3 days followed by annealing with increasing temperatures to 2000° F. It was held at 2000° F for 15 1/2 hours and annealed at 2300° F for 7 hours.

3. Cleaning of 55Ni-25W-20Cr alloy -- Two groups of materials were prepared: one from prealloyed powders procured from a commercial source and another from elemental powders prepared by ball milling. Both materials had considerable impurity oxides after consolidation. The cleaning treatment was the same as that noted in item 1 above.

4. Balls rather than coins were made from a blend of ultrafine Ni-Al$_2$O$_3$ powders. The blending was carried out in a Waring blender for approximately two minutes. Powder blends were packed into a flexible rubber pressing tube which was then tied into segments at approximately 1/4-inch intervals and hydrostatically compacted at 70,000 pounds per square inch. The resulting balls were removed from the pressing tube and cleaned in the same manner as 1 and 3 above.

Metallography

Successfully compacted specimens were mounted in Bakelite and prepared for electron microscopy. Standard metallographic polishing techniques were used for rough polishing, and final polishing was accomplished with 3-micron and 1/2-micron diamond compounds. A low-temperature etching technique was used. Specimens were immersed in liquid nitrogen and then quickly swabbed with an etching solution consisting of 92 percent hydrochloric, 3 percent nitric, 5 percent sulfuric acids diluted in water at a ratio of 4 parts acid to 1 part

water. The low-temperature method was used to slow the etching rate which enabled a fine control of the degree of etching, and minimized specimen staining.

Determination of Particle Parameters

The parameters (i.e., volume percent of particles, interparticle spacing, and particle size) were determined by using measurements taken from electron micrographs. Representative electron micrographs were selected and area analysès were made of them. A Zeiss-Endter particle size analyzer was used to determine the numbers of particles of given diameters in each electron micrograph. The area of each particle counted was visually equated to a circle of light, of comparable area, produced by the counter. For each micrograph, the total area occupied by the particles was determined after the number of particles of given diameters were obtained. The volume fraction of particles was taken as the ratio of the total particle area to the total area scanned.

The average particle sizes and interparticle spacings were calculated by using the following equations:

$$\overline{IPS} = \pi \frac{A}{P} \left(\frac{1}{f_{ox}} - 1 \right)$$

and

$$\overline{Z} = \pi \frac{A}{P}$$

where

$\overline{IPS}$ average interparticle spacing of oxide particles in a three-dimensional array

A   total particle area determined from micrograph (assuming circular plane sections for particles)

P total particle perimeter determined from micrograph (assuming circular

    plane sections for particles)

f_{ox} volume fraction of oxide (area of particle phase divided by total area

    scanned)

$\bar{Z}$ average particle intercept dimension, defined as the average intercepted

    length on randomly oriented straight lines through a random three-

    dimensional array of particles

$\dfrac{V}{S}$ ratio of volume to surface area for dispersoid phase in finished composite

    alloy

The above equations are slight modifications (i.e., substituting $\dfrac{\pi A}{P}$

for $4\dfrac{V}{S}$ of those derived in reference 7, which in turn, were based in part

on topological concepts derived in reference 8.

RESULTS

Preliminary Experiments

It was noted earlier in preliminary experiments, that coins of Ni-Al$_2$O$_3$

ranging in thickness from 1/32 to 1/4 inch were cleaned and annealed. The micro-

structure of a 1/4 inch coin shown in figure 4 illustrates graphically the

relationship between cleaning partially consolidated powder blends and retention

of fine oxide particles. This is shown by the fact that the edge, after exposure

to hydrogen, has a much better dispersion of fine particles than the center.

Wet and Dry Coin Experiments with Ni-Al$_2$O$_3$

Figure 5 shows the "as-blended" structure of aluminum oxide dispersed in

nickel which was cold consolidated with the cartridge-actuated press. The

microstructure of this material compares very favorably in parameters with those

produced by other methods. Some of this material was cleaned in coin form in

the successive steps described previously and the results are indicated in

figures 6 and 7. Figure 6(a) shows the microstructure of the coin which was heated to 2000° F. The particle sizes were relatively uniform. Note also that there is no microstructural evidence of porosity in the matrix. Figure 6(b) shows the results of the 2300° F stability anneal. The uniformity and fineness of the particles are evident but the particle sizes have increased relative to those obtained during cleaning at 2000° F. As was the case before annealing, there is no evidence of porosity in the material. In the case of the stability anneal at 2300° F and 2600° F (fig. 6(c)) there was a somewhat further coarsening of the particles, but the structure was still nonporous even though the final temperature was above 98 percent of the melting point of Ni.

Figure 7(a) shows the results for a specimen produced by dry coining and cleaning at temperatures ranging up to 2000° F. These coins show fine particles and some apparent porosity which was due to incomplete sintering. Figure 7(b) shows a specimen that had been cleaned at 2000° F and has subsequently been stability annealed at 2300° F. Although some of the particles shown are larger than those obtained by the wet method, some are very fine. Upon annealing the material to temperatures as high as 2600° F some fine particles remained, although many particles grew larger.

Figure 8 shows optical micrographs of coins made by the wet and dry processes. The wet produced material has no significant amount of porosity and the dry produced product has a considerable amount of microporosity as a result of incomplete sintering.

