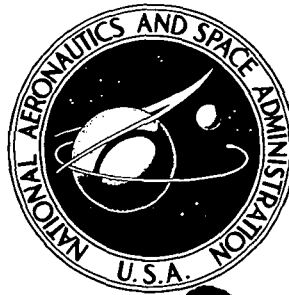


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**OXIDE DISPERSION STRENGTHENED NICKEL  
PRODUCED BY NONREACTIVE MILLING**

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16. Abstract It is shown that oxide dispersion strengthened alloys can be produced by a postulated nonreactive milling mechanism whereby the dispersoid is trapped at the interface between welding metal powder particles. This interparticle welding is possible because, without a suitable and sufficiently vigorous chemical reaction between the metal powder particles and the milling fluid, no protective, weld-preventing reaction coating is formed on these particles. Using water as the nonreactive milling fluid, Ni - 1.8-vol % thoria and Ni - 1.8-vol % yttria alloys with 1093° C tensile strengths ranging from 122.3 to 141.5 MN/m <sup>2</sup> (17 900 to 20 500 psi) were produced by nonreactive milling.			
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# OXIDE DISPERSION STRENGTHENED NICKEL PRODUCED BY NONREACTIVE MILLING

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## SUMMARY

This investigation has shown that oxide dispersion strengthened nickel alloys can be produced by a postulated nonreactive milling mechanism. Nickel - 1.8-volume-percent thoria and nickel - 1.8-volume-percent yttria powders were milled for 640 hours using water as the milling fluid; samples of powders after various milling times were examined by electron microscopy; the amounts of dispersoids taken up by the nickel as a function of milling time were determined; and the high-temperature strengths of the consolidated alloys were obtained.

The rate at which the yttria was kneaded into the nickel decreased with milling time; all the yttria was removed from the liquid in about 80 hours. Thoria was kneaded into the nickel at an approximately constant rate; all the thoria was removed from the liquid in about 145 hours. The milled powders were relatively coarse and nonpyrophoric. Micrographs showed them to be multilayered agglomerates of nickel lamellae welded together with the dispersoid trapped at the welded lamellar interfaces. For the nickel-yttria run, the thicknesses of the lamellae varied from about 0.5 to 0.06 micrometer after 46 and 640 hours milling time. Because lamellae stretch and become thinner with milling time, it is deduced that there is a minimum milling time required for optimum dispersoid distribution; this distribution cannot be improved by further milling.

Because of the nonreactivity of nickel with water, nickel powder cakes on nickel balls and mills due to welding. However, the protective oxide coating that forms on the stainless-steel balls and mill surfaces, by reaction with water, prevents welding to the nickel powder during milling.

The 1093° C ultimate tensile strengths of the ODS nickel alloys, about the same for nickel-thoria and nickel-yttria, range from 122.3 to 141.5 meganewtons per square meter. The 0.2 percent yield strengths range from 113.1 to 131.0 meganewtons per square meter, and the elongations at fracture from 2.7 to 5.0 percent. These values compare favorably with those reported in the literature for nickel - 1.8 volume percent thoria.

Micrographs of the consolidated alloys show dispersoid sizes and distributions that are comparable to those of the best ODS nickel alloys reported in the literature.

## INTRODUCTION

One of the most versatile methods for obtaining dispersion strengthened alloys is ball milling. Generally, it has been assumed that production of a good dispersion by ball milling required the use of a very fine dispersoid and ultrafine submicron size metal powders (refs. 1 to 4). In fact, oxide dispersion strengthened (ODS) nickel of excellent quality has been produced at NASA Lewis Research Center using the milling approach (refs. 2, 5, and 6). In these and other investigations, the use of extremely fine metal powders was deemed necessary because the interparticle spacing of the dispersoid was assumed to depend on metal particle size (as well as on dispersoid particle size). This assumption implies that the ground ultrafine powders used were mixtures of loose dispersoid and metal particles. These ultrafine powders are usually pyrophoric and hazardous to health. Therefore, they usually require handling in an inert atmosphere enclosure (dry box). In addition, these ultrafine powders may require special handling techniques to prevent the (assumed) shifting and subsequent agglomeration of the loose dispersoid during sintering (ref. 7). The assumption that ultrafine metal powders were required for dispersion strengthening by means of the milling approach has led to a number of investigations at NASA dealing with the milling of various metals potentially useful in dispersion strengthened alloys (refs. 3, 8, and 9). In one of these investigations (ref. 8) the present author has shown that extensive comminution of ductile metals into ultrafine powders requires the chemical reaction of the metal being milled with the milling fluid. Conversely, if no chemical reaction occurs, bare metal surfaces are created, and the metal particles weld to each other forming multilayered agglomerates of metal flakes. As a result of this work, it was theorized (ref. 8, p. 19) that, if a dispersoid were present in the milling fluid during this nonreactive milling, the dispersoid would be trapped at the interface between the metal particles being welded during milling and thereby produce an alloy powder containing a dispersed oxide. This powder could then be used either alone or mixed with other similarly produced dispersion strengthened metal powders to produce consolidated alloys by standard powder metallurgy techniques.

The objective of the present investigation was to show that dispersion strengthened metals can be produced by the postulated mechanism of nonreactive milling and to judge the relative merits of this process by analyzing the microstructures obtained and determining high-temperature tensile strengths. To meet this objective, nickel powder was ball milled with either thoria or yttria dispersoid powders using water as the milling fluid and helium as a cover gas; samples of the milled powders were examined by electron microscopy; and the amounts of dispersoid taken up by the milled nickel powder as a function of milling time were determined.

To allow comparisons with data for ODS nickel reported in the literature and to thereby determine the relative merits of the nonreactive milling approach, the ODS

nickel powders produced in the present investigation were consolidated by standard powder metallurgy techniques, the high-temperature tensile strength was determined, and electron micrographs were obtained.

## MATERIALS AND PROCEDURES

### Materials

The materials used in this investigation, nickel, thoria, yttria, and water, are listed and characterized in table I.

### Procedure for Obtaining Samples of Milled Powders and Dispersoids

The flow chart in figure 1 outlines the procedure used for obtaining samples of milled nickel and of the dispersoid remaining in the milling water at various milling times. A more detailed description of the procedure is given in this section.

Loading mills. - Gas tight, stainless-steel, 10-centimeter-inside-diameter mills provided with pressure gages and vacuum valves were loaded with about 3500 grams of 1.27- and 0.95-centimeter-diameter stainless-steel balls, 750 milliliters of distilled water, 368 grams of nickel powder, and 4.03 grams of yttria ( $Y_2O_3$ ). From previous milling experiments the pickup (material worn off the balls and mill) was estimated to be 28 grams; consequently, the total amount of milled material would be (nominally) 400 grams. This is equivalent to a nominal 1.0 weight percent or 1.8 volume percent yttria in the consolidated alloy. For the same reasons 364 grams of nickel powder and 8.0 grams of thoria ( $ThO_2$ ) were used in the Ni- $ThO_2$  run. This is equivalent to 2.0 weight percent or 1.8 volume percent thoria in the consolidated alloy.

After loading, the mills were evacuated, purged with helium, and then pressurized with helium to about 170.3 kilonewtons per square meter absolute (24.7 psia).

Milling and slurry sampling. - Milling was carried out at 100 rpm. At various milling times 5- to 10-gram samples of the nickel-dispersoid - water slurry were siphoned off the mill. The nickel was separated from the water-dispersoid mixture magnetically and washed with distilled water. Both the dispersoid and the nickel were separately dried and weighed to determine the amounts of dispersoid in the milling water.

