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SUMMARY

Until now no really conclusive comparison of blending methods for submicron powders had been made because agglomeration of dispersoid particles during the cleaning and consolidation steps subsequent to blending could alter the structure of the blend before it could be examined. In this investigation, a newly developed cartridge-actuated press was used to compact blended powder specimens to densities adequate for examination with the electron microscope while avoiding agglomeration due to prolonged heating at high temperatures. An automatic film scanner developed specifically for lineal analysis of dispersion microstructures was used to obtain microstructural parameters that were based on much more extensive and intensive examination than had previously been feasible.

Blends consisting of 0.054-micron nickel powder with 5.4-volume-percent 0.025-micron aluminum oxide were prepared by various wet and dry methods. Wet blending methods proved to be superior to dry methods and yielded interparticle spacings as small as 0.96 micron (mean free path). This result was only twice as large as that predicted for an ideal random mixture of the powders, which indicated a high efficiency of blending. The results obtained indicate that high-efficiency blending methods for submicron powders have been developed that can give interparticle spacings in the range desired for dispersion-strengthened alloys.

INTRODUCTION

The increased operating temperatures in advanced aerospace propulsion systems now under development require materials for prolonged service at temperatures close to their melting points. Dispersion strengthening of metals and alloys is a promising means of obtaining the required high strengths at service temperatures. The microstructure of an ideal dispersion-strengthened material is characterized by a uniform distribution of fine dispersoid particles in a metal or alloy matrix. Particle sizes of a few hundredths of a micron and interparticle spacings of less than 1 micron are desired. One of the processing procedures most widely investigated to obtain these microstructural parameters has been mechanical mixing of the metal and dispersoid powders with subsequent consolidation by standard powder-metallurgy techniques (ref. 1). Many of the early investigators recognized that extremely fine starting powders were required to achieve the desired microstructural parameters, and oxide powders of submicron particle size were used. However, submicron metal powders were not generally available, and thus powders in the 1- to 10-micron size were used in experimental studies of blending. In an investigation by Cremens and Grant (ref. 2), various wet and dry blending methods including tumbling with and without baffles, ball milling, and agitation in a Waring Blendor were studied. After examination of the structures of sintered and extruded specimens, it was concluded that dry methods were generally better than wet methods, and that the Waring Blendor was the most effective apparatus. Subsequently, Bonis and Grant (ref. 3) indicated that further improvement resulted from exposure during blending to a source of radioactivity to reduce electrostatic attraction between particles.

An equation relating the minimum achievable interparticle spacing to the volume fraction of oxide and to the initial powder sizes was derived by Cremens (ref. 4). The equation, which is also equation (4) of the present paper, shows that it is essential to use submicron metal as well as submicron oxide powder to achieve an interparticle spacing of 1 micron or less. Predicted minimum interparticle spacing would be realized, however, only if perfect blending of the matrix and dispersoid powders were accomplished. With less than perfect blending, interparticle spacing larger than the predicted value would result. Thus, achievement of the desired microstructural parameters in the final product depends strongly on the efficiency of the blending step even if submicron starting powders are used.

Methods of grinding metal powders to submicron dimensions by ball milling were developed by Quatinetz, Schafer, and Smeal (ref. 5) by using liquid media containing various grinding aids. Several manufacturers have developed other processes for the production of metal powders in particle sizes smaller than 0.1 micron.

Using a high-speed mixer to dry blend submicron powders (0.02 micron nickel and 0.02-micron aluminum oxide), Nelson, Zwilsky, and Grant (ref. 6) found that the blends were not adequately dispersed. Preliminary experiments at the Lewis Research Center also indicated that consolidated blends made with submicron metal and submicron oxide often resulted in poorer dispersions than those made with 1- to 5-micron metal powders. Thus, it became evident that the problem of blending submicron powders could not be readily solved by existing methods, and further blending studies were undertaken.

Because of the submicron dimensions of the oxide dispersoid particles, direct observation of the microstructure requires electron microscopy. Until recently, the usual practice was to consolidate blended powder samples by application of both heat and pressure (cold pressing and sintering, or hot pressing) in order to obtain a specimen sufficiently dense for examination with an electron microscope. If the resulting microstructure exhibited coarse particles nonuniformly distributed, it was impossible to determine whether the blending of starting powders had been inadequate or whether a satisfactory blend had been achieved and then subsequently lost during the consolidation process.

The development of high-energy-rate cold-compaction methods has made possible the preparation of small, dense specimens in an essentially as-blended condition suitable for examination by electron microscopy. The cartridge-actuated compaction press used at Lewis for this purpose has been described in detail by Reinhardt, Cremens, and Weeton (ref. 7). With this device, the oxide distribution present at the end of the blending process is "locked" in place without prolonged heat treatment. The efficiency of the blending process can then be judged by examination of electron micrographs prepared from the compacted specimens.

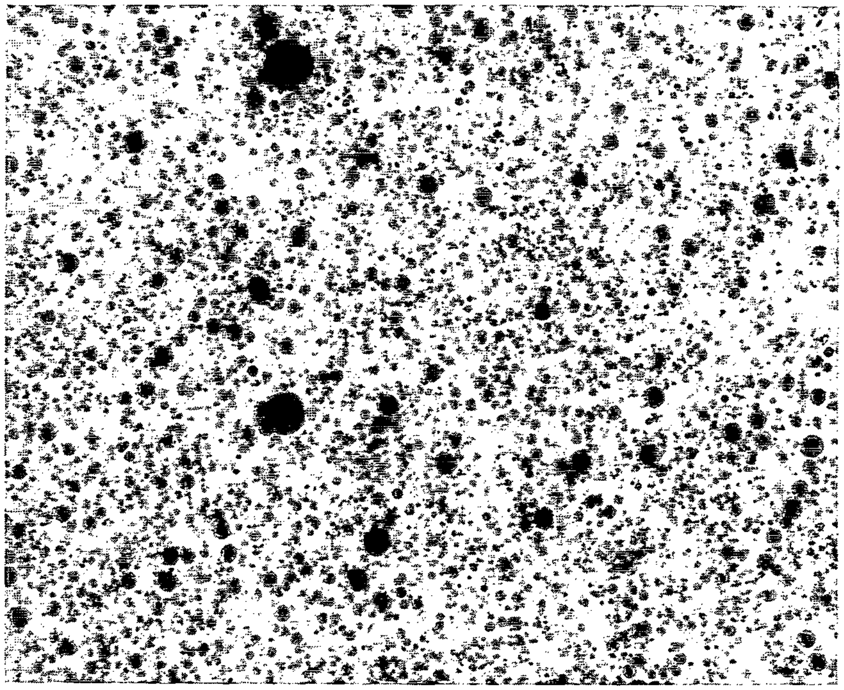
The present study was conducted to compare various blending techniques by examination of the blend microstructures. Blends of submicron nickel and submicron aluminum oxide (alumina) powders were prepared by various wet- and dry-blending methods, consolidated in a cartridge-actuated compaction press, and examined by optical and electron microscopy. The following blending methods were employed: wet milling, homogenizing a slurry in a colloid mill, dry milling, and dry blending in a Patterson-Kelly Twin-Shell V-Blender and in a Waring Blendor. All blend microstructures were compared qualitatively; quantitative evaluation was made of selected microstructures on the basis of average interparticle spacing and average dispersoid particle size. These results gave an indication of the relative efficiencies of the blending methods.

MATERIALS AND PROCEDURES

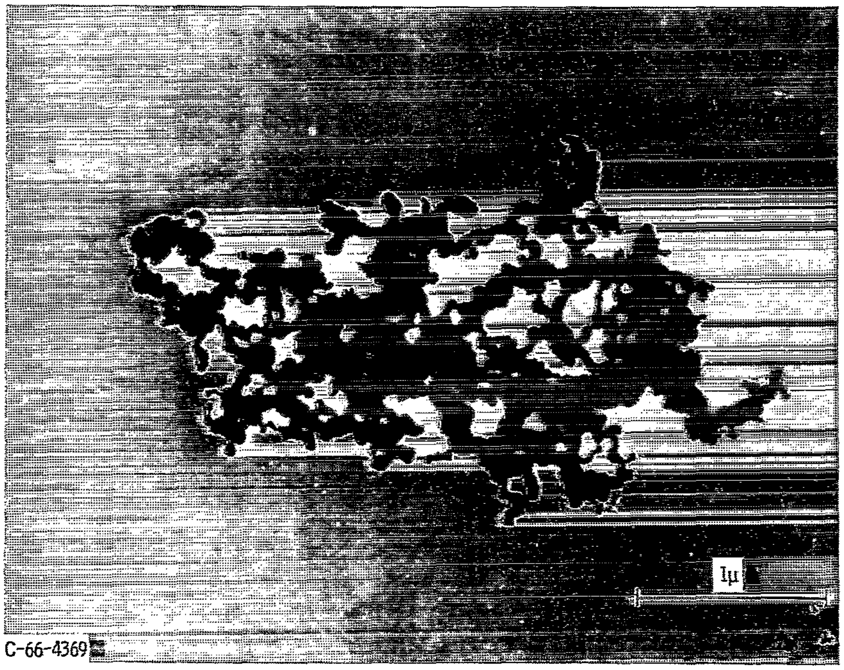
Starting Powders and Pretreatment

One lot of submicron nickel powder and one lot of submicron alumina powder were used in the preparation of all the blends. Pertinent characteristics of these powders, including particle size data, are summarized in table I. Electron micrographs of the starting powders are given in figure 1. The composition of all blends was nickel with 5.4-volume-percent alumina.

The nickel and alumina powders were separately precleaned in vertical nickel-alloy-steel retorts through which hydrogen, purified with a palladium purifier, was passed. The temperature was raised slowly (over a period of 27 hr) to the final cleaning temperatures of 650° F (for nickel) and 900° F (for alumina); each was held for 18 hours at temperature. Measurement of the specific surface area of the powders showed that there had been no significant change during precleaning and thus no appreciable sintering had



(a) Alumina powder. Original magnification, X50 000.