To summarize some of the results shown in the photomicrographs just described on a more quantitative basis, particle parameter measurements were made. These are presented in table I. The number of the particle measurements used in this study was not very great. In most cases only one photomicrograph of the

material was measured. The measured interparticle spacing of the "as-blended" material was 1.04μ and the median particle size was 0.022μ. Such dimensions (although obtained from a non-sintered specimen), compare favorably with those of some of the better dispersion-strengthened products, including TD-Ni. The cleaning of the wet material at a temperature of 2000° F increased the interparticle spacings to 1.8μ and the median particle size to 0.042μ which is almost double that of the initial size. A 2300° F stability anneal increased the median particle size to 0.13μ and the interparticle spacing to 3.4μ. In this case, there was a relatively large amount of growth of the oxide. Annealing at 2600° F resulted in a further growth of the oxide particles (median size 0.19μ) and increased the interparticle spacing to 6.03μ; however, some oxide particles as small as 0.05μ were still present. In all cases the volume percent oxide measured was low relative to the nominal quantity added to the ball mill. The dry coins cleaned at 2000° F exhibited a larger interparticle spacing than did the wet ones (3.57 versus 1.84 micron) but the median particle size (0.042 micron) was the same for both. Annealing at 2300° F increased the interparticle spacing to 4.67 micron. Again, the median particle size was approximately the same as for the wet coins, 0.14 micron. Increasing the annealing temperature to 2600° F resulted in a further increase in both particle size and interparticle spacing.

Wet and Dry Coin Experiments with Ni-ThO$_2$

Preliminary experiments at Lewis Research Center have shown the effectiveness of the cleaning techniques described above for Ni-ThO$_2$ compositions. In one series of experiments, Ni powder 200 - 300 Å in size and contaminated with 0.25 w/o sulfur was wet mixed with 8 v/o ThO$_2$ in a homogenizer. The resulting mixture was dried, the powder cleaned in H$_2$ at 1100° F for 80 hours, and then

sintered at 1900° F in H_2. The resulting microstructure is shown in figure 9. The same Ni-8v/o ThO_2 mixture was processed into coins of both the "wet" and "dry" types by methods similar to those described for the Ni-Al_2O_3 specimens. The resulting "micros" are shown in figures 10(a) and 10(b). It is evident that the thoria particles present in figure 10 are much finer than those of figure 9. Figure 10(c) shows an electron micrograph of the oxide particles after the nickel had been leached away from the powder blend. The oxides are very fine, of the order of 200 to 300 angstrom; however, in some areas they have agglomerated or have not been dispersed by the homogenizer. On the other hand, in large areas of the background, the fine oxides are dispersed. This would indicate that the larger oxides shown in figures 10(a) and 10(b) are caused by the agglomeration of the clusters of oxide particles and that the smaller oxides that are dispersed in the matrix are some of the original fine particles. Thus, the coin method shows up even better than indicated by some of the photomicrographs.

Recently relatively pure thorium oxide powders of an ultrafine size were obtained. These particles had a size of 50 to 150 $\overset{o}{A}$. Figure 11 shows a microstructure of a dry pressed coin produced from a ball milled blend, cleaned and annealed at 2000° F and further annealed at 2300° F. The microstructure appears most promising: particle sizes ranged from 0.018 to 0.382 microns, the median being 0.059 and the interparticle spacing was 2.26 microns. This structure should be compared with those of figures 6 and 7, the parameters for which are noted in table I.

Experiments with Ni-25W-20Cr Alloys

Figure 12 shows some results of cleaning dry compacted coins of a chromium bearing nickel alloy of the composition 55Ni-20Cr-25W. No stable oxide particles were added to this material. The material in figure 12(a) shows an

unusually large quantity of impurity oxides in the consolidated powder. This material was compacted by the cartridge-actuated compaction press. Most of the oxides that are present are believed to be chromium oxides. This was borne out by the fact that most of the oxide was retained after cleaning the powder in H_2 at 800° F (fig. 12(b)). Figure 12(c) shows the same material in the form of a coin after cleaning at a temperature as high as 2300° F in hydrogen. Note that most of the oxides have been cleaned up. The particles visible in the matrix are probably intermetallic compounds. The picture in figure 12(d) shows the same composition made from elemental metal powders by ball milling and subsequent cleaning at temperatures as high as 2300° F. The cleaning process here again appears to have removed the oxides from the matrix.

Figure 13(a) shows cleaned and uncleaned balls produced by hydrostatic compaction in a rubber tube. Figure 13(b) shows an electron photomicrograph which reveals many fine particles distributed in the matrix and no porosity. Although some relatively large particles of oxides were present in the material (not shown in the photomicrograph) it is believed that with refinement the treatment could have achieved as good results as were obtained with some of the coins.

DISCUSSION

Capabilities have been established to produce dispersion-strengthened materials containing ultra-fine dispersoids via mechanical blending or grinding techniques, to consolidate the blended products to a suitable density by a cold compaction method that permits electron microscopic examination of the disper-soids in the matrix, and to clean and consolidate the products so produced so that the resulting microstructures are stable. Microstructural stability, as used in this paper, involves consideration of both the agglomeration of oxides

and resistance to pore formation of the matrix at high temperatures.

Stability - Cleaning Relationships

The importance of the relationships of impurities to oxide agglomeration has been evident to a number of investigators for some time. Solutions to the problem of cleaning matrix powders, while known to be essential, has been most difficult. It is believed that, in the area of cleaning powders or powder blends produced by the mechanical mixing or grinding of materials, that relatively little success has as yet been achieved. In an earlier study conducted at the Lewis Research Center (ref. 9) an edge effect was noted on billets which had been hot pressed in a graphite die. It was felt that the carbon available cleaned the periphery of the material. The center which was uncleaned had larger, agglomerated oxides. Others working with Ni-base materials also have noted the importance of specific impurities as they effect agglomeration of oxides (refs. 5 and 10). Most of the work noted above was concerned with the stability of the oxides per se. In the work of reference 5, it was observed that matrix instabilities were associated with breaks in the slopes of stress-rupture curve representing several different types of dispersion-strengthened materials. Further, it was observed that very high temperature heat treatments produced microporosity in the matrix of the materials that exhibited strength instabilities. One of the best dispersion-strengthened materials, TD-Ni, showed no evidence of agglomeration of ultra-fine oxides or pore formation when it was heated to temperatures of the order of 85 percent of the melting point. Therefore, abnormally high heat treatments; that is, treatments well above the intended use temperature of the product were felt to be a good criterion for the determination of the stability of the material.