Microscopic examination of milled nickel powder. - The samples of dry, milled nickel powder recovered from the slurry samples were used for electron microscopy examinations. The powder samples were mixed with liquid epoxy resin and hardener, and the resin was allowed to harden while in a magnetic field (fig. 2). This procedure was used both to align the powder and to concentrate it near the plane to be polished.

After polishing and etching the powder particles were examined by electron microscopy using the replication technique. In one powder sample the shell technique (ref. 10) was used to determine whether the dispersoid was kneaded into the milled nickel powder. This technique involves holding the powder particles between porous carbon films while the matrix metal is dissolved away with an acid; insoluble oxides are retained between the carbon films.

The specific surface areas of samples of milled nickel from the nickel-yttria run after 46 and 640 hours milling time were determined by the Brunauer, Emmett, and Teller (BET) method.

### Procedure for Making ODS Nickel Sheet

The flow chart in figure 3 outlines the procedure used for making ODS nickel sheet. Details of the procedure are given in this section.

Powder preparation. - The stainless-steel mills were loaded with the same amounts and sizes of stainless-steel balls as well as the same amounts of nickel, dispersoids, and water as described previously for obtaining slurry samples.

The powders were milled for 640 hours at 100 rpm. The mill pressures were monitored during the runs. At the end of the milling runs, the slurries were separated from the balls by sieving. Most of the water in the slurries was separated from the powders after decanting for about 10 minutes. The wet powder was then dried by heating at about 100° C while stirring it.

Hydrogen cleaning and sintering. - The dry nickel powders were placed in retorts (described in ref. 11) and cleaned at 350° C (662° F) in flowing hydrogen (~300 l/hr) to a dew point of -40° C. This required about 20 hours cleaning time. The retorts were transferred (still filled with H<sub>2</sub>) to a helium filled glove box and unloaded. The powders were then cold pressed into 7.5- by 2.5- by 1.9-centimeter (3- by 1- by 3/4-in.) slabs at 55.2 meganewtons per square meter (8000 psi). The slabs were incased in flexible plastic tubing and isostatically cold pressed at 483 meganewtons per square meter (70 000 psi). After removing the plastic tubing in the glove box, the slabs were placed in a retort and transferred to the hydrogen cleaning rig under helium. The slabs were sintered in flowing hydrogen (at ~300 l/hr) at 1125° C (2057° F) for about 3 hours to about 70 percent of their theoretical density. After cooling to ambient temperature, the retort was unloaded in air.

Hot working and thermomechanical processing. - The sintered slabs were placed in stainless-steel cans and the cans were then electron-beam welded. These canned slabs were then hot rolled, warm rolled, decanned, and cold rolled as follows: The canned slabs were hot rolled at 1038° C (1900° F). Total reduction was approximately 46 percent in three passes. The still canned slabs were then warm rolled at 760° C (1400° F)

at a 10 percent reduction per pass. Total reduction was approximately 78 percent. The warm rolled slabs were decanned, and the resulting strips surface ground to remove surface blemishes. The warm worked strips were annealed in hydrogen at 1205° C (2200° F) for 1/2 hour followed by a 10 percent reduction cold roll. The 1205° C, 1/2-hour anneal and 10 percent cold-roll cycles were continued with alternate straight and cross rolling passes for a total reduction of about 82 percent. The resulting sheets were about 0.025 centimeter (0.010 in.) thick.

Specimen preparation and testing. - Specimens having 1.27-centimeters (0.5-in.) gage length and 0.318-centimeter (0.125-in.) width were punched out of the as-cold-rolled sheet for tensile testing.

Tensile tests were carried out in vacuum at 1093° C (2000° F) at a crosshead speed of 0.025 centimeter per minute (0.010 in./min). The elongations of the specimens were determined from the stress-time recorder charts.

Part of the cold-rolled sheets were used to obtain electron micrographs and for chemical analysis for oxygen, carbon, and metallic elements presumably picked up from balls and mills.

#### Milling with Nickel Balls in Nickel-Lined Mill

Since it is known the nickel does not react with water during ball milling (ref. 8), the Ni-Y<sub>2</sub>O<sub>3</sub> run was repeated in a nickel lined mill loaded with nickel shot to demonstrate that the powder welds to the balls and mill surfaces unless these surfaces are protected by an oxide coating (such as that formed on stainless steel by its reaction with water during milling). To demonstrate this effect, 400 grams of nickel - 1.0-weight-percent yttria powder mixture was ball milled with 3500 grams of nickel shot (ranging in size from 1.27 to 0.3 cm in diam) and 750 milliliters of distilled water. The rest of the milling procedure was the same as that used for milling powders intended for making ODS nickel sheet, except that the milling was discontinued after 270 hours because about half of the powder had caked to the balls and mill walls and could not be scraped loose.

### RESULTS AND DISCUSSION

Analysis of slurry samples. - The data in figure 4 show that the amounts of residual dispersoid in the milling water decreases with milling time. This indicates that somehow the dispersoid is kneaded into the nickel powder during milling. The calculated amounts of dispersoid kneaded into the nickel as a function of milling time is also shown in figure 4. It may be noted that in the nickel-yttria run all the yttria is kneaded into the

nickel in about 80 hours and that the rate at which the yttria is kneaded into the nickel decreases with milling time. In the nickel-thoria run on the other hand, all the thoria was kneaded into the nickel after about 145 hours, and the rate at which the thoria was kneaded into the nickel was approximately constant.

The differences in kneading rates and in milling times required for complete removal of the dispersoid from the milling water are attributed to the fact that the thoria used in this study was observed to form a sol with water (hydrosol). This ability of thoria to form a hydrosol indicates electrical charges surrounding the particles. These charges tend to separate the particles not only from each other but also from other oxides such as those that normally coat the stainless-steel balls and mill surfaces. Thus, the thoria would be taken up by the nickel at a relatively slower rate than the yttria (which was observed not to form a hydrosol) and, consequently, would also remain longer than yttria in the milling water.

Microstructure of milled powders. - In figure 5 are shown electron micrographs of milled Ni-Y<sub>2</sub>O<sub>3</sub> powders at various milling times. As shown in this figure the milled powders are composed of welded nickel lamellae. Figure 6 shows the structure of milled Ni-Y<sub>2</sub>O<sub>3</sub> after 490 hours milling time at higher magnification than in figure 5. This micrograph clearly shows many nickel lamellae welded to each other but some fissures or pockets are visible.

The fact that the amounts of dispersoid remaining in the milling water decrease with milling time (fig. 4) indicates that the dispersoid is being trapped between welding nickel particles during ball milling. The presence of yttria, however, cannot be ascertained from the micrographs in figures 5 and 6, perhaps, because yttria is soluble in the (acid) etchant used to reveal the microstructure. However, other evidence shows that the dispersoid particles are indeed trapped within the agglomerates formed by the welded nickel lamellae (i. e., the milled powder particles). Thus, some thoria dispersoid particles are clearly visible in the micrograph of a powder particle from the Ni-ThO<sub>2</sub> run after milling time of 160 hours (fig. 7). In addition, in figure 8 are shown a very large number of thoria particles remaining after leaching the nickel out of a single agglomerate of milled powder from the Ni-ThO<sub>2</sub> run after 640 hours of milling time. Electron microscopy showed that these thoria particles (which appear as black or gray circles in fig. 8) range in size from 0.005 to 0.015 micrometer; this is also the electron microscopy size range of the original thoria powder. The micrograph shown in figure 8 was obtained by the "shell technique" (ref. 10).