(b) Nickel powder. Original magnification, X50 000.

Figure 1. - Electron micrographs of submicron powders used to prepare all blends.

occurred. However, the powders tended to form a loosely packed "clump" in the cleaning retort; this clump was broken up by passing it through a 40-mesh sieve. All weighing and handling of the fine powders in the dry state was conducted in a dry box with high purity (99.997 percent) argon atmosphere.

Preparation of Blends

The processes used to prepare the blended specimens for optical and electron microscopy are outlined in the flow charts in figure 2. In each case, a limited number of blends was prepared with each apparatus. Conditions were used that were believed to be "good practice" on the basis of previous experience. These experiments are summarized in table II. No attempts were made to improve the operations. Details of each of the operations are described in the following paragraphs.

Dry blending. - The processing of all blends shown in figure 2(a), except blend 5, included tumbling the nickel powder prior to precleaning. This operation was expected to break down some of the powder agglomerates and thus permit more effective precleaning and blending. Blend 5 was run as a control sample, duplicating blends 3 and 4, to determine if the tumbling had a measurable effect. The unblended nickel powder was tumbled for 2 minutes in a stainless-steel, 1-gallon, Patterson-Kelly Twin-Shell V-Blender rotating at 24 rpm with its intensifier cage operating at 1725 rpm. The amount of powder in the blender was adjusted to fill it to the level of the axis of the intensifier cage.

Blend 1 - Waring Blendor: A 307-gram charge of the nickel and alumina powders was loaded into the 1-quart glass container of the Waring Blendor, filling it to about two-thirds of capacity. Blending was carried out for 10 minutes at a speed of approximately 15 000 rpm.

Blend 2 - Twin-Shell V-Blender: The Patterson-Kelly Twin-Shell V-Blender used in the tumbling operation was also used in this experiment. Because of the large volume of the vessel, a 1200-gram charge was required for effective operation. The mill was operated for 4 minutes at 24 rpm with the intensifier cage rotating at 1725 rpm.

Blends 3 and 4 - plastic mill: A 1-quart plastic jar (4-in. in diam and 8-in. long) was loaded with a 307-gram powder charge and a volume of 1/4-inch glass balls equal to one-half the volume of the powder. The plastic mill was sealed in a dry box and then rolled in the air at 60 rpm for 24 hours. The mill was unloaded in a dry box.

Blend 5 - plastic mill: Blend 5 was a control sample that duplicated blends 3 and 4 except that the nickel powder was not tumbled prior to hydrogen precleaning.

Blend 6 - stainless-steel mill: The mill used was a 1-quart-capacity mill ($4\frac{1}{2}$ in. in diam and 5 in. long) with a cover that sealed securely with a rubber gasket. The mill had three longitudinal internal ribs (1/4 in. by 1/4 in.) that were welded to the wall. Loading

TABLE I. - CHARACTERISTICS OF POWDERS BLENDED

Characteristic	Nickel	Aluminum oxide
Source	Union Carbide Metals	Vitro Corporation
Crystal structure	FCC	FCC (γ)
Specific surface area, S, m^2/g	8.4	43.9
Average particle size[a], Z, microns	0.054	0.025
Particle size range, microns	0.02 to 0.5	0.002 to 0.3
Average agglomerate size, microns	1.7	-----------
Bulk density, g/cc	0.15	0.14

[a] Calculated from eqs. (7) and (8) of ref. 4, $Z = 4/\rho S$, where $\rho_{Ni} = 8.90$ and $\rho_{Al_2O_3} = 3.64$ (calculated from X-ray diffraction analysis).

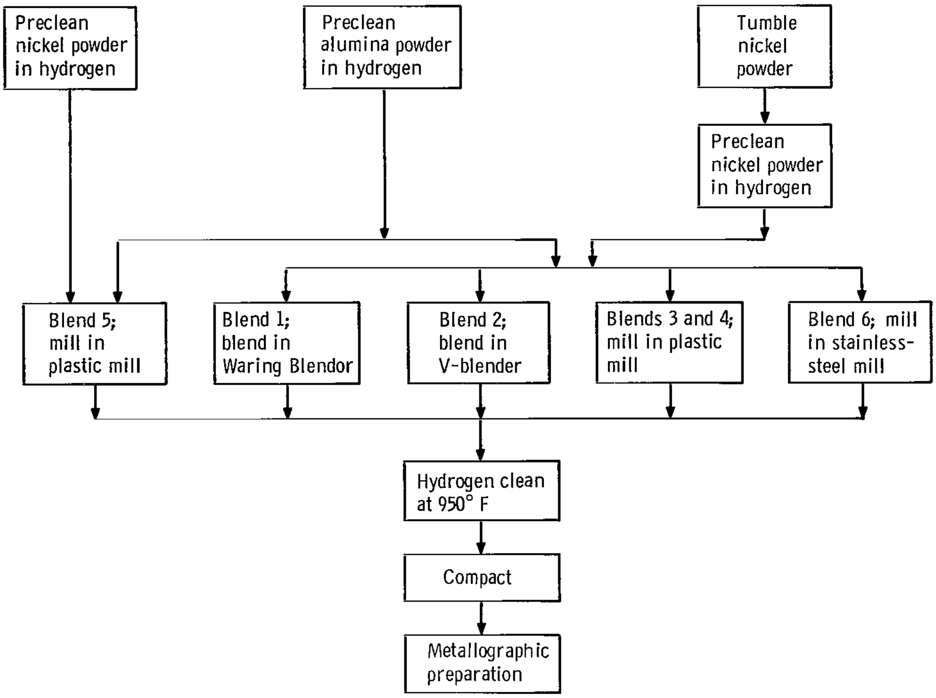
TABLE II. - SUMMARY OF BLENDING EXPERIMENTS

Blend	Apparatus	Blending Procedure	Photomicrographs located in figure -
		Dry blend	
1	Waring Blendor	10 min at 15 000 rpm[a]	3(a), 4(a)
2	Twin-Shell V-Blender	4 min at 24 rpm with intensifier rotating at 1725 rpm[a]	3(b), 4(b)
3	Plastic mill with glass balls	24 hr at 60 rpm[a]	3(c), 4(c)
4	Plastic mill with glass balls	24 hr at 60 rpm[a] (repeat of blend 3)	3(d), 4(d)
5	Plastic mill with glass balls	24 hr at 60 rpm (control)	3(e), 4(e)
6	Stainless-steel mill with nickel balls	24 hr at 60 rpm[a]	--------
		Wet blend	
7	Homogenizer	5 passes at 6000 psi[b]	3(f), 4(f)
8	Stainless-steel mill with nickel balls	48 hr at 60 rpm[c]	3(g), 4(g)
9	Plastic mill with glass balls	24 hr at 60 rpm[c]	3(h), 4(h)

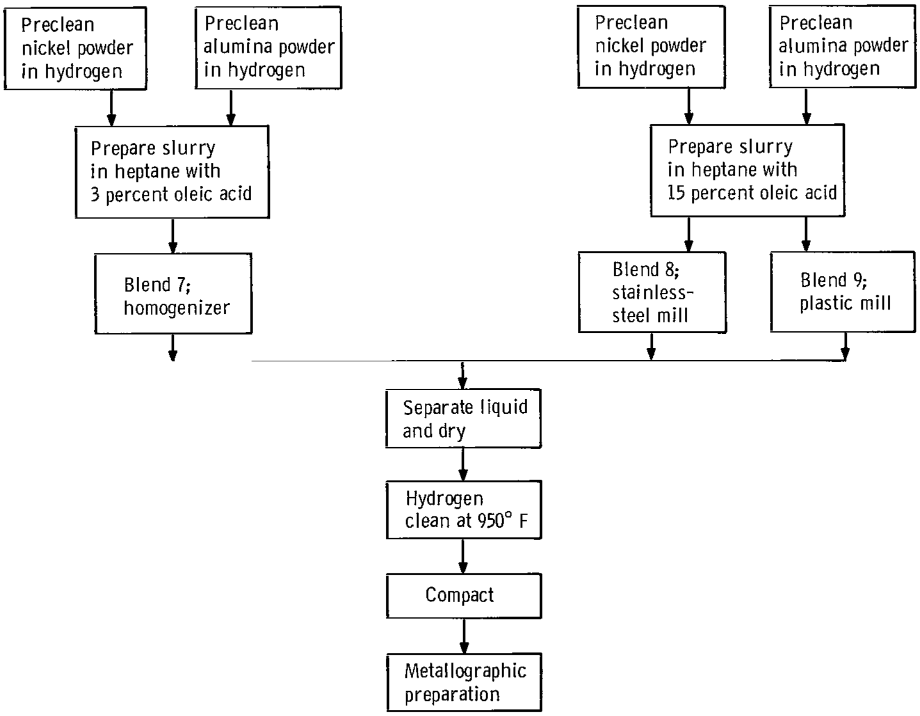
[a] Nickel powder tumbled 2 min in Twin-shell V-blender prior to precleaning treatment.

[b] Liquid medium, heptane with 3-percent oleic acid.

[c] Liquid medium, heptane with 15-percent oleic acid.



(a) Dry-blending techniques.



(b) Wet-blending techniques.

Figure 2. - Preparation of blends.

and milling procedures were the same as for blends 3 to 5 except that 1/4-inch nickel balls were used instead of glass balls.

Wet blending. - Preparation of the slurries for wet blending, as indicated in figure 2(b), consisted of adding the precleaned nickel and alumina powders to the liquid media and premixing for 2 minutes in a Waring Blendor. Composition of the slurry was nominally 460 grams of powder per liter of n-heptane with oleic acid added as a dispersing agent. The concentration of oleic acid was equal to 3 weight percent of the powder weight in blend 7 (homogenizer) and equal to 15 weight percent in blends 8 and 9 (ball mill).

