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PROCESS DEVELOPMENT FOR A DISPERSION STRENGTHENED COBALT BASE ALLOY

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CURTISS WRIGHT
Buffalo Facility

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS 3-11161
Fred H. Harf, Project Manager

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FINAL REPORT

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NASA Lewis Research Center
Cleveland, Ohio
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FOREWORD

This report was prepared by personnel of the Buffalo Facility of the Curtiss-Wright Corporation, Buffalo, New York, and describes original work performed under Contract NAS 3-11161.

The contract was awarded to Curtiss-Wright by the NASA-Lewis Research Center. Technical monitoring was provided by the Project Manager, Mr. Fred Harf, of the Materials and Structures Division of the NASA-Lewis Research Center.

Bernard H. Triffleman of the Buffalo Facility served as the Curtiss-Wright Project Manager; Keki K. Irani was Project Engineer.

Numerous Curtiss-Wright personnel contributed to the program. In particular we wish to acknowledge the efforts of the following: S. Allen, J. Bona, R. Crotty, D. Gress, D. Halloran, D. Perry, E. Truhn, F. C. Wagner, and G. G. Weart.

The electron metallography was performed under the direction of James L. McCall of Battelle Memorial Institute, Columbus, Ohio. Additional and vital electron metallography was performed by Mr. Bruno C. Buzek, Materials and Structures Division, NASA-Lewis Research Center.

The contract work was performed over the period from June 25, 1968 to March 24, 1969.

ABSTRACT

Co-18Cr-20Ni-4^{v}/o ThO_2 powders were prepared by the Flash Drying Selective Reduction Process starting with an aqueous solution of metal salts containing colloidal ThO_2. Procedures were developed for processing the powders into extruded rods of substantially 100% of theoretical density. The best procedure resulted in a rod containing a median ThO_2 size of 210 Å after a 100 hour, 1205°C stability heat treatment.

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I. SUMMARY

The objective of the program was to produce a cobalt base dispersion-strengthened alloy from a flash dried aqueous solution containing the dispersoid in colloidal form.

Four lots of 11 kg each of Co-18Cr-20Ni-4 $^{v}/o$ ThO_2 powder were pilot produced using various processing conditions.

X-ray diffraction showed the reduced powders to be essentially a cobalt base solid solution containing a ThO_2 addition. Micrographs of extracted dispersoid particles of one lot of powder showed a median particle size of 195 Å.

Procedures were developed for pressing and sintering 110g billets of each lot of powder and for extruding these billets into rod of substantially 100% of theoretical density.

The microstructural parameters on the extrusion showing the best combination of properties before and after a 100 hour, 1205 °C stability heat treatment were as follows:

		As Extruded	As Heat Treated
Volume Fraction - %	-	4.53	6.26
Mean Free Path - microns	-	1.98	1.40
Average Particle Diameter - Å	-	1410	1470
Median Particle Diameter - Å	-	--	210*

*Extracted Particle Micrograph

II. INTRODUCTION

New air breathing engine designs require materials with high temperature strength and oxidation resistance exceeding those of materials now commercially produced. A need exists for a superalloy with a stress rupture life of at least 3,000 hours at 2,000 °F (1,100 °C) and at 15,000 PSI (100 N/mm^2).

Nickel and cobalt superalloys which are generally used in present day aircraft are only useful up to a maximum temperature of 1,800 °F (1,000 °C). These alloys are generally strengthened by precipitation of carbide and gamma prime particles but the particles dissolve or agglomerate above 1,800 °F (1,000 °C). To exceed this temperature a more stable particle has to be used.

A promising approach for achieving high temperature strengths is the utilization of dispersion strengthening mechanisms by insoluble, hard, ultrafine thoria particles which are uniformly incorporated in a metal matrix. T-D Nickel has demonstrated the feasibility of producing a thoria dispersion-strengthened alloy with 1,800 °F (1,000 °C) stress rupture properties in excess of the best cast or wrought nickel or cobalt base alloys. However, the oxidation resistance and lower temperature properties of this material are low. To overcome these deficiencies alloying has been attempted. Efforts to create such dispersion-strengthened oxidation-resistant alloys have run into difficulties because of an inability to disperse fine thoria particles in the metal matrix in a completely random and homogeneous manner (1, 2, 3, 4, 5).