The specific surface areas of milled Ni-Y<sub>2</sub>O<sub>3</sub> powders were 1.48 and 1.42 square meters per gram after 46 and 640 hours of milling time, respectively. However, from the micrographs shown in figure 5, it is calculated that the thicknesses of the lamellae decreased from about 0.5 to about 0.06 micrometer on going from 46 to 640 hours milling time. Since the size of the agglomerates remains approximately constant and the



thicknesses of the lamellae decrease, it follows that the agglomerates either break up or fold over and then reweld during ball milling.

Microstructure of cold rolled ODS nickel alloys. - Figures 9 and 10 are electron micrographs of consolidated and cold worked Ni - 1.8 volume percent  $\text{ThO}_2$  and Ni - 1.8 volume percent  $\text{Y}_2\text{O}_3$ . In these micrographs the dispersoid is clearly visible and well distributed, thus confirming that the dispersoid particles were trapped between welded lamellae during ball milling. The size and distribution of dispersoids in these micrographs are comparable to those of the best ODS nickel reported in the literature (refs. 2, 5, and 12).

Pressure increase during ball milling. - During both the Ni- $\text{ThO}_2$  and the Ni- $\text{Y}_2\text{O}_3$  runs, there was a pressure increase during milling. As shown in a previous investigation (ref. 8), this pressure increase was caused by the hydrogen released during the reaction between the water in the mill and the metal abraded off the stainless-steel balls and mills (pickup). Since this abrasion removes the protective oxide skin from balls and mill wall surfaces the water also reacts with these surfaces. Consequently, the oxide skin on these surfaces is continuously renewed. It is this oxide skin that prevents welding of the metal particles to the balls and mill walls, as was clearly demonstrated by the extensive welding that occurred on milling Ni- $\text{Y}_2\text{O}_3$  with nickel balls in a nickel lined mill. (See the experiment in Milling with Nickel Balls in Nickel Lined Mill section.)

The ball mill pressures as a function of milling time for both the Ni- $\text{ThO}_2$  and the Ni- $\text{Y}_2\text{O}_3$  runs are shown in figure 11. Note that the pressure increases were negligible up to about 190 hours milling time during the Ni- $\text{ThO}_2$  run and up to about 350 hours milling time during the Ni- $\text{Y}_2\text{O}_3$  run. The reason for the difference in the milling time required for significant hydrogen release is not clear; it may be due to the different abrading properties (i. e., shape and hardness) of the dispersoid and to its ability to armor (ref. 13) or loosely coat the balls and mill walls. Be that as it may, it is clear that, since hydrogen evolution is due to pickup formation, it should be possible to reduce this pickup by ball milling no longer than the time it takes for hydrogen evolution to become significant (knees of the curves in fig. 11). However, it is not known whether milling up to the knees in the curves would yield powders with dispersoid distributions suitable for making dispersion strengthened alloys.

Chemical analysis of cold-rolled ODS nickel alloys. - Table II lists the chemical analyses of the cold-rolled, ODS Ni- $\text{ThO}_2$  and Ni- $\text{Y}_2\text{O}_3$  alloys. The analyses show that during the Ni- $\text{ThO}_2$  run 6.51 weight percent iron and 1.42 weight percent chromium were picked up from the stainless-steel balls and mill; 3.1 weight percent iron and 2.58 weight percent chromium were picked up during the Ni- $\text{Y}_2\text{O}_3$  run. At present no explanation for the different iron-chromium ratios for the two runs is apparent.

The iron and chromium pickup shown in table II is of concern mainly because these metals may be undesirable for compounding into superalloys. However, the pickup may be limited to either iron or chromium by the simple expedient of milling with balls and

mills made from these metals. Since both iron and chromium oxidize in water, they should also form protective oxide coatings during ball milling in water. The possibility of reducing the pickup by milling up to the knees in the pressure-milling time curves has already been discussed.

The oxygen in excess of the calculated stoichiometric amount in the dispersoid is much smaller in the Ni-ThO<sub>2</sub> alloy (0.008 wt %) than in the Ni-Y<sub>2</sub>O<sub>3</sub> alloy (0.197 wt %). The excess oxygen does not appear to be detrimental either to the high-temperature tensile properties (table III) or to the dispersoid size and distribution in the alloys (figs. 9 and 10). Since the origin of this excess oxygen is not known, no suggestion can be made at this time on how to reduce it.

The carbon content of the alloys (40 and 56 ppm) was much smaller than the 989 ppm carbon in the starting nickel powder because of the hydrogen cleaning process.

High-temperature tensile properties of ODS nickel alloys. - The 1093<sup>o</sup> C (2000<sup>o</sup> F) ultimate tensile strength (UTS), 0.2-percent yield strength (YS), and percent elongation of the thermomechanically processed Ni - 1.8-volume-percent ThO<sub>2</sub> and Ni - 1.8-volume-percent Y<sub>2</sub>O<sub>3</sub> sheet are shown in table III. These properties are about the same for the Ni-ThO<sub>2</sub> and the Ni-Y<sub>2</sub>O<sub>3</sub> alloys. The UTS's range from 122.3 to 141.5 meganewtons per square meter (17 900 to 20 500 psi); the YS's range from 113.1 to 131.0 meganewtons per square meter (16 400 to 19 000 psi); and the elongations ranges from 2.7 to 5.0 percent. By comparison, a Fansteel brochure (ref. 12) giving properties of TD nickel shows a guaranteed 1093<sup>o</sup> C UTS minimum of 98 meganewtons per square meter (14 000 psi), typical UTS values of 112.0 to 126.0 meganewtons per square meter (16 000 to 18 000 psi), typical YS's of about 105 meganewtons per square meter (15 000 psi), and average elongations of about 6.5 percent.

The relatively high 1093<sup>o</sup> C tensile properties of the ODS alloys produced in this investigation can only be possible with a good dispersoid distribution. This further confirms that the dispersoid is indeed well kneaded into the nickel during the nonreactive milling.

Considering that only one milling time (640 hr), one method of cold rolling, and only an 82 percent cold reduction were carried out, the tensile properties indicated in table III may be amenable to further improvement by optimizing the processing variables. This optimization, however, is beyond the scope of the present investigation.

## MODEL FOR NONREACTIVE MILLING AND IMPLICATIONS

From the preceding RESULTS AND DISCUSSION, the nonreactive milling process is visualized as depicted in figure 12. Although in this figure the milling process is depicted as taking place in stages, it must be understood that the transition from one stage into the next is gradual.

During the initial ball milling stage, particles of the material being milled (Ni and dispersoid, in this case) are caught between the colliding and sliding balls and between the balls and mill walls. Thereby, the surfaces of the balls and mill walls become armored (ref. 13) with nickel and dispersoid particles (i. e., loosely attached to surfaces much like fish scales). During this armoring process, the nickel particles are flattened into flakes, and their surface area increases. Consequently, the original oxide skin coating the nickel particles is ruptured and bare nickel surfaces are created. Since these nickel flakes armor the balls and mill wall surfaces, the surfaces of these nickel flakes not only become themselves armored with the dispersoid during the sliding and colliding of the balls, but they weld to other similarly flattened nickel particles armoring other balls. Hence, the dispersoid armoring the nickel particles becomes trapped between the welding surfaces. This is the reason that the dispersoid is gradually removed from the milling water, as already discussed.

During the intermediate milling stage, the welding nickel particles become agglomerates of multilayered nickel lamellae, while flattening of nickel into flakes and imbedding of dispersoid between welding particles continues. Concurrent with the build up into multilayered agglomerates, the agglomerates themselves become flattened so that the lamellae become thinner; hence, the still unwelded portions of interlamellar surfaces become stretched and create new bare metal surfaces, which in turn weld to each other "in situ" and make the agglomerate stronger.