Blend 7 - homogenizer: After the slurry was preblended in a dry box, 700 cubic centimeters of it were transferred to the air for homogenizing. The apparatus was a Manton-Gaulin Sub-Micron Disperser (SMD). In operation, the slurry is pumped at high pressure through a small orifice (homogenizing valve) used to control the pressure. As it passes the homogenizing valve, the slurry is subjected to a high shear and impacts at high velocity against a cylindrical surface (impact ring). The slurry was passed through the apparatus for five complete cycles at a nominal pressure of 6000 pounds per square inch. To prevent overheating, the slurry was cooled to less than 70° F prior to each successive pass.

Blend 8 - stainless-steel mill: A mill similar to that used for blend 6 was loaded with about 630 cubic centimeters of preblended slurry and 330 cubic centimeters of 1/4-inch nickel balls in a dry box. The mill was removed from the dry box and rolled in air at 60 rpm for 48 hours.

Blend 9 - plastic mill: The procedure for this experiment was the same as for blend 8 except that the plastic mill used for blends 3 to 5 was used with 1/4-inch glass balls and the milling time was 24 hours.

Filtration and drying. - The slurries used for blends 7 to 9 were separated by vacuum filtration. The damp filter cake was transferred to a tray for freeze drying. The tray was placed in a vacuum chamber fitted with a shelf and cooled with liquid nitrogen to freeze the heptane remaining in the filter cake. After the filter cake had been cooled below the freezing temperature of the heptane, the chamber was evacuated and held with the pump running until a vacuum of about 1×10^{-2} torr was achieved. The temperature was then raised to approximately 170° F while the vacuum was maintained; the chamber was filled with high-purity argon and the tray sealed. The trays were transferred to a dry box for unloading.

Hydrogen Cleaning and Powder Compaction

Powders from the dry-blending experiments (blends 1 to 5) and freeze-dried powders from the wet-blending experiments (blends 7 to 9) were loaded into retorts and cleaned with purified hydrogen. (Blend 6 was discarded for reasons that are explained in the section RESULTS.) The temperature was raised slowly to 950° F over a period of 30 hours and held until reduction at that temperature was essentially complete, as indicated by a low-moisture content in the effluent hydrogen (less than 10 ppm). Time at temperature varied from 10 to 20 hours.

As a result of this cleaning operation, the powders had a tendency to sinter, and it was necessary to crush the material manually in a stainless-steel mortar. The powder was crushed fine enough to pass through a 40-mesh sieve.

Metallographic Procedures

Small samples of each blend were compacted in a 0.45-caliber cartridge-actuated compaction press and then polished and etched for metallography, according to the methods described in reference 7. Some specimens were examined after compaction and others after compaction and annealing for 1 hour at 1700° F in hydrogen. The annealing treatment was used to increase particle-to-matrix contrast, as discussed in reference 7.

Six of the blends warranted evaluation beyond a qualitative inspection of optical and electron photomicrographs. Measurements of volume-percent dispersoid, average interparticle spacing, and average particle intercept were made of both unannealed and annealed blends by using the specially designed Flying Spot Particle Quantizer and Lineal Analyzer, an automatic film scanner manufactured by the Airborne Instrument Laboratory of Cutler-Hammer for Lewis (ref. 8). The film scanner uses a raster generated on a cathode-ray tube to scan a film. Variations in intensity of the light spot, after it has passed through the film and a high-resolution optical system, are sensed by a photomultiplier tube that feeds logic circuits. A digital display counter is controlled by the output from the logic circuits. A high-contrast 35-millimeter film of the blend microstructures was prepared from the electron micrographs by an overlay-copy technique recently reported (ref. 9). Particle images were copied onto overlay sheets at print magnifications of 46 000. Magnification was reduced to 5300 on the 35-millimeter film used for automatic scanning. This method of processing large amounts of quantitative metallographic data makes feasible numerical comparisons that have a reasonable degree of statistical validity. Fifteen micrographs (equivalent to a total specimen area of approximately 170 square microns) of each blend and condition were measured.

Microstructural parameters were obtained from film-scanner data from the following equations:

$$\text{Volume percent dispersoid} = \frac{L_a}{L_a + L_m} 100 \text{ percent} \qquad (1)$$

$$\text{Average interparticle spacing} = \frac{L_m}{N_a} 3.77\times10^{-3} \text{ microns} \tag{2}$$

$$\text{Average particle size} = \frac{L_a}{N_a} 3.77\times10^{-3} \text{ microns} \tag{3}$$

where

L_a total distance traversed across particle phase by the raster scan line

L_m total distance traversed across matrix phase by the raster scan line

N_a total number of particle intercepts

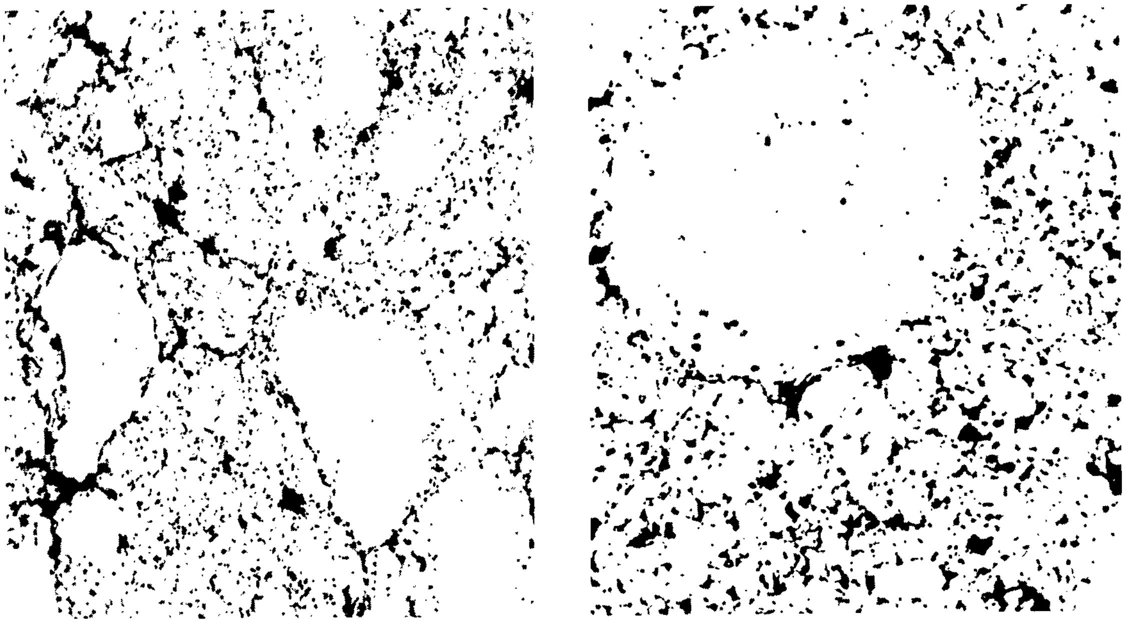
The calibration constant (3.77×10^{-3}) in equations (2) and (3) includes film magnification and converts numerical data from the scanner into metallographic parameters in units of microns. The average particle size is defined as the average particle intercept and corresponds to the parameter Z in the notation of Cremens (ref. 4). The film scanner was also used to count the number of individual particles in the field of each micrograph.

Data from all micrographs of each specimen were used to calculate average values for L_a, L_m, and N_a. Then a criterion was applied to reject micrographs that showed either abnormally large agglomerates or dispersoid free regions. This criterion called for discarding data from all micrographs whose value of N_a was either less than one-half or more than twice the average value of N_a for that specimen. New average values of L_a, L_m, and N_a were calculated and used in subsequent calculations. This rejection criterion typically removed one of the 15 electron micrographs for each set of blend conditions.

RESULTS

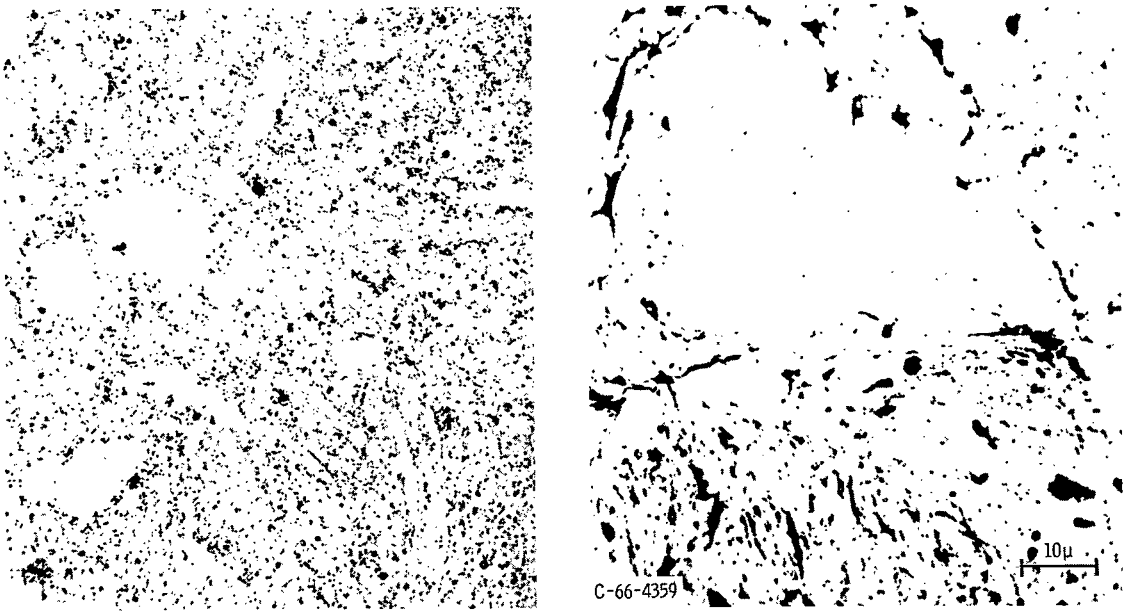
Eight of the nine blends were successfully compacted into pellets and examined by light and electron microscopy. In preparing blend 6, the powder became welded to the balls in the mill, and several attempts to remove it without altering the blend were unsuccessful. The entire lot was discarded and no further use was made of this blending method.