The objective of NASA Contract NAS 3-11161 was to determine whether a cobalt base alloy of acceptable characteristics and properties could be made from a flash dried solution containing the dispersoid in colloidal form.

It has been previously demonstrated that homogeneous alloy powders could easily be made by Flash Drying Selective Reduction Process (4). However, when this process was used for flash drying a solution containing the base metals and thorium nitrate, an alloy resulted in which the thoria particles were generally large and unevenly distributed. This was attributed to an uneven and insufficient formation of thoria nuclei during the oxide formation from the nitrates. It was therefore proposed that the problem be overcome by starting with a solution in which the thoria particles were already present so that nucleation of the thoria could be bypassed. The addition of thoria in colloidal form to a solution of the base metals prior to flash drying seems to be the logical path to follow. The question to be resolved here is whether such colloidal particles will agglomerate during the processing of the alloy. Ideally, and as required by the contract, these thoria particles should form a dispersoid of 4 volume percent having an average particle size of 0.1 micron or less and an average interparticle spacing of less than 2 microns. Also impurity particles should constitute less than 15% of the thoria particle volume. These requirements are based on the work of Gensamer and Co-workers (6, 7) Lenel and Ansell (8) and others who both calculated and demonstrated that for the oxide particles to be effective strengtheners, the sizes and interparticle spacing must be as given above.

The purity requirement is based upon the observations that the impurity particles tend to agglomerate and weaken the alloy and thus should be kept as low as practicable.

The alloy matrix composition was chosen from the studies performed by A. L. Mincher (9) who found that a thoria dispersion strengthened cobalt base alloy with 20Ni and 18Cr had desirable properties over the temperature range of interest.

III. PROCESS OUTLINE

The general process used for the manufacture of the powders and for the powder consolidation is shown in step chart form in Figure 1.

The process has been divided into four major sequences:

1. Preparing the oxides, (Steps 1 - 4).
2. Reduction Processes (Steps 5 - 8).
3. Consolidation and Extrusion (Steps 9 - 15).
4. Evaluation of the Extrusions (Steps 16 - 18).

IV. PREPARATION OF OXIDES

A. Colloidal ThO_2

Colloidal ThO_2 of four size ranges were purchased and these were checked for size using X-ray diffraction on the solids and areal analyses on electron photomicrographs supplied by the manufacturer. Comparisons of the manufacturer's analyses, topographical analyses, and X-ray diffraction analyses are shown in Table 1. The micrographs used for the topographical analyses are shown in Figures 2, 3 and 4. The 50 - 150 Å colloidal ThO_2 was chosen for this work because it represented the smallest size and a size where the topographical and X-ray diffraction analyses checked with the manufacturer's stated size range.

B. Formulation of Metal Salt-Colloidal ThO_2 Solutions

The objective was to develop a solution-colloidal ThO_2 suspension formulation which would be stable so that the resulting solution-suspension could be fed to the Flash Dryer before agglomeration or precipitation of the ThO_2 occurred. A desirable formulation would contain salts in high concentration so that the flash drying could be practiced at a practical rate.

A series of experiments described in Appendix I, were performed to develop this formulation. It was concluded that the best formulation would be to start with a 35% nitrate salt solution and to meter into this solution just before the Flash Dryer, a colloidal ThO_2 suspension of 30-100g/dm^3 concentration.

The stock solutions for the various constituents of the alloys for this program were prepared as follows:

a. The cobalt nitrate stock solution was made by dissolving 1 part of cobalt powder in 7 parts of 45 per cent (by weight) nitric acid in a jacketed stainless steel reactor. The solution was filtered and pumped into a stainless steel storage tank. A total of 280 gallons ($1.06m^3$) of stock solution was prepared; the solution was analyzed at ambient temperature for cobalt (approximately 13.5%) and used for formulations for the various alloys.

b. Nickel Nitrate Stock Solution - In a manner similar to above, nickel powder was converted into 280 gallons ($1.06m^3$) of a 12.75% nickel solution.

c. Chromium Solution - A weighed amount of chromium nitrate ($Cr(NO_3)_3 9H_2O$) was dissolved in an equal weight of cold water.

d. Thoria Solution - 58g of colloidal ThO_2 of 50-150 Å nominal size were dispersed in one dm^3 of distilled H_2O.