The build up into ever larger agglomerates of thin nickel lamellae can not go on indefinitely. After the agglomerates reach a large enough size, they are knocked off the balls. The agglomerates may also break up or bend over and reweld. Hence, an equilibrium agglomerate size is eventually reached during the milling process. Considering that the specific surface areas of the Ni-Y<sub>2</sub>O<sub>3</sub> powder are about the same after 46 and 640 hours milling time, the equilibrium agglomerate size is apparently reached early in the milling process in this system.

During this intermediate milling stage in the Ni-Y<sub>2</sub>O<sub>3</sub> system, the rate at which the dispersoid is kneaded into the nickel decreases as milling time increases, as already discussed. Hence, the interfaces between the nickel particles welded early in the milling process will have more dispersoid per unit area than those interfaces formed later on in the process just before the dispersoid in the milling water is exhausted. This suggests that the dispersoid could be more evenly distributed between the early and late formed interfaces either by adding the dispersoid gradually during ball milling or by diluting the dispersoid in the original milling water (i. e., using more milling water).

During the final milling stage, after the dispersoid in the milling water is exhausted, break up and rewelding of agglomerates continues. Now, since the lamellae become thinner with milling time, as already discussed, the dispersoid becomes better distributed in the agglomerates as milling time continues. The reason for this improved dispersoid distribution is that, since the lamellae are flattened and also become thinner,

the dispersoid particles trapped at the welded lamellar interfaces become closer to each other in the direction normal to the interfaces and more separated from each other in the interfacial planes. From this it follows that, at a certain time during the milling process, the average dispersoid interparticle distance in a direction normal to the lamellar interface will be the same as the average dispersoid interparticle distance along a randomly chosen straight line in the plane of the lamellar interface; hence, an optimum dispersoid distribution results. From the formula for the nearest neighbor distance between randomly distributed dispersoid particles (ref. 14), it is deduced that the lamellar thickness  $t_l$  for optimum dispersoid distribution is given by

$$t_l = \frac{D}{F_v^{1/3}}$$

where  $D$  is the average diameter of the dispersoid particles (in cm) and  $F_v$  is the volume fraction of dispersoid. In this investigation  $D \cong 0.01 \times 10^{-4}$  and  $F_v = 0.018$ , from which we obtain  $t_l = 0.038$  micrometer. This value of  $t_l$  is smaller than the 0.06 micrometer, lamellar thickness estimated for Ni - 1.8-volume-percent  $Y_2O_3$  in this investigation; obviously the theoretical, optimum dispersoid distribution was not achieved. It follows from this discussion that there must be a minimum milling time beyond which no further improvement in dispersoid distribution is possible.

#### COMPARISON OF REACTIVE MILLING, NONREACTIVE MILLING, AND MECHANICAL ALLOYING

Reactive and nonreactive as applied to ball milling are relative terms. A given metal powder-milling fluid system should not be classified as reactive just because a relatively mild reaction occurs if, despite this reaction, the milling process yields milled powders that are equivalent to those obtained by a completely nonreactive milling process. Hence, it is necessary to establish a criterion for distinguishing these two types of milling, based on the differences between them.

Reactive milling is characterized by the following distinguishing features:

- (1) The metal powders react (relatively) extensively with the milling fluid during milling.
- (2) The metal powder is extensively comminuted; that is, it is much smaller than the starting powder.
- (3) If balls and mills are the same metal as the powder, this powder does not weld to them during milling.

Thus, for instance, nickel milled in carbon tetrachloride (ref. 15) or stainless-steel powder milled in water (ref. 8) clearly fall in this category.

In contrast, nonreactive milling is characterized by the following features:

(1) The metal powder either reacts (relatively) mildly or not at all with the milling fluid during milling.

(2) The powder particles weld to each other extensively during ball milling.

(3) If balls and mill are the same metal as the powder, this powder welds extensively to the balls and mill during milling.

Thus, for instance, besides the system used in the present investigation, nickel milled in n-heptane, benzene, and either methyl or ethyl alcohols (ref. 15) have all these features and, hence, can be properly classified as nonreactive milling systems.

With these considerations in mind, the main practical criterion for distinguishing reactive from nonreactive milling is whether balls and mills of the same metal as the powder weld to this powder during milling. It stands to reason that, if the metal powder reacts with the milling fluid so extensively that the reaction products prevent welding of the powder to balls and mill (of the same metal as the powder) then these reaction products will also prevent interparticle welding; by definition, this is reactive milling. Conversely, if the chemical reaction is so mild or of such a nature that extensive welding of the powder to balls and mill occurs during milling then interparticle welding will also occur; by definition, this is nonreactive milling.

During nonreactive milling, welding of powders to balls and mills may occur even if they are a different metal than the powder. This welding may be minimized or eliminated by selecting a milling fluid that forms a protective reaction coating on the balls and mill but reacts mildly or not at all with the powders being milled. This technique has been applied to advantage not only in the present investigation but also in one modification of the so-called mechanical alloying milling process.

The term "mechanical alloying" is applied either to dry milling in a stagnant air atmosphere in a gas-tight mill (ref. 16) or to milling in a flowing atmosphere of nitrogen with about 3.4 volume percent oxygen (ref. 17). The second of these practices apparently provides a controlled and relatively mild reaction rate that allows interparticle welding while preventing excessive welding of the powder charge to balls and mill walls. In addition, most of the micrographs in reference 16 depicting powders made by "mechanical alloying" are quite similar to micrographs of milled powders (Cu, Ag, Ni) produced by the nonreactive milling approach (but without dispersoids) in a previous investigation by the present author (ref. 8).

Thus, reactive and nonreactive milling categories include both wet and dry milling. A milling process can be wet and reactive (as, e. g., Ni milled in carbon tetrachloride), wet and nonreactive (Ni milled in water), dry and reactive (Cr milled in iodine vapor), and dry and nonreactive (Cr milled in vacuum or Ar; ref. 8, p. 20).

## SUMMARY OF RESULTS

This investigation was conducted to show that oxide dispersion strengthened (ODS) alloys can be produced by a postulated mechanism designated as nonreactive milling and to judge the relative merits of the process by analyzing their microstructures and determining their high-temperature tensile strengths. In this study, nickel powder with 1.8 volume percent of either thoria or yttria powders were ball milled in water for up to 640 hours and the following results were obtained:

1. The amounts of dispersoid kneaded into the nickel powder increased with ball milling time. In the nickel-yttria run the rate at which the yttria was kneaded into the nickel decreased with milling time, and all the yttria was removed from the liquid in about 80 hours. In the nickel-thoria run the thoria was kneaded into the nickel at an approximately constant rate, and all the thoria was removed from the liquid in about 145 hours of milling time.

2. Electron micrographs of the cross sections of the milled nickel powder particles showed them to be composed of a large number of very thin nickel lamellae welded together. In the case of the nickel - 1.8-volume-percent yttria milled powder, the thicknesses of the lamellae were about 0.5 and 0.06 micrometer after 46 and 640 hours milling time, respectively.

3. The milled ODS nickel powders are relatively coarse and nonpyrophoric, and they can be handled in air after milling.

4. When milled with nickel balls in a nickel lined mill, the nickel powder welds to the balls and mill liner. This does not happen on milling with stainless-steel balls in a stainless-steel mill because the oxides resulting from the reaction of the stainless steel with water coat the balls and mill and prevent the welding of the nickel powder to them.

5. Electron micrographs of the consolidated ODS nickel show dispersoid sizes and dispersoid distributions that are comparable to those of the best ODS nickel alloys with about the same amounts of dispersoids reported in the literature.