Particular attention was paid in this study to the instabilities of the

matrix as evidenced by porosity. The stability anneals that were used are believed to be a more rapid and reliable indication of the stability of the product than chemical analyses, which are difficult to perform rapidly and accurately.

The evidence obtained in this investigation, showed that after heating to temperatures as high as 2000° F, (reaching this temperature slowly and cleaning on the way to the temperature) only a small increase in interparticle spacing was obtained over that of the blended powder using nickel and 5 v/o aluminum oxide. Even after heating at temperatures of 2300° F and 2600° F (88 and 98 percent of the melting point of the nickel matrix), many fine particles were retained in the microstructures. The median particle size values were below 0.20 microns in the case of the wet compacted coins stability annealed at 2600° F. Also, no catastrophic agglomeration occurred that was comparable to the type of agglomeration observed in earlier work after conventional cleaning and sintering (fig. 9) or in the center of the coin (fig. 4) which was not dense after heating for over 30 hours at 2300° F and 2560° F in a vacuum.

Cleaning Concepts

Conventional processing of materials to produce dispersion-strengthened products generally involved cleaning of the matrix metal powder (before or after blending with oxide) in hydrogen at relatively low temperatures to avoid sintering. The cleaned powder would then be consolidated into a billet by hot pressing or cold pressing and sintering. Despite the fact that monitoring of effluent moisture during the cleaning process seemed to indicate that cleaning was complete, the amount of agglomeration obtained during the subsequent processing, and increased quantities of measured total oxide above the nominal oxide content, suggested that detrimental impurities were not completely removed or that the

powder was recontaminated subsequent to cleaning.

The difficulty in cleaning the loose powder is that low temperatures used to avoid sintering may not be sufficient to thoroughly clean the powder while high temperatures may cause agglomeration of both metallic and oxide constituents. Also, if the powder bed is deep the reaction products, in this case water, are believed to react again with nickel or other upstream powders to reform impurity oxides. This process may occur many times before all of the water is finally swept from the cleaning chamber.

In processing billets made from fine powders two types of edge effects were noted, one in which the sintering was done in a vacuum or inert atmosphere and another in which the sintering was done in a reducing carbonaceous or hydrogen atmosphere. Micrographs of the structures produced and some analysis of the inside and surface or edge of an extruded bar indicated that the insides of the billet had a higher contamination of impurities than the surface. In the case of sintering in a neutral atmosphere it is believed that the higher contamination on the inside is due to sintering of the surface which traps impurities in the center. When sintering with a reducing atmosphere, a cleaning effect at the surface or edge was observed (ref. 9). This occurred simultaneously with the sinter. The edges apparently densified during sinter in such a manner that a good distribution of intentionally added oxides was maintained.

The use of partially densified thin pieces as used in this study takes advantage of the ability of the cleaning gas to penetrate such a specimen and the ability of the gaseous reaction products to escape from the specimen. The method also restricts gross movements and surface diffusion of the added oxide during the simultaneous cleaning and densification. Another possible factor that could facilitate agglomeration of the added oxides in a powder blend might be

the presence of a skin or film of a low free energy oxide on the surface of the metal powders. Such a film could be most detrimental and must be removed by the cleaning process. Preliminary partial densification of the coins probably traps the added oxides in place in the presence of impurities but permits thorough cleaning to occur before densification is complete. A good portion of the cleaning (such as surface skin removal) is believed to occur at low temperatures. Finally, the remaining impurities are eliminated as the temperature is raised in successive steps. The final complete cleaning of the traces of impurities are believed to be accomplished at elevated temperatures. Although thermodynamic considerations indicate that a complete cleaning should be possible at lower temperatures, kinetic considerations probably prevent thorough cleaning from taking place. Finally the process yields a highly dense product which should not readily recontaminate on further handling or processing.

Aluminum Oxide Versus Thorium Oxide

The selection of aluminum oxide for the bluk of this study was predicated on the fact that an ultrafine and relatively pure aluminum oxide could be obtained readily and conveniently.

While both Al_2O_3 or ThO_2 can be agglomerated in Ni if the matrix has impurities, in a clean matrix thoria should be more stable since it has a more negative free energy of formation, and since it does not undergo an allotropic transformation from γ to α (cubic to hexagonal - refs. 11 and 12). Furthermore, thoria does not form spinels which probably are relatively undesirable dispersoids.

Versatility of Cleaning Method

In the results describing the apparent cleaning of the nickel containing sulfur as an impurity and thorium oxide as a dispersoid, it was suggested that other types of impurities in a nickel matrix may be cleaned by the process. It

is believed that materials such as carbon can also be removed by a similar method or, in fact, any other impurity that could be made either volatile or gaseous as a reaction product. The method is also believed to be applicable to materials other than a matrix such as nickel, which has a low stability oxide such as NiO; for example, a chomium bearing material containing large quantities of chromium oxide impurities (but no oxide additives such as thoria), was cleaned to some degree by the process of this study (fig. 12).