C. <u>Flash Drying</u>

Weighed amounts of the various stock solutions calculated to yield a 4.36kg batch of alloy powder were blended by stirring at ambient temperature to form a homogeneous solution. A dual feed system was set up on a Flash Dryer so that a correct proportion of the colloidal ThO_2 suspension was fed to a line carrying the metal nitrate solutions. The point of juncture of the two solutions was just before the solutions entered the Flash Dryer. The junction was made here to prevent possible precipitation of the colloidal ThO_2. The mixed solutions were flash dried by pumping controlled amounts of liquids into a perforated pipe from which droplets fell on a rotating internally heated drum.

The drum was surrounded by a stainless steel housing and connected to an acid recovery system. The temperature of the drum was maintained at 200 °C. The product was scraped off the drum by a stainless steel "doctor blade".

Sufficient blended solutions were flash dried by the above procedure to yield 43.6kg of alloy.

A chemical analysis of the flash dried material showed only 0.003% nitrogen present. This indicated that the decomposition of the nitrate salts was substantially complete.

X-ray diffraction analyses for phases present and ThO_2 particle size were made and the results are shown in Table 2.

D. Calcination

The object of this step was to stabilize the ThO_2 size. Since the chemical analysis on the flash dried material indicated that the evolution of the acid gases was practically complete, it was decided not to calcine one 11 kg batch of powder (hereinafter referred to as Procedure A Powder) and to calcine the remainder. The powder was fed into a rotary calciner and heated at 400 °C for 15 minutes in air.

An X-ray diffraction study was made on this material and the results are shown in Table 2.

The powder from the Flash Dryer and Calciner is approximately 4 mesh and finer. Previous work by this contractor had shown that a - 50 mesh oxide powder is necessary for proper reduction and compaction of the powder. The calcined powder was therefore ground in a hammer mill. Substantially 100% recovery of - 50 mesh powder was obtained.

V. REDUCTION PROCEDURES

The object of the reduction procedures was to reduce the non-ThO_2 oxygen to a level of 0.03% or below without agglomerating the ThO_2. Four procedures were investigated and these are shown in step chart form in Figure 5. The details of the procedures are given below:

First Reduction Procedures A, C, and D.

The object of the first reduction was to remove as much oxygen in a comparatively short time and at a low temperature.

The reduction was carried out in a rotary calciner for 20 minutes at 925 °C. Procedure A powder was reduced under dissociated ammonia while Procedure C and D powders were reduced under hydrogen.

Due to some agglomeration of the powder during the reduction step, it was necessary to regrind the powder to -50 mesh. This step was done in a hammer mill.

A weight loss analysis showed the non-ThO_2 oxygen content to be 6.16% on Procedure A material and 7.3% on Procedure C and D material. A nitrogen analysis showed the Procedure A powder to contain 0.012% N and Procedure C and D material to contain 0.003% N. Thus it can be seen that some nitrogen pickup occurs under dissociated ammonia.

An X-ray diffraction analysis on Procedure A material is shown in Table 2.

Second Reduction Procedure A, C, and D.

At this point graphite sufficient to react with the oxygen present was added. The objectives were non-ThO_2 oxygen and carbon contents of less than 0.03%. Procedure A powder was blended with 4.16% graphite and Procedure C and D powder was blended with 5.45% graphite.

All blending was done in an 8 dm^3 stainless steel twin shell blender.

The blended powders were loaded into perforated boats and reduced in a metal muffle furnace at 1095 °C. Procedure A powder was heated for 5 hours under 75%H_2, 25%N_2; Procedure C and D powders were heated for 2 hours under hydrogen.

Third Reduction Procedure D

The object of this reduction was to further reduce the oxygen and carbon levels. Procedure D powder was put back on the perforated boats and put back in the muffle furnace and reduced under hydrogen at 1205 °C for two hours.

One Step Hydrogen Reduction Procedure B

The object of procedure B was to reduce the oxides directly to metal. A few preliminary reducing experiments were run at 1205 °C for various lengths of time with hydrogen as the reducing gas. The results are shown in Table 3. The bulk of the powder was reduced at 1205 °C for 12 hours because this yielded the lowest oxygen content.

Comminution All Procedures

All the powders sinter together during the reduction step and it is necessary to break the resulting powder cake. A jaw crusher was used to deagglomerate the powder to approximately -4 mesh.