6. The 1093<sup>o</sup> C (2000<sup>o</sup> F) ultimate tensile strengths of the ODS nickel alloys are about the same for the nickel - 1.8-volume-percent thoria and the nickel - 1.8-volume-percent yttria and range from 122.3 to 141.5 meganewtons per square meter (17 900 to 20 500 psi). The 0.2-percent yield strengths range from 113.1 to 131.0 meganewtons per square meter (16 400 to 19 000 psi). And the elongations range from 2.7 to 5.0 percent. These values compare favorably with those reported in the literature for nickel - 1.8-volume-percent thoria (16 000 to 18 000 psi UTS at 1093<sup>o</sup> C (2000<sup>o</sup> F)).

## CONCLUSIONS

From the results of the present investigation the following conclusions can be drawn:

1. The observed milling mechanism whereby oxide dispersoid particles are trapped at the interface between welding nickel particles confirm the assumed nonreactive milling theory.

2. The insight into the milling mechanism gained from the results of the present investigation may lead to improvements in dispersion strengthened alloys made by milling. Thus, for instance, it is surmised that adding the dispersoid gradually during milling or increasing the relative amounts of liquid used could lead to a better distribution of the dispersoid.

3. From considerations based on the fact that the lamellae making up the milled particles become progressively thinner with milling time, it is deduced that during nonreactive milling there is a minimum milling time required to obtain optimum dispersoid distribution; this dispersoid distribution cannot be improved by further milling.

4. The ODS nickel powders made by the methods of this investigation should be suitable for compounding into ODS superalloys.

5. Since only nickel powder, dispersoids, and water are used and since the ball mills can run unattended for long periods of time, the nonreactive milling process is considered to be an economical and simple process for making ODS nickel.

6. Since water is used for milling and the milled powders are relatively coarse, the process used in this investigation is considered safer than other methods using fine powders for producing ODS nickel.

7. Consolidation and thermomechanical processing of ODS nickel powders made by nonreactive milling yield ODS nickel alloys with excellent high-temperature tensile properties. It is believed that even further improvements are possible by optimizing the processing variables.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, September 30, 1975,  
505-01.

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TABLE I. - RAW MATERIALS

Material	Form and size	Source	Manufacturer specifications or chemical analysis
Nickel	Powder; specific surface area, 0.37 m <sup>2</sup> /g (1.2 μm)	International Nickel Co.	Purity, 99.7%; analysis - 0.170 wt % oxygen, 980 ppm carbon, 80 ppm iron
Thoria	Colloidal powder; 0.005 to 0.015 μm	Thorium Ltd.	Purity, 99.9%; analysis - 100 ppm sulfur, 350 ppm (max) calcium, 10 ppm iron, 60 ppm (max) silicon, and 100 ppm (max) sodium
Ytria	Powder; specific surface area, 70 m <sup>2</sup> /g (0.0113 μm)	Research Chemicals	Spectrographic analysis - 5.8 wt % aluminum, 0.13 wt % nickel, 0.04 wt % iron, 0.04 wt % silicon
Water	Liquid	Lewis	Distilled

TABLE II. - CHEMICAL ANALYSES OF COLD ROLLED, ODS NICKEL SHEET

[Made from powders milled for 640 hr.]

Nominal composition	Amount of dispersoid originally added, wt %	Chemical analysis				Oxygen in excess of that in dispersoid, wt %
		Oxygen, wt %	Carbon, ppm	Iron, wt %	Chromium, wt %	
Ni - 1.8-vol % ThO <sub>2</sub>	2.0-ThO <sub>2</sub>	0.234	40	6.51	1.42	0.008
Ni - 1.8-vol % Y <sub>2</sub> O <sub>3</sub>	1.0-Y <sub>2</sub> O <sub>3</sub>	.426	56	3.1	2.38	.197

TABLE III. - 1093° C (2000° F) TENSILE PROPERTIES OF ODS NICKEL SHEET

Nominal composition	Ultimate tensile strength		0.2-Percent yield strength		Elongation, percent	Figure number of electron micrograph
	MN/m <sup>2</sup>	psi	MN/m <sup>2</sup>	psi		
Ni - 1.8-vol % ThO <sub>2</sub>	141.5	20 520	131.0	19 000	3.7	} 9
	124.1	18 000	113.1	16 400	5.0	
	122.3	17 940	118.6	17 200	3.9	
Ni - 1.8-vol % Y <sub>2</sub> O <sub>3</sub>	136.5	19 800	126.2	18 300	3.8	} 10
	136.0	19 720	124.5	18 050	2.9	
	136.0	19 720	121.8	17 670	2.8	
	124.8	18 100	116.2	16 850	2.7	

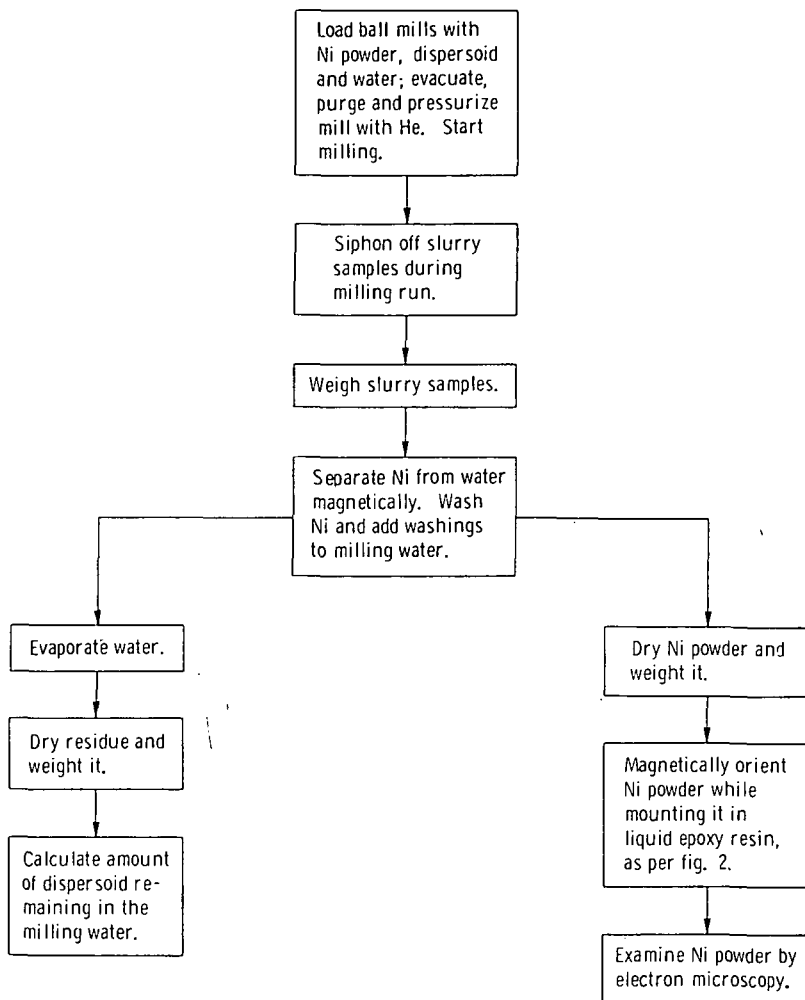


Figure 1. - Flow chart for obtaining nickel powder and free dispersoid samples during ball milling.