Method of Producing Billets or Larger Products

One of the methods that has been conceived to make larger products is to produce billets by stacking coins together, sintering these coins or isostatically hot pressing them, and subsequently canning and extruding or working the products, figure 14. Another method to produce similar products is to make balls or pellets rather than coins. Figure 13(a) shows balls produced by a hydrostatic compaction method. In the center are balls which were cleaned by the cycle described in the procedure for the coins. The significance of this series of photographs is that relatively mechanized methods may be devised to produce pellets or balls or small thin shapes of materials which can be cleaned by the principles described. To produce larger products from such shapes it is conceivable that they could be canned, hot pressed, and forged or hot pressed, and extruded or in some other way consolidated.

SUMMARY OF RESULTS

This investigation was conducted to determine whether stable dispersion-strengthened materials could be produced by a combined cleaning and densification process applied to thin partially consolidated materials. Nickel plus Al_2O_3 or ThO_2 dispersion-strengthened blends prepared by mechanical mixing were produced with microstructural parameters (after cleaning and annealing) comparable to the

better nickel-base materials. The results of the investigation were as follows:

1. $Ni+Al_2O_3$ materials were produced by a wet coining method that showed particle sizes after cleaning to 2000° F of as low as 0.042μ (median size) and an interparticle spacing of 1.84 microns. The range of sizes were 0.017 to 0.31μ.

2. $Ni+Al_2O_3$ specimens produced by the wet coining process stability annealed 24 hours at 2300° F (homologous temperature of 0.88) exhibited particles ranging from 0.046 to 0.51μ; median 0.13μ. Another specimen annealed at 2600° F for 11 hours following a 2300° F anneal exhibited particle sizes of 0.050 to 0.60μ; median 0.19μ. No evidence of matrix instabilities in the form of micropores were observed in these materials. The lack of abnormal growth of particles compared with relatively impure sintered materials is felt to be a good indication of the stability-cleanliness relationship.

3. Cleaning of coins of blended $Ni+Al_2O_3$ produced by a dry method yielded particle sizes comparable to those of the wet pressed coins. Upon annealing the coins, particle size increased somewhat more for the dry than the wet pressed coins. Dry pressed coins did not sinter as completely as the wet pressed coins.

4. A preliminary cleaning experiment with a chromium bearing alloy processed into coins and cleaned appeared promising. Apparently H_2 reduced impurity-chromium oxides that were present in large quantities in the starting material.

5. In a preliminary experiment with $Ni-ThO_2$ a material was produced with very good microstructural parameters after annealing at 2300° F. The median particle size was 0.059μ and the interparticle spacing 2.26μ.

6. A $Ni-ThO_2$ dispersion-strengthened material that had been most difficult to consolidate without agglomeration of oxides due, presumably, to the presence of sulfur was coined, given a cleaning and annealing treatment, and exhibited a stable structure.

7. A mechanical method to produce small balls for cleaning and subsequent consolidation was presented and a method for producing billets from both balls and coins was described.

REFERENCES

1. R. Irmann, Metallurgia, pp. 125-133, Sept. 1952.

2. N. J. Grant and O. Preston, Trans AIME, 209, (1957) 349-360.

3. G. B. Alexander, R. K. Iler and S. F. West, U. S. Patent 2,972,529, Feb. 21, 1961, E. I. duPont de Nemours and Company, Wilmington, Del.

4. G. Reinhardt, W. S. Cremens and J. W. Weeton, NASA TN E-3200.

5. C. A. Hoffman and J. W. Weeton, NASA TN E-2982.

6. M. Quatinetz, R. J. Schafer and C. R. Smeal, NASA TN D-879 March 1962.

7. Cremens, Walter S: Use of Submicron Metal and Nonmetal Powders for Dispersion-Strengthened Alloys. Ultrafine Particles, W. E. Kuhn, ed., John Wiley and Sons, Inc., 1963 pp. 457-478.

8. Smith, Cyril Stanley; and Guttman, Lester: Measurement of Internal Boundaries in Three-Dimensional Structures by Random Sectioning. AIMME Trans., J. Metals, vol. 197, No. 1, Jan 1963, pp. 81-87.

9. R. J. Schafer, M. Quatinetz, and J. W. Weeton, NASA TN D-1167 March 1962.

10. D. K. Worn and S. F. Marton, Powder Metallurgy, Edited by W. Leszynski, Interscience, New York 1961, pp. 309-342.

11. K. M. Zwilsky and N. J. Grant, Trans. Met. Soc. AIME, 221, 1961, pp. 371-377.

12. N. Komatsu and N. J. Grant, Trans. Met. Soc. AIME, 224 August 1962, pp. 705-713.

Table I. - Microstructural parameters of blended, cleaned and annealed Ni − 5 v/o Al_2O_3 coins.

SPECIMEN CONDITION		PARTICLE SIZE, μ	VOLUME, %	INTERPARTICLE SPACING, μ
BLEND	CARTRIDGE ACTUATED COMPACTION STRESS ANNEAL 1600° F, 1 HR VACUUM	0.010 - 0.19 50% -< 0.022	3.44	1.04
WET METHOD	CLEANED THROUGH 2000° F	0.017 - 0.31 50% -< 0.042	3.67	1.84
	STABILITY ANNEALED, H_2 2300° F, 24 HR	0.046 - 0.51 50% -< 0.13	4.14	3.40
	STABILITY ANNEALED, H_2 2300° F, 11 HR 2600° F, 11 HR	0.050 - 0.60 50% -< 0.19	3.31	6.03
DRY METHOD	CLEANED THROUGH 2000° F	0.017 - 0.73 50% -< 0.042	2.66	3.57
	STABILITY ANNEALED, H_2 2300° F, 24 HR	0.050 - 0.66 50% -< 0.14	3.48	4.67
	STABILITY ANNEALED, H_2 2300° F, 11 HR 2600° F, 11 HR	0.086 - 0.60 50% - 0.23	2.73	7.96