The course powders were then ground to approximately -50 mesh in a hammer mill.

Analyses of Reduced Powders

All the powders were analyzed for carbon, oxygen and minor elements. Procedure A powder was also analyzed for major elements, phosphorus and nitrogen. The chemical analysis data is shown in Table 4. It is not clear why the non-ThO_2 oxygen was so high in Procedure A powder.

Procedure A and B powders were also analyzed for phases present and ThO_2 crystallite size and the results are shown in Table 2. It can be seen that a complete alloying was achieved and that there was an apparent difference in crystallite size between Procedure A and Procedure B powders.

In order to determine whether crystallite size and particle size were the same, it was decided to check the particle size of Procedure A powder by two methods. A sample of the powder was to be pressed and brought up to full density by explosive compaction. Electron photomicrographs using replication techniques were to be made on the densified piece, and particle size determined by lineal analysis. A particle extraction was also to be made on the densified piece, the extracted particles were to be analyzed by electron diffraction, and a particle size determination was to be made by A Quantimet (QTM) Image Analyzing Computer. Unfortunately, the powder only compacted to 70% of theoretical density using explosive compaction. The powder was then canned and warm rolled but full density was not achieved. The electron photomicrographs showed many voids and was not suitable for lineal analyses. However, the extraction of the particles was more successful and two electron photomicrographs are shown in Figures 6 and 7. Two electron diffractions were made on two different areas and except for a few lines which are unidentified, the pattern agrees with the standard pattern given by ASTM for ThO_2. The data is shown in Table 5.

The medium particle size was shown to be 195 Å which is close to the X-ray diffraction crystallite size. A histogram of the particle sizes is shown in Figure 8.

VI. CONSOLIDATION, EXTRUSION, AND EVALUATION

A. General

It has been found advantageous from previous work to press and sinter billets and to extrude the resulting billets into rod. The sintering of the billets removes the residual oxides in the powders. Extruding pressed and sintered billets versus extruding loose powders simplifies the can design. The extrusion completes the densification of the sintered billets to substantially 100% of theoretical density.

B. Sintering

Two consolidation procedures were used as shown in Figure 9. Powders from Procedures B, C, and D reductions were low in non-ThO_2 oxygen and would be used without further reductions. Powder from the Procedure A reduction was high in oxygen. Therefore in order to use this powder, an additional reduction had to occur during the sintering. An addition of graphite sufficient to reduce it to 0.03% maximum was made. Specifically each 2.25kg batch of Procedure A powder was blended with 0.3 weight % graphite (99.9% C) in a twin shell 4 dm^3 stainless steel blender.

1.5" (3.8 cm) O.D. x 1.5" (3.8 cm) long slugs were pressed of each powder in a spring-loaded die on a 200 ton (1.8×10^6N) hydraulic press. Procedure A powder was pressed at 40 TSI (560 N/mm^2) because it was desired to have a billet dense enough for the carbon to diffuse evenly and to react with the non-ThO_2 oxygen.

Pressed billets of Procedures B, C, and D powders were to be sintered in a hydrogen atmosphere and therefore low density billets were desirable for reaction of the oxides with the gas. The powders were therefore pressed at 10 TSI (140 N/mm^2).

The pressed slugs were sintered at temperatures and times shown in Table 6. Sintering run Nos. 1 and 2 were made to study the effects of temperature difference in sintering in vacuum. The higher sintering temperature increased the density of the billets, drove the carbon-oxygen reaction more to completion and did not increase the average ThO_2 crystallite size. Sintering run Nos. 1 and 3 were made to study the effect of time differences in sintering in vacuum. The longer sintering time did not increase the density of the billet but seemed to have driven the carbon-oxygen reaction more to completion. Sintering run Nos. 3 and 8 were made to study the effect of sintering in vacuum and in dissociated ammonia (75% H_2, 25% N_2). Sintering in dissociated ammonia did not increase the density of the billet as much as in vacuum but apparently drove the carbon-oxygen reaction more to completion. Sintering run Nos. 3 and 9 were made to study the effect of sintering for 8 and 12 hours in vacuum. The comparatively large increase in density in run No. 9 billet and non comparative chemical analyses can only be ascribed to the fact that a new lot of powder was used in run No. 9. Run Nos. 1 and 10 were made to study the effects of sintering under the same conditions (2 hours in vacuum) two lots of powder. While the density of the billets were the same, the carbon and oxygen analyses were not comparable. Whether the difference in the carbon and oxygen analyses were due to differences in reactivity of two lots of powder or inaccuracies of chemical analyses is not known at the present time. Sintering run Nos. 12 and 20 were made to study the effects of sintering different lots of powder in hydrogen for 4 and 2 hours and at the same temperature. Fairly comparative densities and chemistries were obtained. Sintering run No. 19 was made to study the effect of sintering for 2 hours in hydrogen at 1095 °C. The larger carbon and oxygen content of the resulting billet when compared to run Nos. 12 and 20, can be ascribed to the lower sintering temperature.