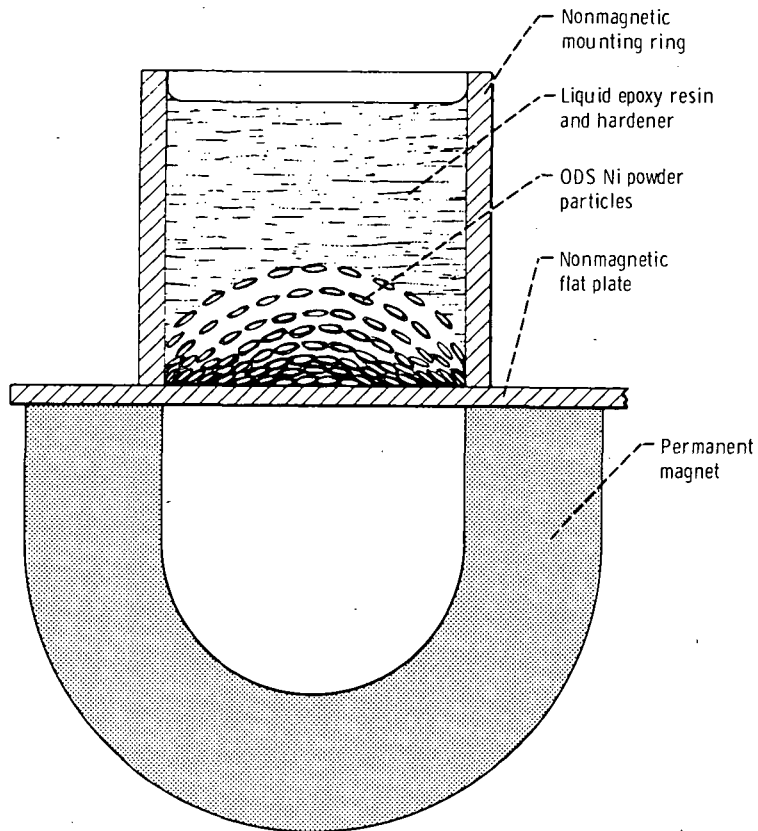


Figure 2. - Method of mounting ODS nickel powder for microscopic examination.

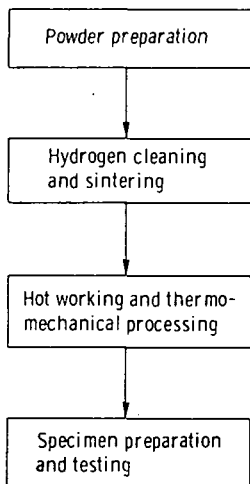


Figure 3. - Flow chart for making ODS nickel sheet.

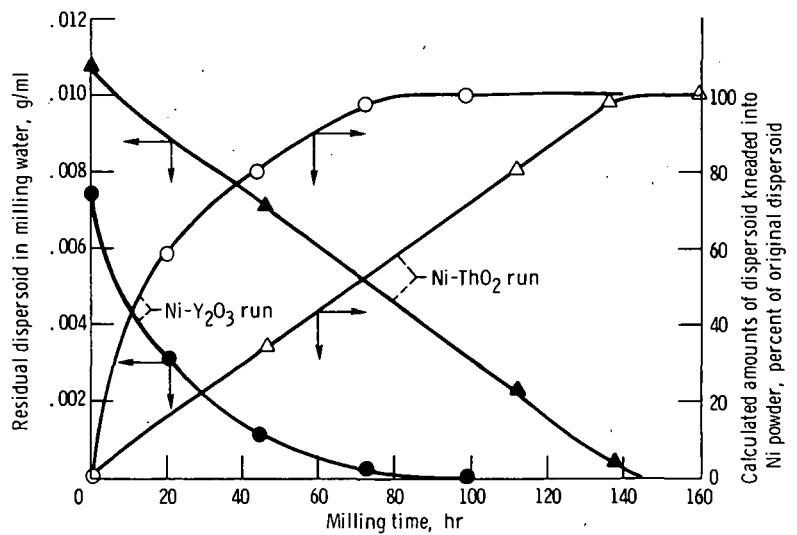
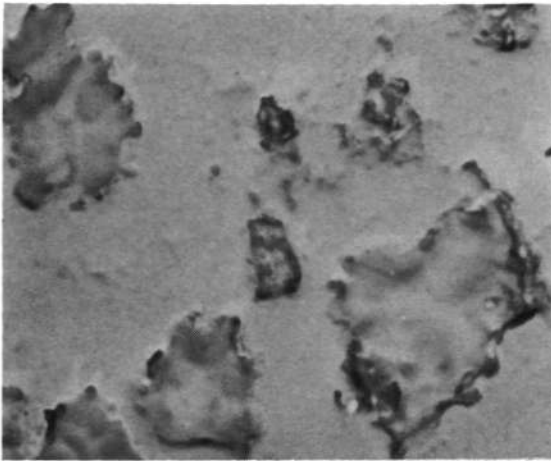
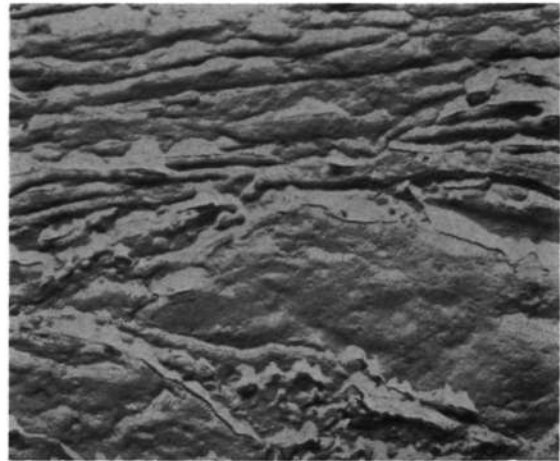


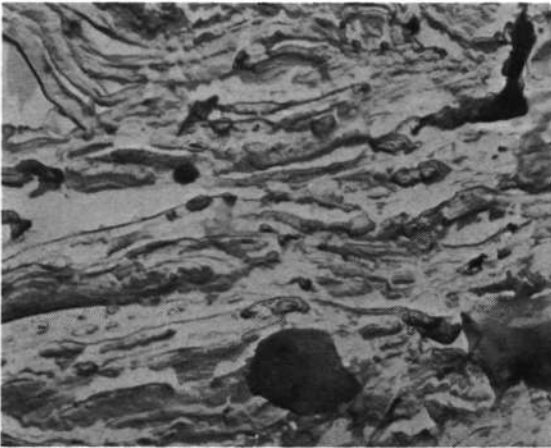
Figure 4. - Residual amounts of dispersoid (ThO<sub>2</sub> or Y<sub>2</sub>O<sub>3</sub>) in milling water and calculated amounts of dispersoid kneaded into nickel powder as function of milling time.



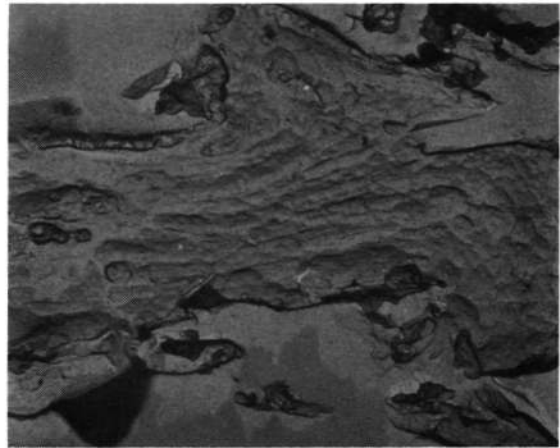
(Raw nickel powder) not milled



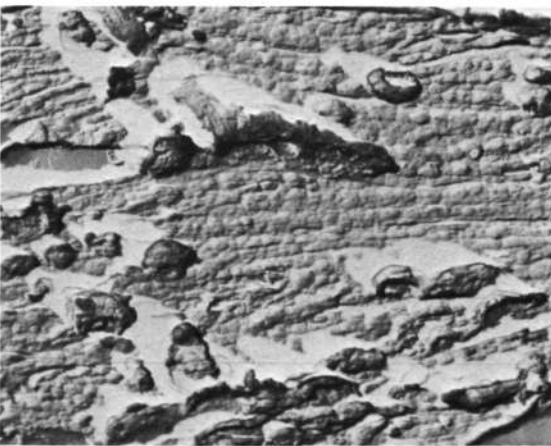
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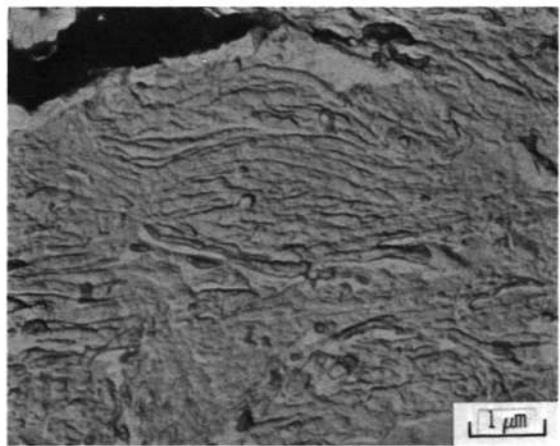
120 hr