CS-40008

Ni CONTAINER, STIRRER, AND BALLS
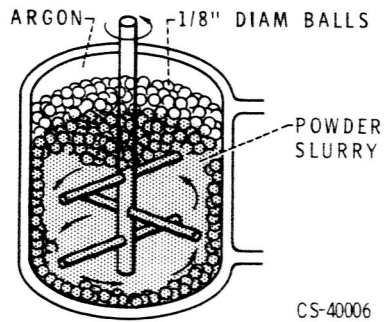
Figure I. - Attritor mill used for grinding ultrafine
powders of metals and oxide.
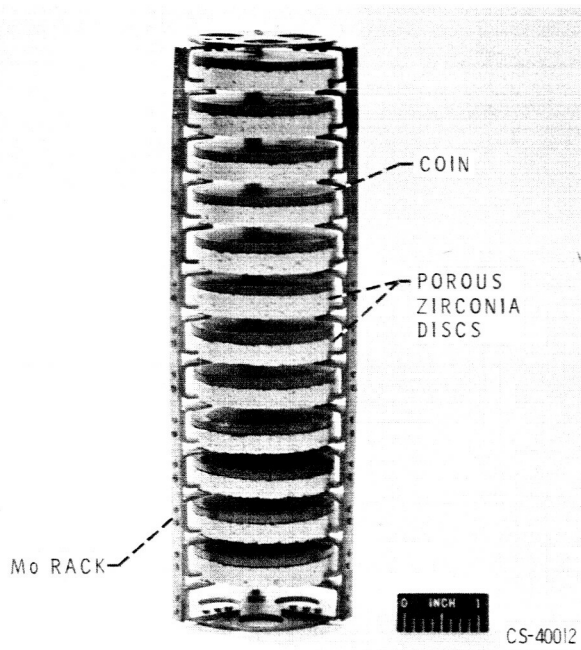
Figure 2. - Coins made from powder blends stacked on cleaning rack.
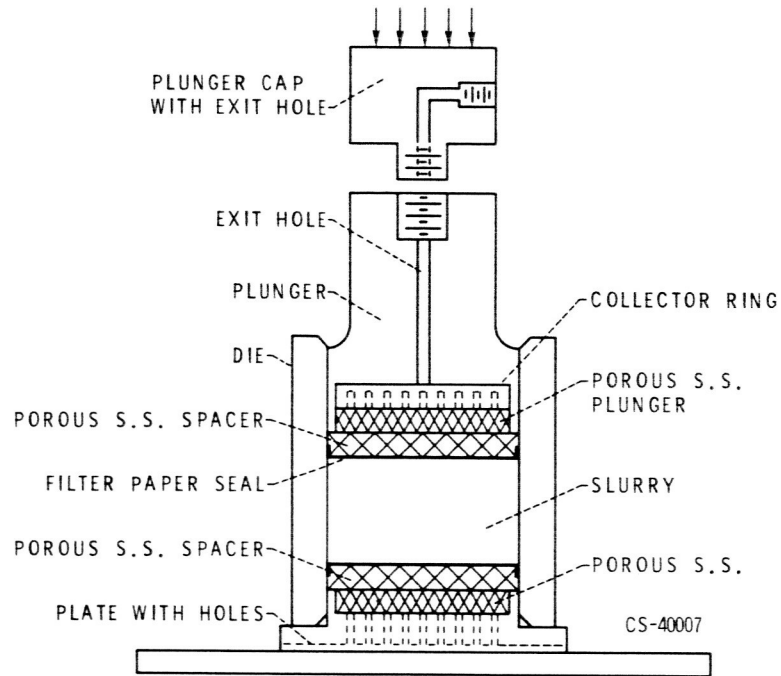
Figure 3. - Die for preparing coins from slurry of blended powders.
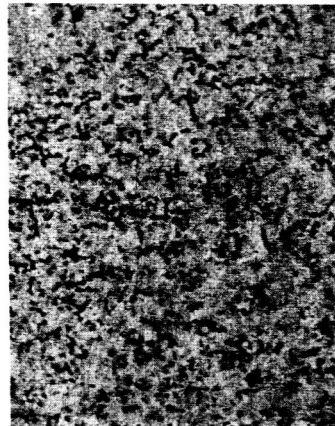

(A) EDGE   (B) CENTER   CS-40015
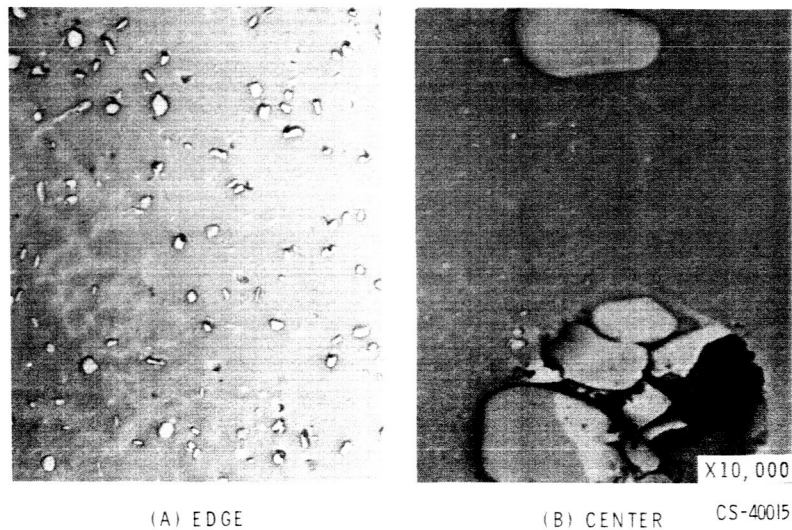
SINTERED AT 2000° F FOR 2 HR WITH H_2 AND FOR 6 HR IN VACUUM.
ANNEALED AT 2000° F FOR 20 HR WITH H_2 AND FOR 4 HR IN VACUUM;
ALSO AT 2300° F FOR 32 HR IN VACUUM, AND AT 2560° F FOR 35 HR
IN VACUUM.