Optical micrographs of blends 1 to 5 and 7 to 9 are given in figure 3. Figures 3(a), (b), (d), and (e) illustrate the unsatisfactory dispersoid distributions achieved in this study by dry-blending methods. Figure 3(c), blend 3, shows a possible exception to this general trend. This more uniform distribution was not obtained, however, when the



(a) Blend 1; dry blended in Waring Blendor.

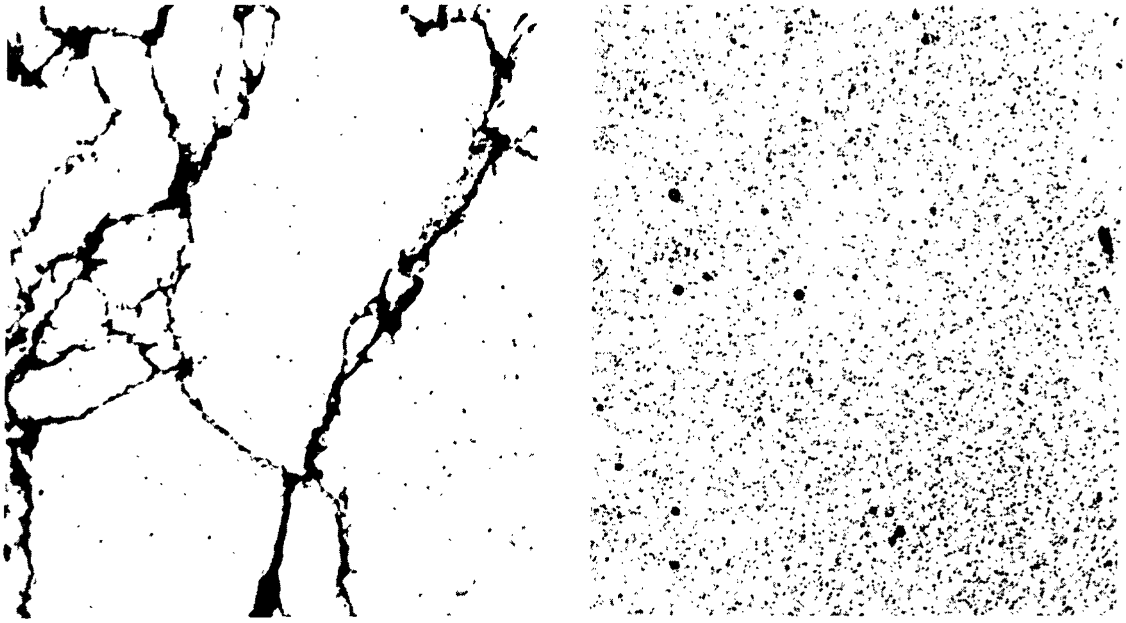
(b) Blend 2; dry blended in Twin-Shell V-Blender.



(c) Blend 3; dry blended in plastic mill with glass balls.

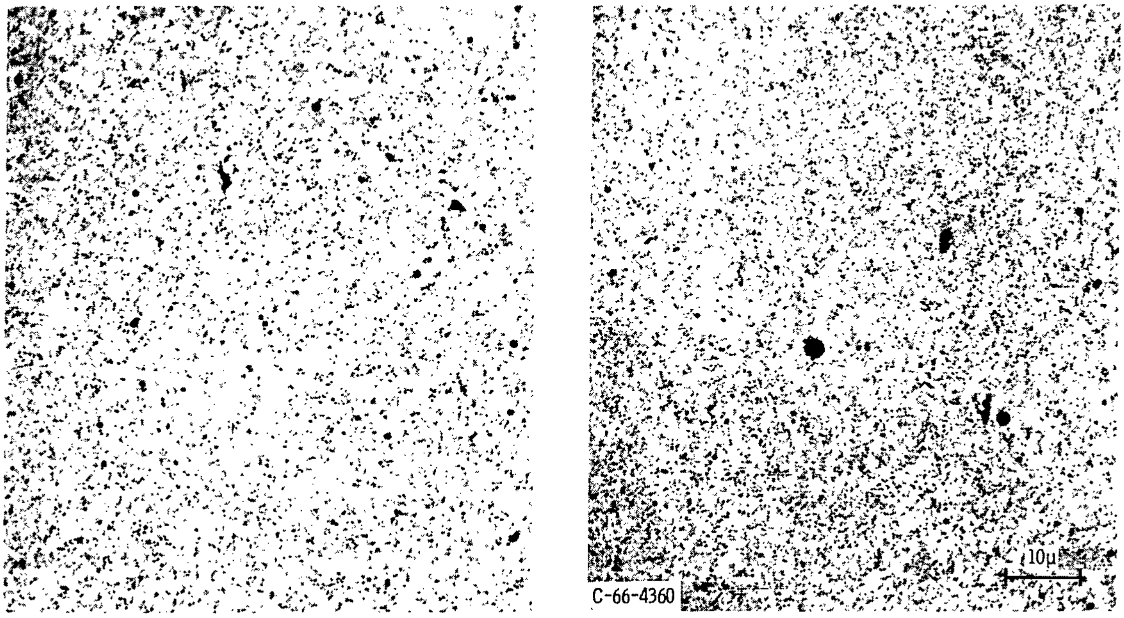
(d) Blend 4; dry blended in plastic mill with glass balls (repeat of blend 3).

Figure 3. - Optical micrographs of blend specimens. Original magnification, X1000.



(e) Blend 5; dry blended in plastic mill with glass balls; pretumbling omitted.

(f) Blend 7; wet blended in homogenizer.



(g) Blend 8; wet blended in stainless-steel mill with nickel balls.

(h) Blend 9; wet blended in plastic mill with glass balls.

Figure 3. - Concluded.

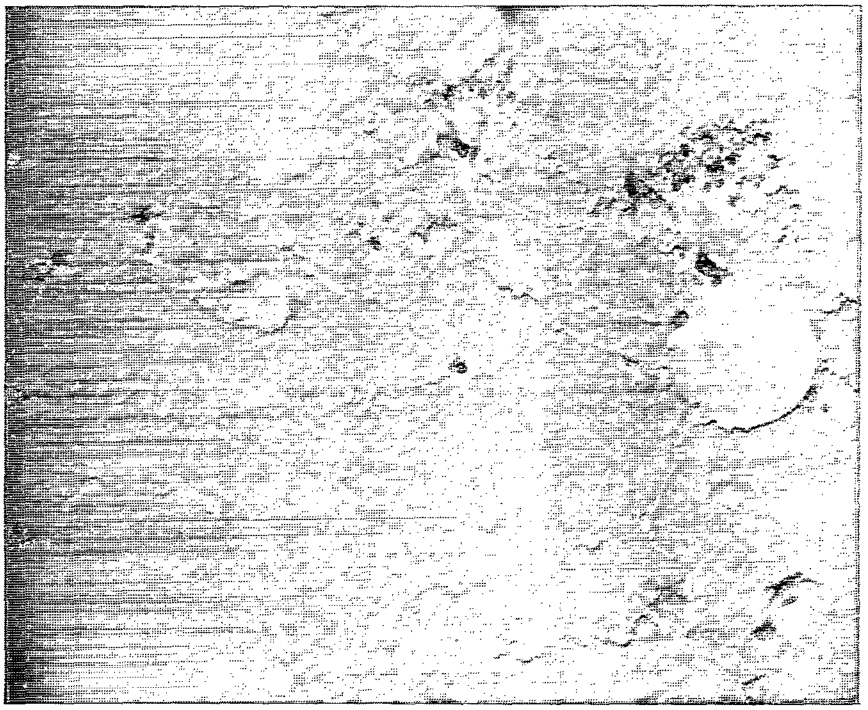
experiment was repeated, as can be seen in figure 3(d), blend 4. Blend 5 differed in preparation from blends 3 and 4 only in omitting the tumbling step that preceeded ball milling. The oxide particles in blend 5 (fig. 3(e)) appear to be concentrated primarily in the boundaries of agglomerated nickel powder particles. Blends 2 and 4 also exhibited marked segregation of the dispersoid.

Figures 3(f) to (h) demonstrate the uniform blending achieved by the wet methods employed in this study. No large-scale segregation was observed in optical micrographs of wet-blended specimens. Measurement of microstructural parameters from electron micrographs was necessary to determine whether there were significant differences among these blends. Electron micrographs were made from most blend specimens both as-compacted and as-compacted and annealed for 1 hour at 1700° F. Representative electron micrographs are presented in pairs in figure 4 for comparison of the unannealed with the annealed structures. Approximately 15 electron micrographs were measured for each condition to obtain the microstructural parameters shown in table III (p. 22). As mentioned earlier, the annealing treatment was intended to show particles more clearly. The desired clarification of the structure was obtained for dry blend 1 and for all the wet blends (7 to 9), as shown in figure 4. However, two of the dry blends (3 and 4) showed severe agglomeration on annealing, as shown in figures 4(c) and (d). Values for average particle size before and after annealing are detailed in table III.