340 hr



490 hr



640 hr

Figure 5. - Replica electron photomicrograph of Ni - 1.8 -vol%  $Y_2O_3$  powder after milling times indicated.

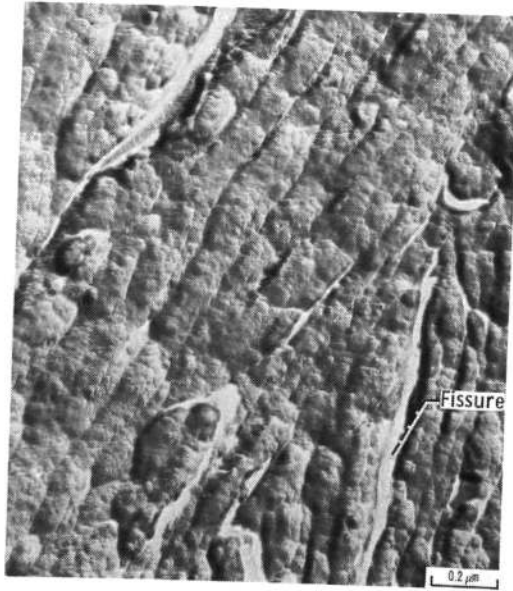


Figure 6. - Microstructure of Ni - 1.8 - vol%  $Y_2O_3$  powder after milling 490 hours in water.

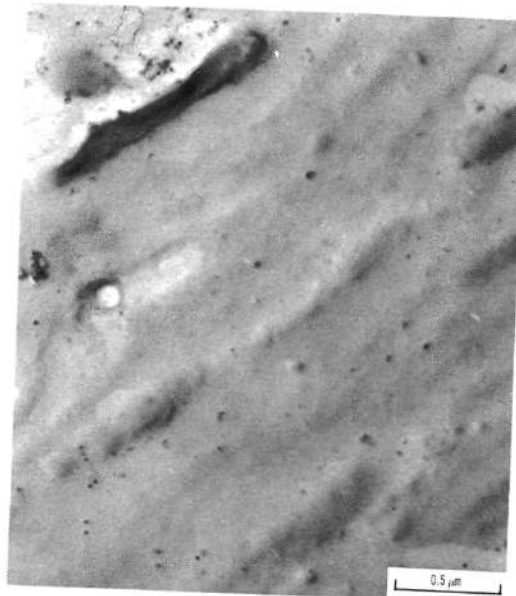


Figure 7. - Microstructure of Ni - 1.8 - vol%  $ThO_2$  powder after milling 160 hours in water.

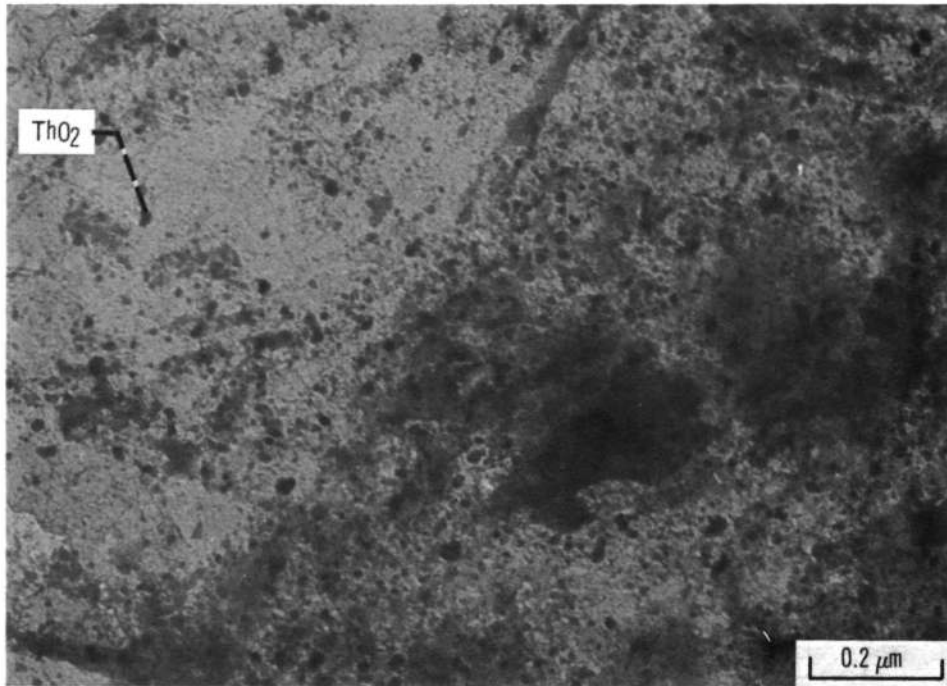


Figure 8. - Ni - 1.8 -vol% ThO<sub>2</sub> powder milled 640 hours in water showing distribution of ThO<sub>2</sub> after leaching nickel by shell technique (ref. 10).

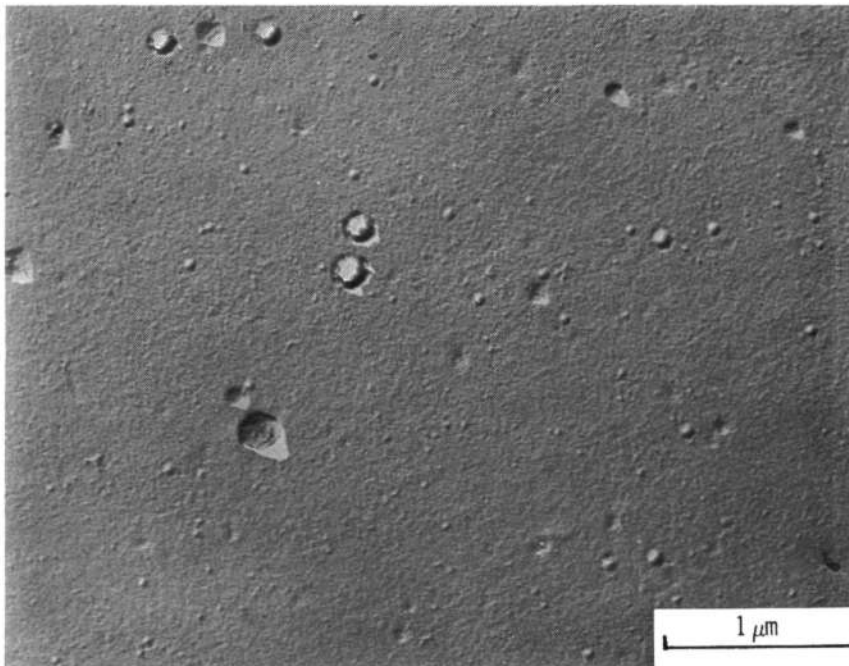


Figure 9. - Replica electron photomicrograph of Ni - 1.8 -vol% ThO<sub>2</sub> after cold rolling.