Figure 4. - Microstructure of edge and center of 1/4" thick Ni − 5 v/o Al_2O_3 partially
cleaned and annealed coin.
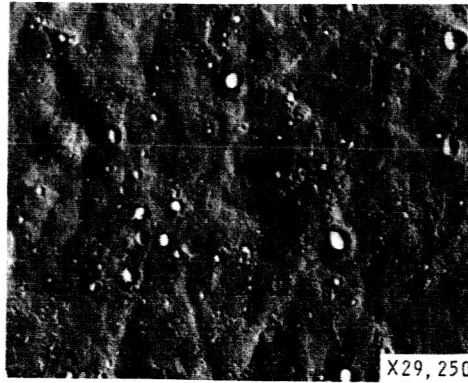
X29,250   CS-40013

STRESS RELIEF ANNEALED AT 1600° F FOR
1 HR IN VACUUM.

Figure 5. - As blended and cold compacted Ni + 5 v/o Al_2O_3
ball milled powder.
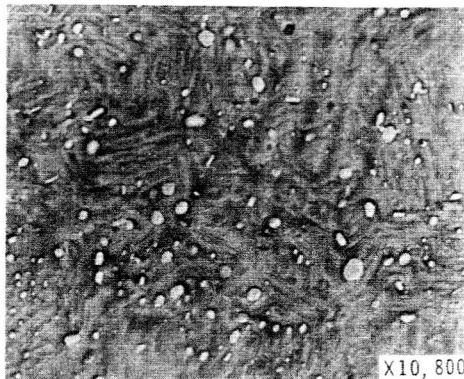
X29,250

(A) CLEANED AT 2000° F FOR 2 HR WITH H_2
AND FOR 6 HR IN VACUUM.

X10,800 CS-40018

X10,800

(B) CLEANED AT 2000° F FOR 2 HR WITH H_2
AND FOR 6 HR IN VACUUM. ANNEALED
AT 2000° F FOR 20 HR WITH H_2 AND FOR
4 HR IN VACUUM; ALSO AT 2300° F FOR
·24 HR WITH H_2.

(C) CLEANED AT 2000° F FOR 2 HR WITH H_2
AND FOR 6 HR IN VACUUM. ANNEALED
AT 2000° F FOR 20 HR WITH H_2 AND FOR
4 HR IN VACUUM; ALSO AT 2300° F FOR
11 HR WITH H_2; AND AT 2600° F FOR
11 HR WITH H_2.

Figure 6. - Microstructures of cleaned and annealed Ni + 5 v/o Al_2O_3 coins produced by wet method.
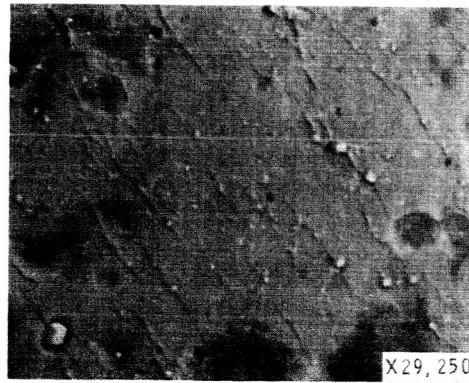
(A) CLEANED AT 2000° F FOR 2 HR WITH H₂ AND FOR 6 HR IN VACUUM.

CS-40017
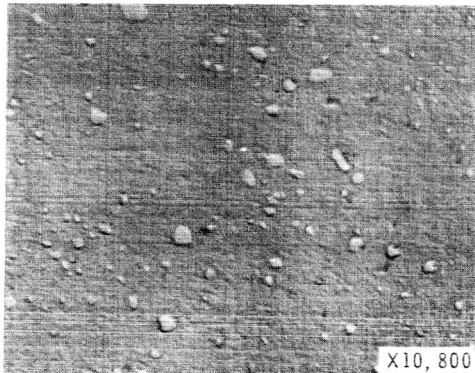
(B) CLEANED AT 2000° F FOR 2 HR WITH H₂ AND FOR 6 HR IN VACUUM. ANNEALED AT 2000° F FOR 20 HR WITH H₂ AND FOR 4 HR IN VACUUM; ALSO AT 2300° F FOR 24 HR WITH H₂.
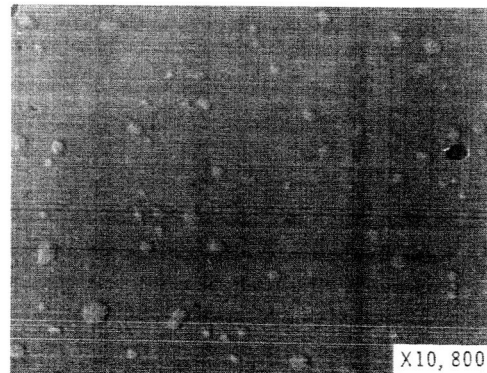
(C) CLEANED AT 2000° F FOR 2 HR WITH H₂ AND FOR 6 HR IN VACUUM. ANNEALED AT 2000° F FOR 20 HR WITH H₂ AND FOR 4 HR IN VACUUM; ALSO AT 2300° F FOR 11 HR WITH H₂, AND AT 2600° F FOR 11 HR WITH H₂.

Figure 7. - Microstructures of cleaned and annealed Ni + 5 v/o Al₂O₃ coins produced by dry method.