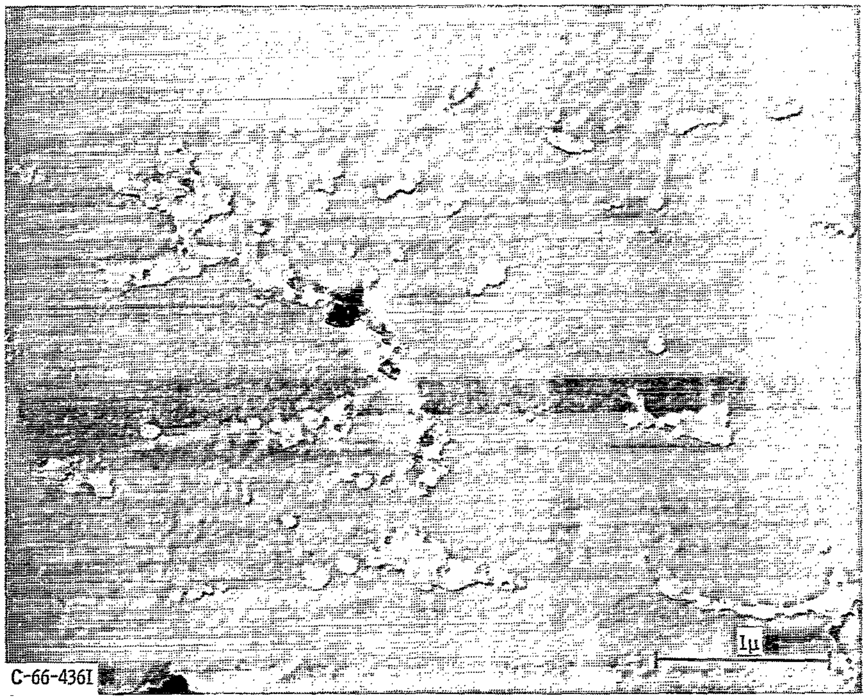
Based on the evidence of the electron micrographs, the microstructural parameters for annealed specimens were considered more representative of the blend microstructures except for blends 3 and 4. Parameters for the unannealed specimens were considered more representative of these two blends. These choices were supported by the fact that they gave, in every case, closer approximations of the 5.4-percent dispersoid indicated by charge analysis. The high volume percentage measured in the unannealed specimen of blend 1 (8.5 percent) is believed to be the result of the segregation observable in the optical photomicrograph of figure 3(a). (Other sources of error are discussed in the appendix). For the conditions chosen as representative of the various blends (table III), the variation of measured volume percentage from the charge-analysis value ranged from 2 to 15 percent higher than that value. The exact value of 5.4 percent measured for the annealed specimen of blend 1 appears to be fortuitous in view of the segregation observed in that specimen.

The average interparticle spacings of wet-blended specimens were, in general, smaller than those of dry-blended materials. This relation was valid for both the unannealed and annealed conditions. Measured interparticle spacing increased with annealing for the dry-blended specimens but decreased for the wet-blended samples.

Table III also lists the total number of particles counted in each series of micrographs. For each of the more uniform blends examined in this study (blends 3 and 7 to 9), approximately 2000 particles were scanned. Although approximately the same number of



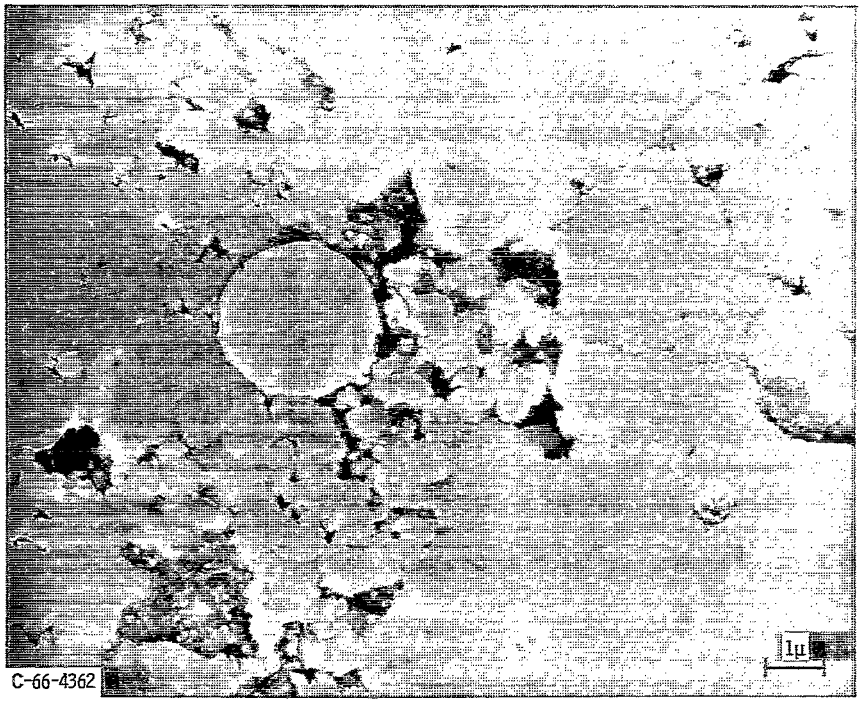
Unannealed



Annealed for 1 hour at 1700° F

(a) Blend I; dry blended in Waring Blendor. Original magnification, X46 000.

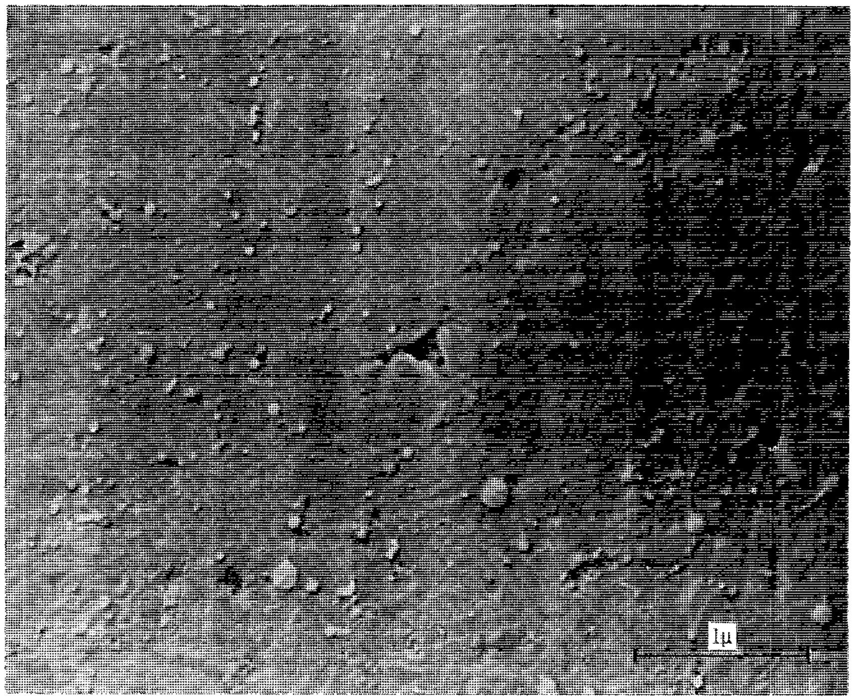
Figure 4. - Electron micrographs of blend specimens.



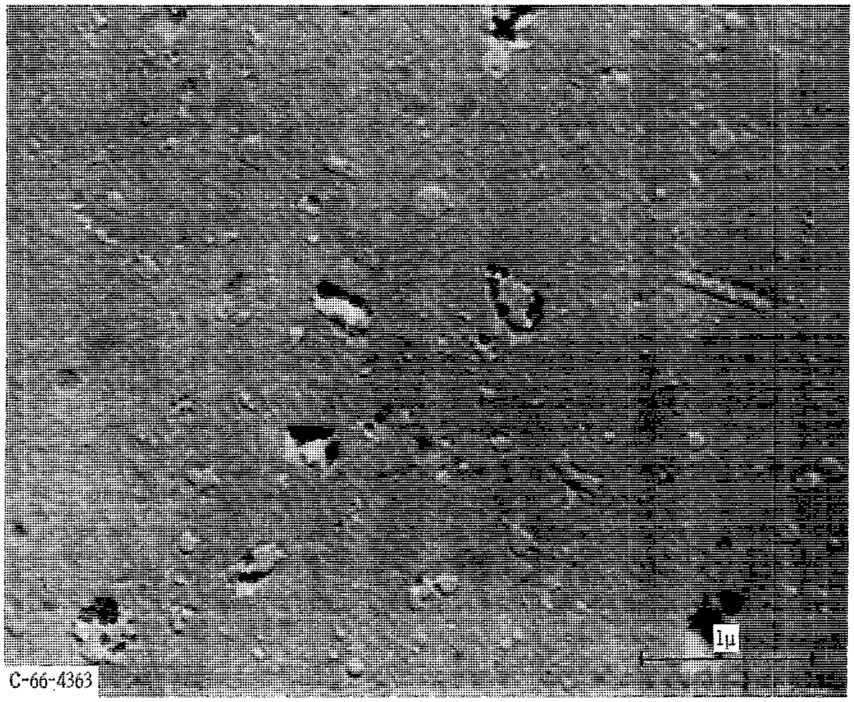
Unannealed

(b) Blend 2; dry blended in Twin-Shell V-Blender. Original magnification, X16 400.

Figure 4. - Continued.