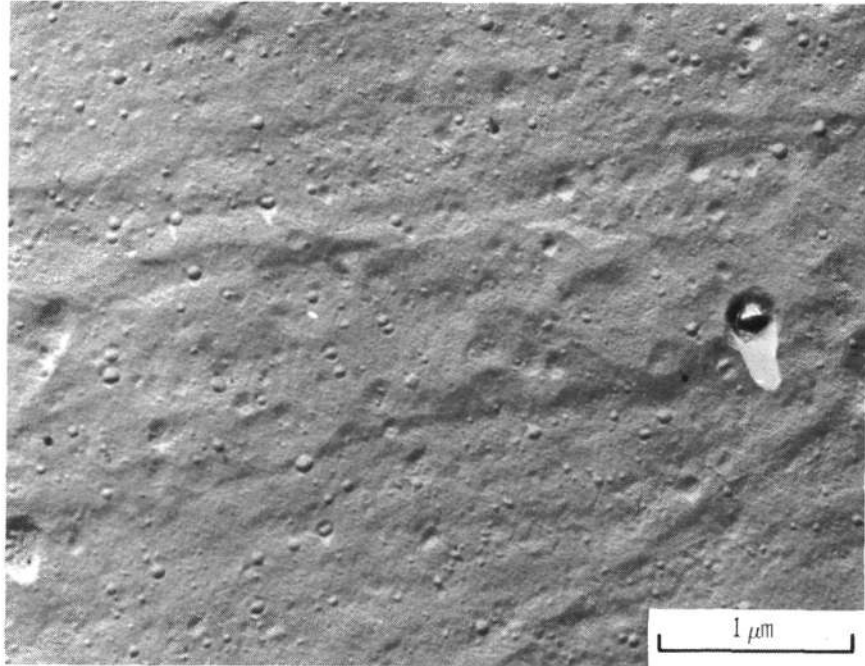


Figure 10. - Replica electron photomicrograph of Ni - 1.8 -vol%  $Y_2O_3$  after cold rolling.

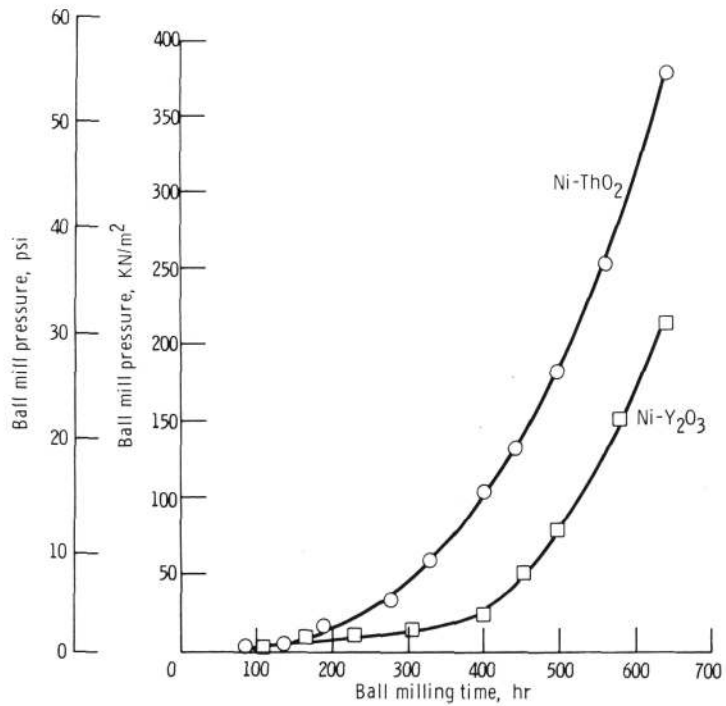
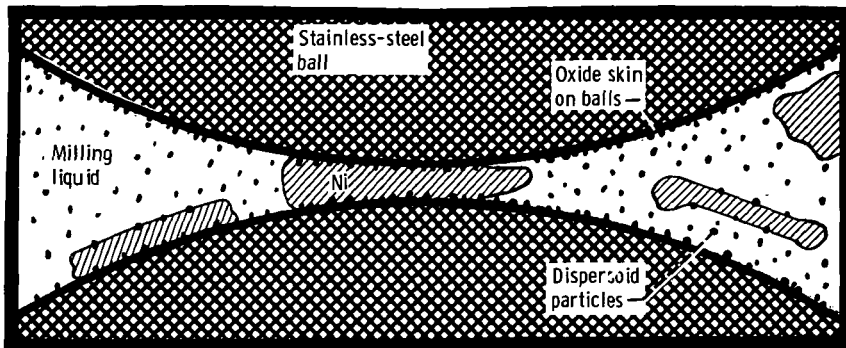
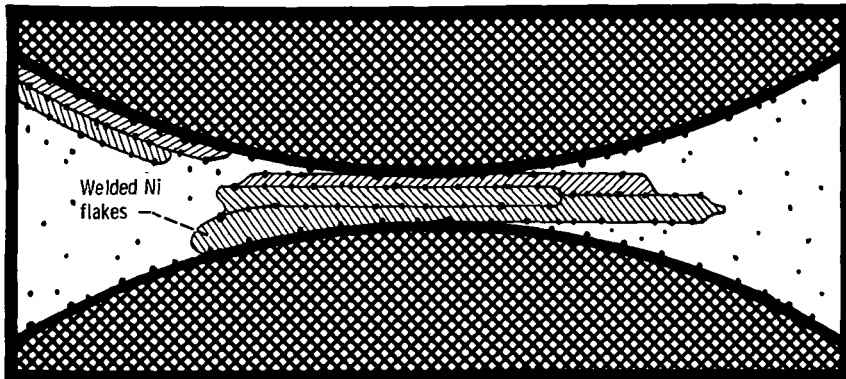


Figure 11. - Ball mill pressure as function of milling time.

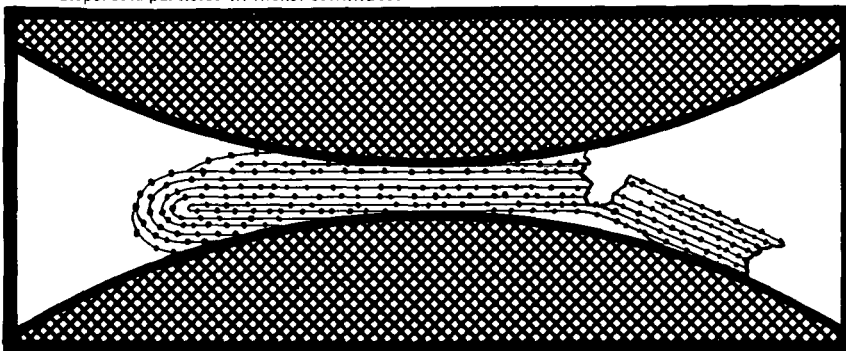




(a) Initial milling stage: nickel flattened into flakes; dispersoid imbedded in nickel particles.



(b) Intermediate milling stage: nickel flake formation continues; flakes weld; imbedding of dispersoid particles in nickel continues.



(c) Final milling stage: multilayered nickel flakes fold and/or break and reweld; all dispersoid kneaded into milled powder.

Figure 12. - Pictorial representation of nonreactive milling process. Both nickel and dispersoid particles are much smaller than shown in figures, in relation to ball sizes.



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