CS-40016
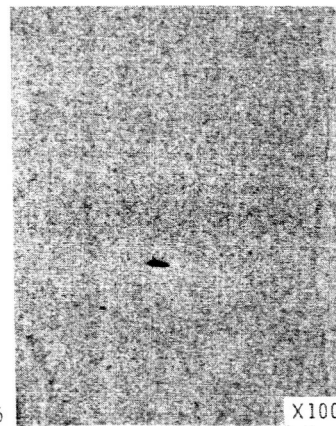
(A) PREPARED BY DRY METHOD

(B) PREPARED BY WET METHOD

CLEANED AT 2000° F FOR 2 HR WITH H₂ AND FOR 6 HR IN VACUUM. ANNEALED AT 2300° F FOR 24 HR WITH H₂.

Figure 8. - Low magnification microstructures of cleaned and annealed Ni + 5 v/o Al₂O₃ coins produced by wet and dry methods.
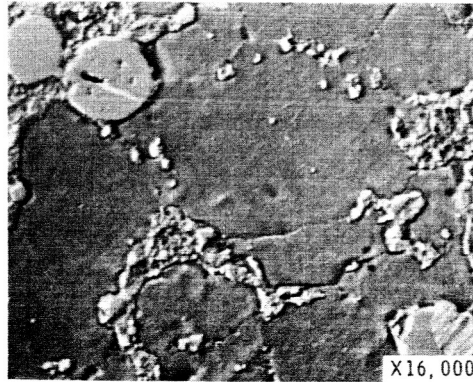
X16,000   CS-40010

CLEANED AT 1100° F FOR 80 HR WITH H$_2$.
SINTERED AT 1900° F FOR 5 HR WITH H$_2$.

Figure 9. - Microstructure of conventionally blended and
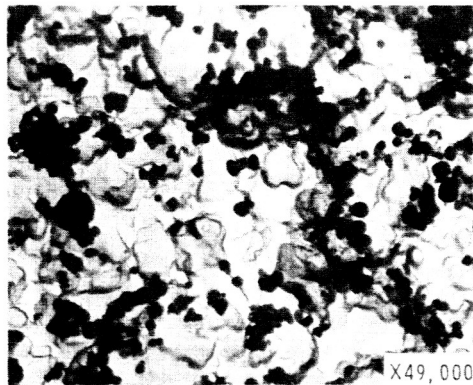cleaned Ni + 8 v/o Th O$_2$; initially contaminated with
0.25 percent sulfur.
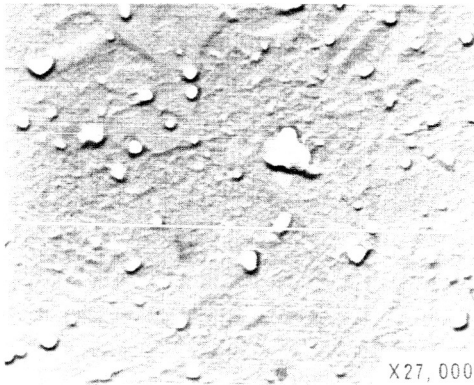
X27,000 CS-40020

(A) CLEANED AT 800° F FOR 2 HR WITH H$_2$;
ALSO AT 2300° F FOR 2 HR WITH H$_2$.
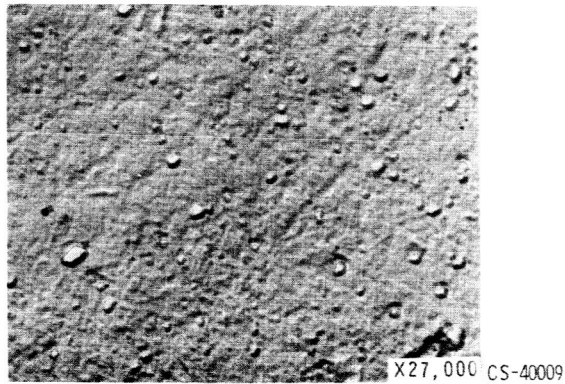ANNEALED AT 2300° F FOR 24 HR WITH H$_2$.
COMPACTED DRY.
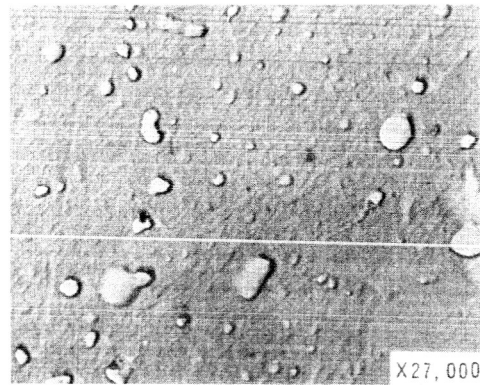
X27,000

(B) CLEANED AT 800° F FOR 2 HR WITH H$_2$;
ALSO AT 2300° F FOR 2 HR WITH H$_2$.
ANNEALED AT 2300° F FOR 24 HR WITH H$_2$.
COMPACTED WET.

X49,000

(C) CARBON REPLICA OF POWDER BLEND;
WITH Ni DISSOLVED SHOWING OXIDE
PARTICLES.

Figure 10. - Microstructures of cleaned and annealed Ni + 8 v/o Th O$_2$ coins; initially contaminated with 0.25
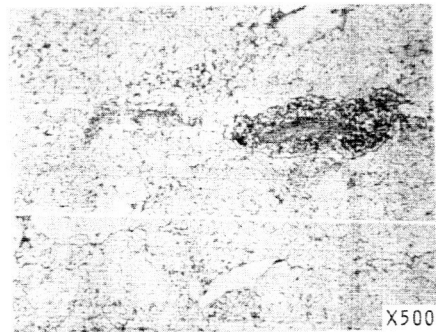percent sulfur.