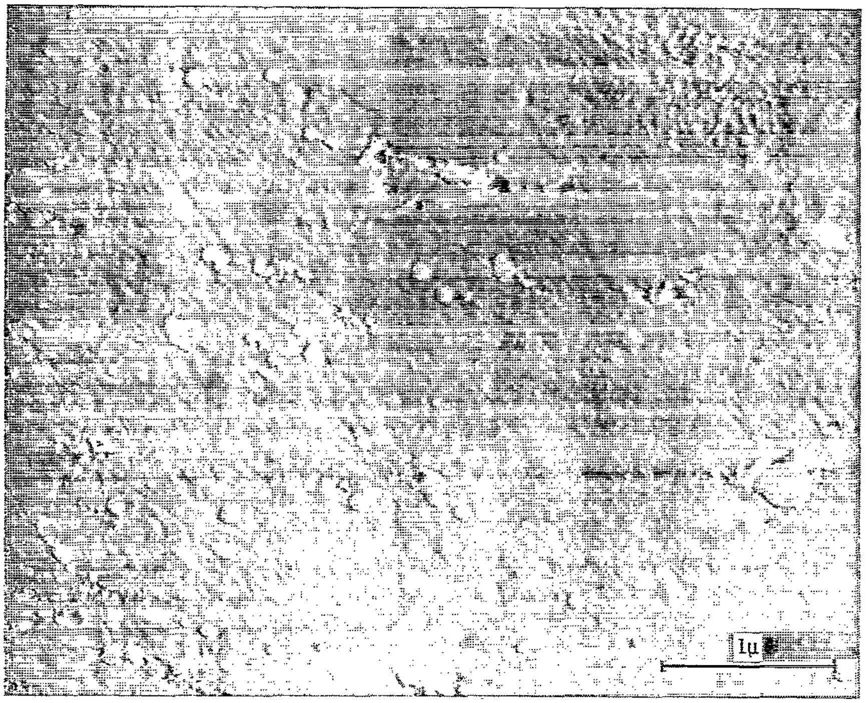
Unannealed



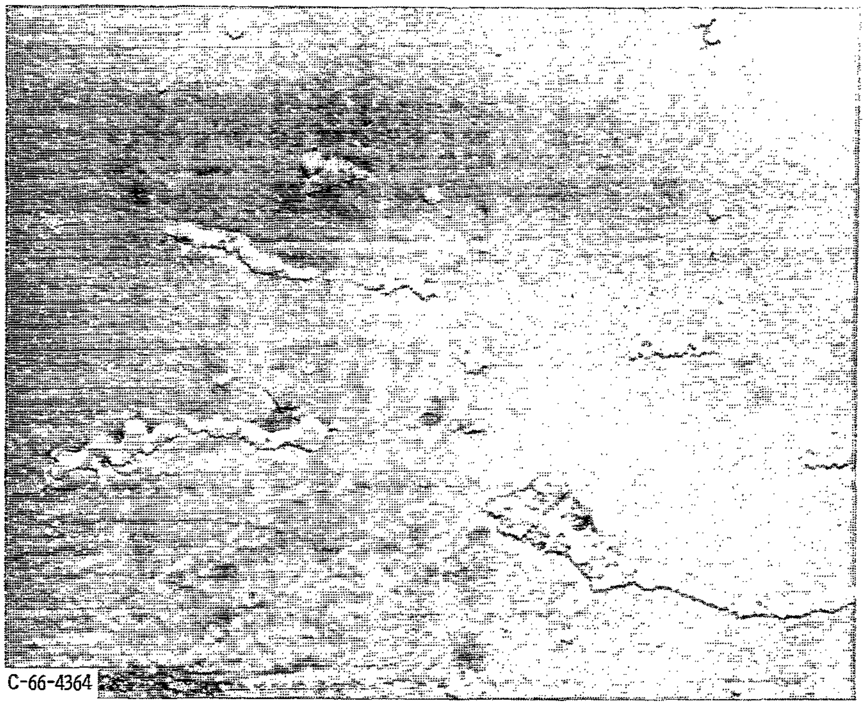
Annealed for 1 hour at 1700° F

(c) Blend 3; dry blended in plastic mill with glass balls. Original magnification, X46 000.

Figure 4. - Continued.



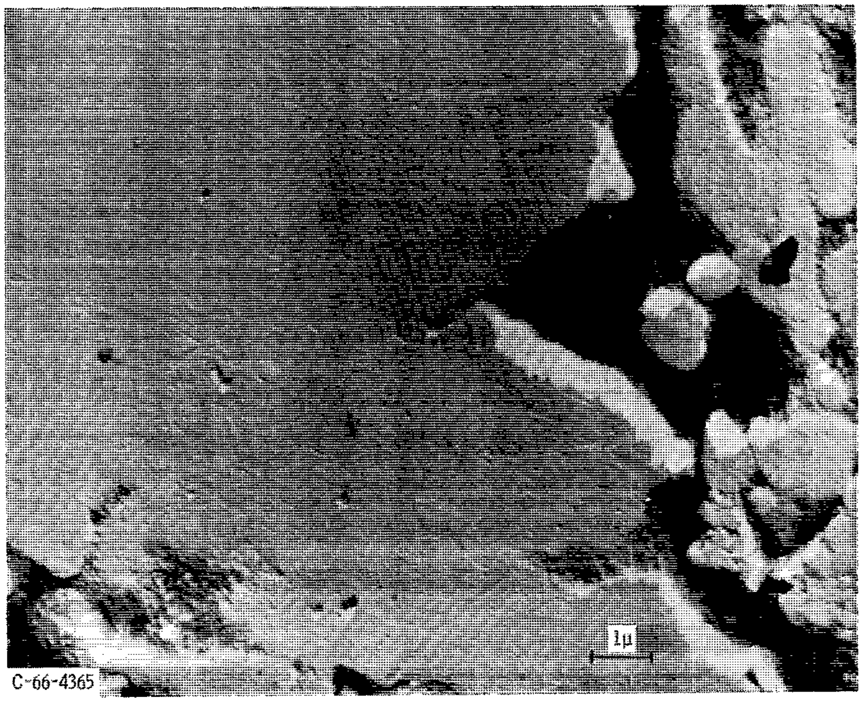
Unannealed



Annealed for 1 hour at 1700° F

(d) Blend 4; dry blended in plastic mill with glass balls (repeat of blend 3). Original magnification, X46 000.

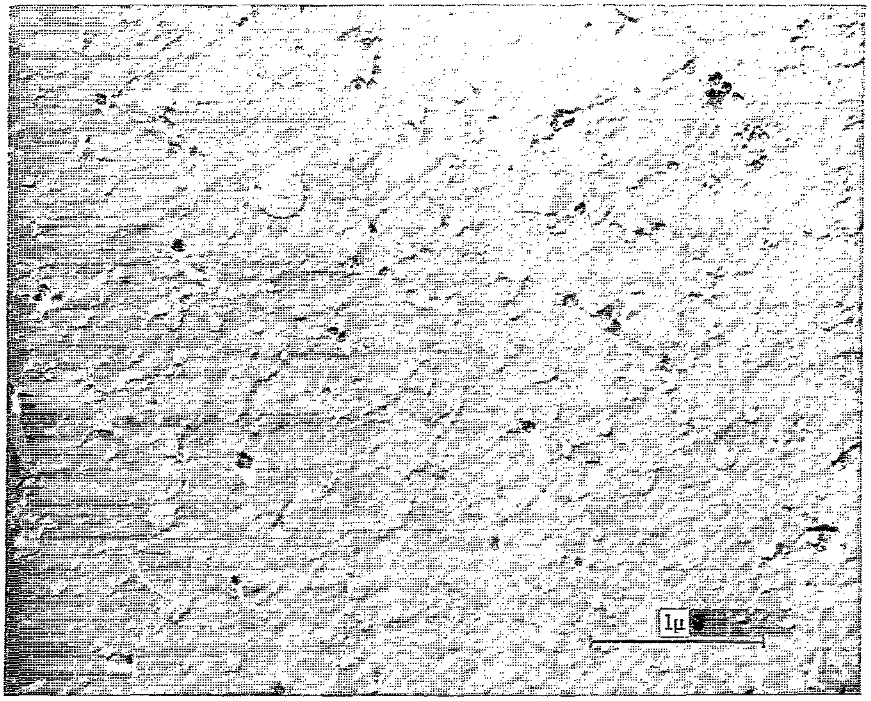
Figure 4. - Continued.



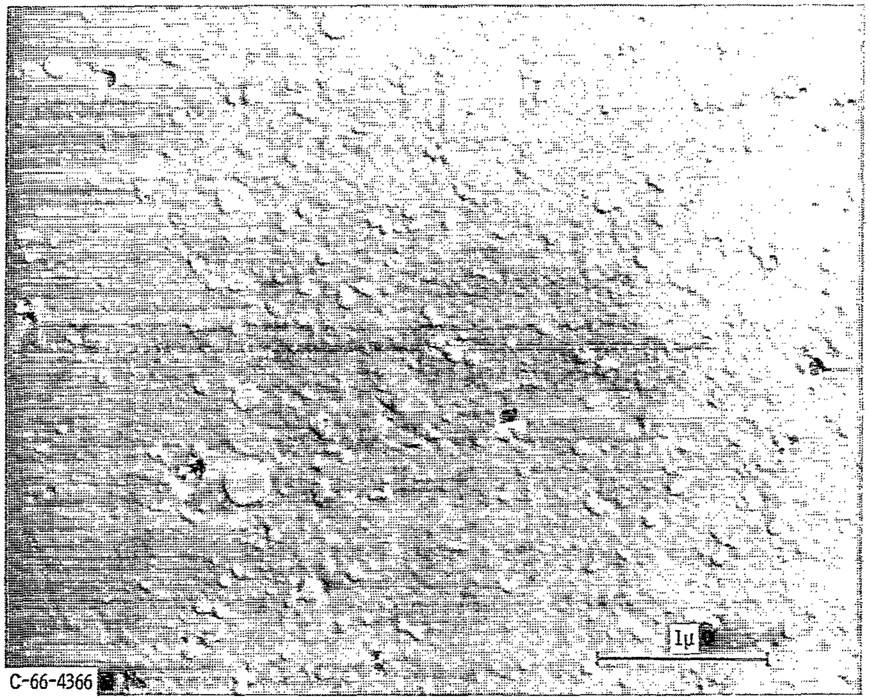
Unannealed

(e) Blend 5; dry blended in plastic mill with glass balls; pretumbling omitted. Original magnification, X16 400.

Figure 4. - Continued.