PRE-CLEANED AT 800° F WITH H$_2$ TOWER FOR
3 DAYS. CONSOLIDATION OF COINS ~ 6700
PSI. CLEANED COINS TO 2000° F WITH H$_2$,
HELD 15-1/2 HR. ANNEALED AT 2300° F FOR
7 HR.

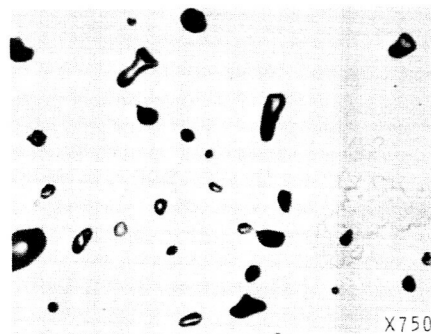Figure 11. - Microstructure of cleaned and annealed coins
of Ni + 5 v/o Th O$_2$.
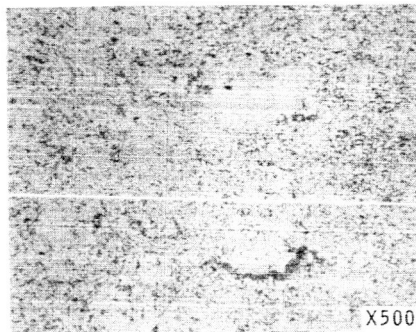
(A) COLD COMPACTED AS-RECEIVED.
PREALLOYED POWDER. ANNEALED 1
HR AT 1700° F.

B) COLD COMPACTED PREALLOYED
POWDER. ANNEALED 1 HR AT 1700° F.
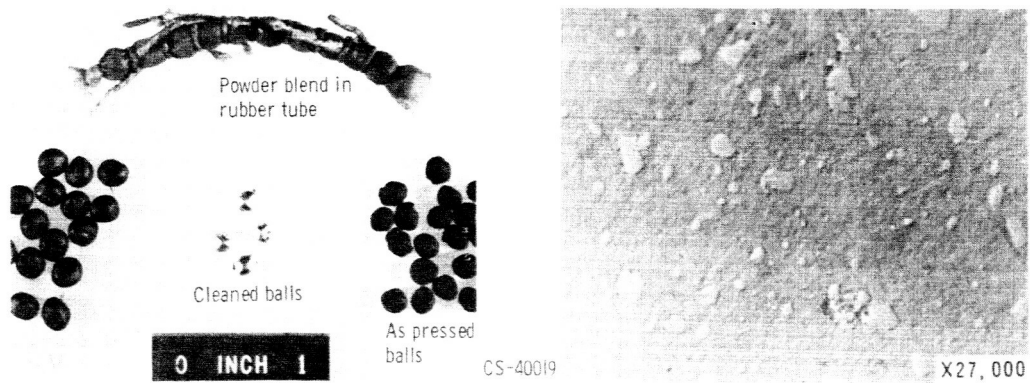CLEANED WITH H$_2$ FOR 96 HR AT 800° F.

(C) DRY COMPACTED PREALLOYED
POWDER COIN (1/8 IN. THICK).
CLEANED WITH H$_2$ AT 800° F FOR 2 HR
FOLLOWED BY 2 HR WITH H$_2$ AT 2300° F.

CS-40014

(D) DRY COMPACTED ELEMENTAL
POWDER COIN (1/8 IN. THICK).
CLEANED WITH H$_2$ AT 800° F FOR
2 HR FOLLOWED BY 2 HR WITH H$_2$
AT 2300° F.

Figure 12. - Microstructure of chromium bearing nickel alloy (55 Ni - 25 W - 20 Cr) cleaned after coining.

Powder blend in
rubber tube

Cleaned balls

As pressed
balls

0 INCH 1

CS-40019

X27,000

(A) PREPARATION OF COLD PRESSED AND
SINTERED BALLS.

(B) PHOTOMICROGRAPH OF CLEANED
Ni-Al$_2$O$_3$ BALL CLEANED AT 800^0 F
FOR 2 HR WITH H$_2$; ALSO AT 2300^0 F
FOR 2 HR WITH H$_2$.

Figure 13. - Application of cleaning method to hydrostatically pressed 1/4" Ni - 4 v/o Al$_2$O$_3$ balls made from powders.
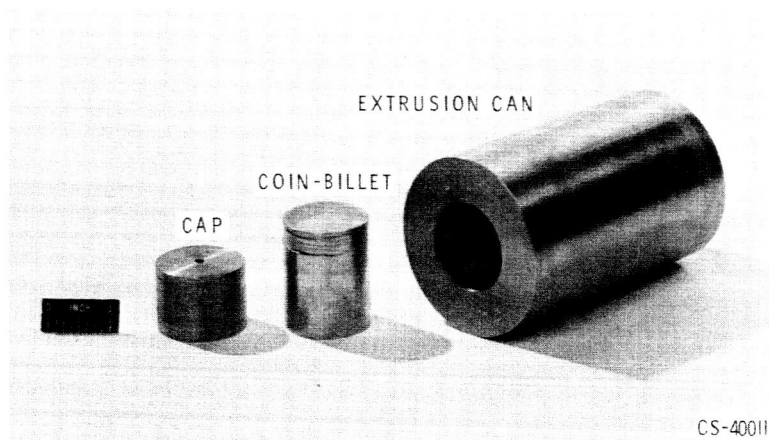

EXTRUSION CAN

COIN-BILLET

CAP

CS-40011

Figure 14. - Bonded and machined coins and extrusion can.