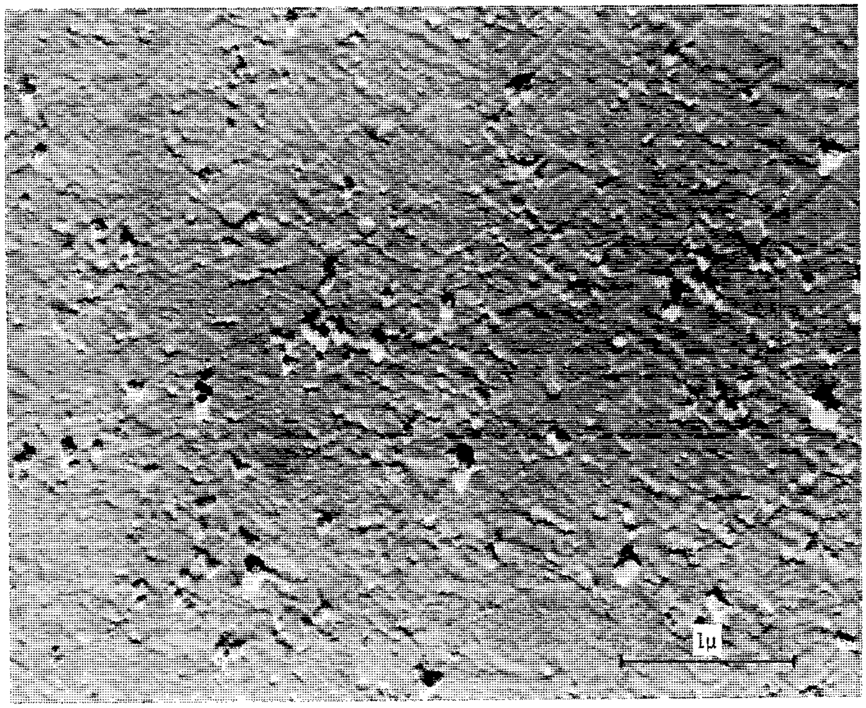
Unannealed



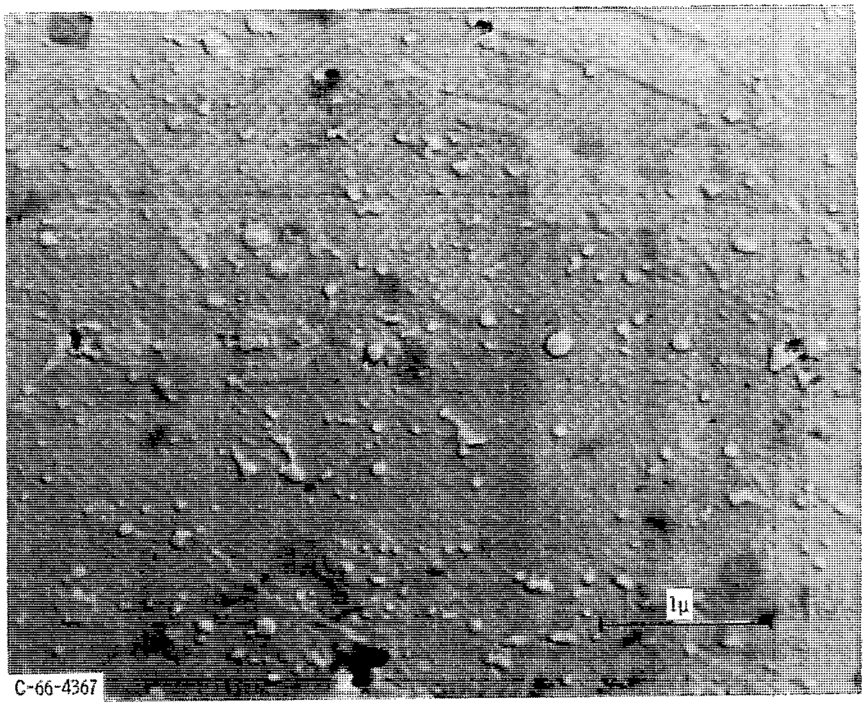
Annealed for 1 hour at 1700° F

(f) Blend 7; wet blended in homogenizer. Original magnification, X46 000.

Figure 4. - Continued.



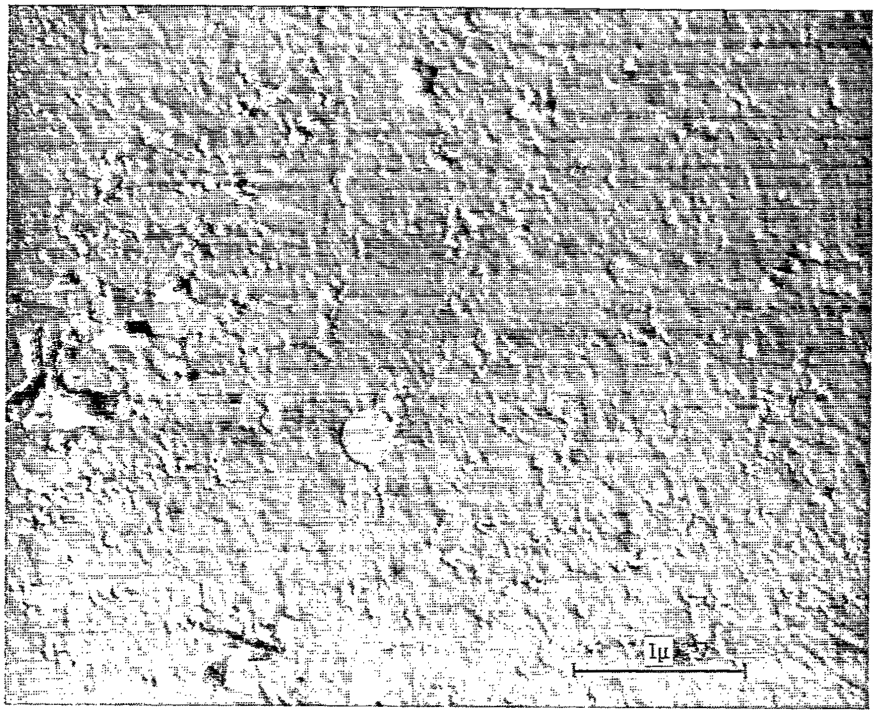
Unannealed



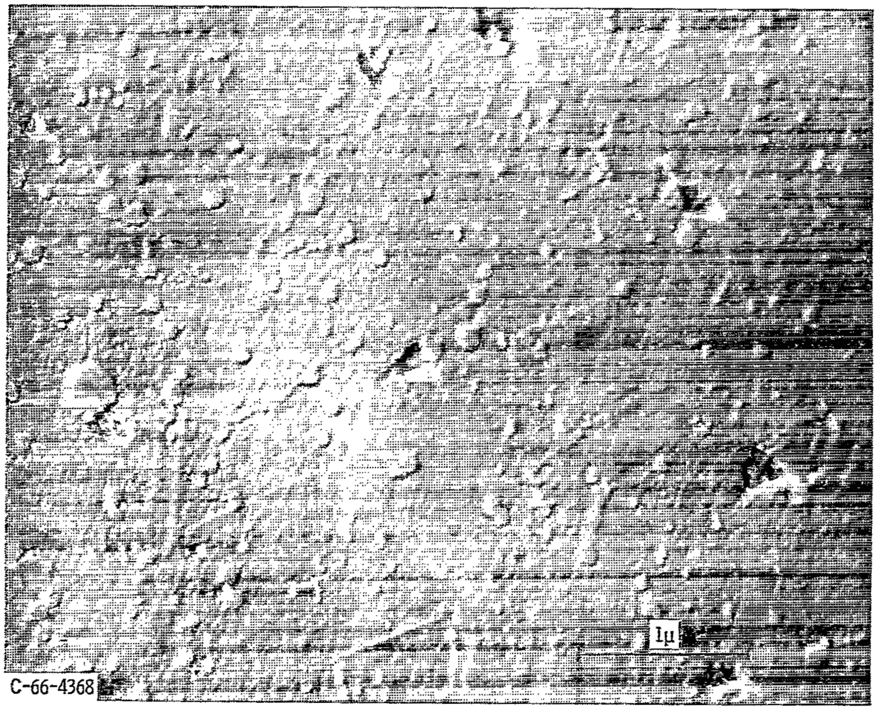
Annealed for 1 hour at 1700° F

(g) Blend 8; wet blended in stainless-steel mill with nickel balls. Original magnification, X46 000.

Figure 4. - Continued.



Unannealed



Annealed for 1 hour at 1700° F

(h) Blend 9; wet blended in plastic mill with glass balls. Original magnification, X46 000.

Figure 4. - Concluded.

TABLE III. - RESULTS OF QUANTITATIVE METALLOGRAPHY OF BLEND MICROSTRUCTURES

Blend[a]	Apparatus	Dispersoid, volume percent		Average interparticle spacing[b], microns		Average dispersoid particle size[c], microns		Number of particles counted	
		Unannealed	Annealed	Unannealed	Annealed	Unannealed	Annealed	Unannealed	Annealed
				Dry blends					
1	Waring Blendor	8.5	[e]5.4	2.0	[e]2.4	0.19	[e]0.14	759	[e]591
2	Twin-Shell V-Blender[f]	---	----	----	----	----	----	----	----
3	Plastic mill with glass balls	[e]5.6	6.8	[e]1.3	1.8	[e].078	.13	[e]1934	980
4	Plastic mill with glass balls	[e]5.5	7.6	[e]2.3	2.6	[e].13	.21	[e]838	502
5	Plastic mill with glass balls[d, f]	---	----	---	---	----	----	----	---
6	Stainless-steel mill with nickel balls[g]	---	----	---	---	----	----	----	---
				Wet blends					
7	Homogenizer	3.9	[e]5.7	1.6	[e]1.1	0.066	[e]0.076	1979	[e]2371
8	Stainless-steel mill with nickel balls	3.3	[e]6.1	1.6	[e].96	.056	[e].062	2139	[e]3519
9	Plastic mill with glass balls	4.2	[e]6.2	1.6	[e]1.1	.069	[e].073	1997	[e]2060

[a] See table II for more detailed description and micrograph references.

[b] Mean-free-path interparticle spacing, $\overline{IP}$.

[c] Defined as average intercept, Z.

[d] No preblend tumbling of powder (see fig. 2(a)).

[e] Value chosen as more representative of microstructure (see p. 13).

[f] Poor distribution, no measurements made.

[g] No specimen; powder welded to balls.

electronmicrographs was analyzed for each specimen, the total particle counts varied widely. Microstructures that had uniform distributions of fine particles had higher particle counts than those that had coarser distribution.

Blends 3 and 4 were prepared by the same method. However, large differences between measured interparticle spacings and particle sizes of these two blends suggests that there were important variables which were not controlled in this dry-blending method.

DISCUSSION

Until now, no really conclusive comparison of blending methods as such had been made because there was no way to examine submicron powder blends. The recent use of high-energy-rate compaction to prepare blend specimens made possible examination of the blend with minimum disturbance. By using this technique, this study has demonstrated that good dispersion microstructures can be produced by mechanically blending submicron powders. The dispersion microstructures of the three wet-blended specimens were particularly good with interparticle spacings of about 1 micron. It is believed that this spacing, if retained in the end-product alloy, would be of the proper magnitude for effective dispersion strengthening. Measurements on commercial dispersion-strengthened alloys such as S.A.P. and TD Nickel, for example, have shown interparticle-spacing values of 0.4 and 1.5 microns, respectively. The interparticle spacings referred to in this study are equivalent, by definition, to the average matrix-intercept length (see eq. (2)). It has been shown previously (ref. 4) that the smallest interparticle spacing that can be achieved by ideal random mixing of two given powders can be predicted from the relation

$$\overline{IP}' = Z_{oxp}\left(\frac{1}{f_{ox}} - 1\right) + Z_{mp} \tag{4}$$

where

$\overline{IP}'$ predicted average interparticle spacing

Z_{oxp} particle size (average intercept) of oxide powder

Z_{mp} particle size (average intercept) of metal powder

f_{ox} volume percent of oxide

For the powders used in this study, the predicted ideal value of interparticle spacing was 0.49 micron. The best blend examined (prepared by wet milling for 48 hr with 1/4-in. nickel balls) had an interparticle spacing of 0.96 micron, only twice the value predicted for ideal random mixing. Other wet-blending methods resulted in spacings of 1.1 microns.

Wet blending produced consistently better microstructures than dry blending. Interparticle spacings of wet-blended specimens were generally less than one-half those of dry-blended materials. Good results from wet-blending methods have been observed in many more instances than the three experiments reported herein. Some other examples, illustrative of a large body of unpublished work, appear in reference 7.

A reason for the superiority of wet blending is suggested by the findings of Meissner, Michaels, and Kaiser (ref. 10). Considering the behavior of submicron zinc oxide particles, they reported "spontaneous pelletization", the formation of relatively strong agglomerates, on dry tumbling. They also noted that the agglomerates retained some strength in nonpolar liquids (cyclohexane and dioxane) but fell apart spontaneously in water. They concluded that agglomeration was caused by cohesive forces of the van der Waals type rather than by electrostatic forces. If the phenomenon of spontaneous pelletization does operate during dry blending of submicron powders, results could not be expected to be better than if coarse particles (of the size of the agglomerates) had been used originally. However, liquid media could be expected to dissipate the cohesive forces and permit individual metal and oxide particles to mix.

Quatinetz, Schafer, and Smeal (ref. 5) demonstrated the beneficial effects of using surfactants and a liquid medium in the process of grinding metal powders to ultrafine dimensions. They noted that the surfactant formed an adsorbed layer on individual particles and thus inhibited agglomeration. It could also be expected that, during blending, a liquid would provide a means of transferring shear forces and thus break up unblended agglomerates.

A relatively good interparticle spacing of 1.3 microns was measured on one dry blend, blend 3. However, examination of the optical micrograph of this blend (fig. 3(c)) shows that the blend was not uniform by comparison with the wet-blended specimens shown in figures 3(f) to (h) (p. 12). When blends 3 and 4 were rerun, an interparticle spacing of 2.3 microns was obtained. Dry blending may be susceptible to variable surface factors such as humidity. This susceptibility is in striking contrast to the wet blends that gave similar results despite marked changes in blending method and slurry composition.

Although no agglomeration was expected to result from a 1-hour anneal at 1700° F, severe agglomeration was observed in two of the dry blends but not in any of the wet blends. These results may indicate that the blended structure was "locked" in place during the drying process subsequent to wet blending, while paths for migration of oxide particles were not similarly impeded in the dry-blended specimens.

While it seems clear that the wet-blending methods used here are superior to the dry methods studied, it is also apparent that some room for improvement remains in the wet-blending methods. Definitive answers as to how closely wet-blending results can be made to approach the ideal random blend and which wet-blending method should be preferred will require further work. The examination and analysis techniques used here to evaluate current methods can also guide refinement of the best of those methods. Furthermore, these examination and analysis techniques can also be used to observe and avoid dispersoid-particle agglomeration in billet-scale batch processes subsequent to blending (e.g., powder cleaning and consolidation).

Detailed statistical error analyses for the microstructural parameters measured in this study are beyond the scope of this report. However, the most probable sources of error are discussed in the appendix.

CONCLUSIONS

This investigation, which was undertaken to compare various methods of blending submicron metal and oxide powders, yielded the following conclusions:

1. Interparticle spacings of about 1 micron were achieved by blending either by wet ball milling or by using a homogenizer apparatus. This spacing is in the range desired for dispersion-strengthened alloys.

2. Blending was consistently better by wet methods than by dry methods. There were no substantial differences between the blends prepared by the three wet-blending methods.

3. Compacts made from two dry blends showed severe agglomeration when annealed at 1700° F. Blends prepared by wet methods showed little coarsening as a result of annealing. While this low-temperature exposure is not a stringent test, the results suggest that dispersions produced by wet methods are more likely to be retained during subsequent processing than those produced by dry methods.

4. Comparison of the smallest interparticle spacing measured (0.96 micron) with the value predicted for ideal random mixing of the powders (0.49 micron) indicated that further improvement in blending could be expected. The techniques used in this study for evaluating powder blends can also be used to optimize the most promising blending methods.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 16, 1966,
129-03-01-05-22.

APPENDIX - SOURCES OF ERROR IN METALLOGRAPHIC MEASUREMENTS

In table III (p. 22) there is considerable variation in the metallographically measured volume percentage of dispersoid for the blend specimens. According to charge analysis, the amount of dispersoid added was 5.4 volume percent. The variations are important because an accurate volume percentage can be taken as a measure of the validity of metallographic representation of the structure. There are at least six sources of error to be considered:

(1) The sample could be too small for the scale of inhomogeneity in a poor blend. This error could account for the wide range of volume percentages measured for the dry blends (figs. 3(a) to (e), pp. 11-12).

(2) Inadequate resolution in the micrographs could cause fine particles to be missed; the volume percentage measured would be correspondingly low. This is believed to be the case for the unannealed wet blends (7 to 9 in table III, p. 22).

(3) Etching of the metallographic specimen could undercut fine particles and thus cause them to be lost. Etching might also uncover more of a large particle than would appear in an ideal plane-of-polish.

(4) Fine particles might be enlarged during overlay copying. This problem can be minimized by adjusting the magnification to ensure that particles will be sufficiently large in the micrograph.

(5) Contaminants, such as nickel oxide, might be included in the measured volume percentage.

(6) Signal threshold settings in the automatic film scanner could cause a variation in the volume percentage measured. Since this calibration is done once for an entire data series, any such error would be systematic and would not affect relative values.

With so many possibilities for error, the variations in volume percentage shown in table III are not unreasonably large. The best data, those for annealed wet blends, show volume percentages about 10 percent higher than charge analysis. The unannealed wet-blend results are believed to be low because of inadequate resolution of fine particles. Thus, use of the volume percentage as a check value led to the choice of the annealed specimens as most accurately representing all the wet blends.

In the dry blends, however, the particles were coarse enough to be observed in the unannealed condition. Annealing was not beneficial for the dry-blended specimens, since it resulted in agglomeration (fig. 4(a) to (d), pp. 14 to 17). The annealed condition was, however, more representative for the case of blend 1. Sampling errors are believed to cause the large volume-percentage measured in the unannealed blends.

REFERENCES

1. Bunshah, R. F.; and Goetzel, C. G.: A Survey of Dispersion Strengthening of Metals and Alloys. Summary Tech Rep. (WADC TR 59-414), New York University, July 1959.
2. Cremens, Walter S.; and Grant, Nicholas J.: Preparation and High Temperature Properties of Nickel-Al_2O_3 Alloys. Proc. ASTM, vol. 58, 1958, pp. 714-730.
3. Bonis, Laszlo J.; and Grant, Nicholas J.: Influence of Processing Variables on the Properties of Nickel-Al_2O_3 Alloys. AIME Trans., vol. 218, no. 5, Oct. 1960, pp. 877-881.
4. 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.
5. Quatinetz, Max; Schafer, Robert J.; and Smeal Charles: The production of Submicron Metal Powders by Ball-Milling with Grinding Aids. AIME Trans., vol. 221, no. 6, Dec. 1961, pp. 1105-1110.
6. Nelson, R. C.; Zwilsky, K. M.; and Grant, N. J.: Evaluation of Ultrafine Metal Powders for Dispersion Hardening Purposes. Final Report (Contract NOw 61-0672-f), New England Materials Lab., Inc., Aug. 31, 1961.
7. Reinhardt, Gustav; Cremens, Walter S.; and Weeton, John W.: Cold Consolidation of Metal Plus Dispersoid Blends for Examination by Electron Microscopy. NASA TN D-3511, 1966.
8. Mansberg, H. P.: Photo - Optical Field Measurement by Flying Spot Scanners for Biomedical Applications. Soc. Photographic Instr. Eng. J., vol. 2, Feb. - Mar. 1964, pp. 83-88.
9. Norris, L. Fredrick; Cremens, Walter S.; and Weeton, John W.: Overlay Copy Technique to Provide High-Contrast Electron Micrographs for Automatic Metallographic Analysis. NASA TN D-3658, 1966.
10. Meissner, H. P.; Michaels, A. S.; and Kaiser, Robert: Spontaneous Pelletization in Fine Powders. Ind. Eng. Chem. Process Des. Dev., vol. 3, no. 3, July 1964, pp. 197-201.

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