C. Extrusion of Billets

The billets from sintering run Nos. 8, 12, 19, and 20 were canned in mild steel cans of dimensions shown in Figure 10 and the cans were evacuated to one micron absolute pressure and sealed off.

The cans were heated for 30 minutes at temperatures indicated in Table 6 and extruded on a 700 ton (6.2×10^6N) press converted for small vertical extrusions. Figure 11 shows the appearance of a sintered billet, canned slug, degassed and sealed can, and an extruded specimen. Figure 12 shows the equipment and the steps used in the vertical extrusion used for this work.

The extruded specimens were decanned with hot 50% nitric acid.

D. Evaluation of the Extrusions

The extruded rod was evaluated in the as extruded and heat treated conditions. The heat treated rods were held at 1205 °C for 100 hours in vacuum (10^{-4} torr). The purpose was to check the stability of the microstructure by comparing the microstructure parameters before and after the heat treatment. The evaluation consisted of the hardness and density checks (Table 7) and microstructural examinations comparing the dispersoid parameters, types of precipitates and void formation.

1. As Extruded Rods

Structures obtained by optical and replica electron photomicrography are shown in Figures 13 through 20. Lineal analyses were made on the electron micrographs and the results are presented in Table 7.

The large volume percentage of dispersoid in Extrusion No. 8 was unexpected. Even if one is to assume that all the non-ThO_2 oxygen is tied up as Cr_2O_3 and the carbon as Cr_3C_2, the volume fraction of the dispersoid would only be increased by a maximum of 0.5%. A spectrographic analysis was made on this extrusion and the result can be compared in Table 8 with the spectrographic analysis of the powder. Same pickup of impurities has taken place (probably in the blending step), but this still does not account for the excess percentage of dispersoid. In order to investigate anomalies found in the microstructure of this extrusion more fully, an electron photomicrograph (Figure 21) was made on the extracted particles. The size distribution of the particles was plotted, (Figures 22 and 23). The median particle diameter of 207 Å compares favorably with the median particle diameter of 195 Å obtained in the powder sample.

In Extrusion No. 12, the particle diameter obtained by lineal analysis of replication electron photomicrographs is 2020 Å. Therefore, a particle extraction was also made on this extrusion and an electron micrograph made of the particles. The micrograph is shown in Figure 24. The median particle size was found to be 207 Å, the size distribution of the particles are shown in Figures 25 and 26.

It was therefore concluded that the replica electron micrographs were not giving an accurate picture of the particle sizes.

2. Heat Treated Extrusions

Densities and hardness were measured on each rod and can be seen in Table 7. The hardness dropped on each extrusion and Extrusions 8 and 19 had the largest decrease. No explanation can be given at this time for this hardness decrease. The density changes were small for all extrusions and are probably within experimental error.

Optical photomicrographs and replica electron micrographs were made on each heat treated rod and these are shown in Figures 27 through 34. It should be noted on the electron micrographs that no voids were formed, that no new phases precipitated and that the dispersoids tended to spherodize. Lineal analyses made on the electron micrographs are shown in Table 7.

Since it was found on the extruded rods that surface replica micrographs were not showing the smallest particles, electron micrographs were again made of the extracted particles. Examples of the resultant micrographs are shown in Figures 35 (Extrusion No. 19) and 36 (Extrusion No. 20). The median particle sizes were found to be 157 Å and 210 Å. The size distribution plots are shown in Figures 37 through 40.

An additional set of extraction replicas on the same two extrusions were obtained from NASA-Lewis Research Labs and these are shown in Figures 41 and 42. About 96% of the particles on each micrograph are 217 Å or below which is in fair agreement with the median particle size determinations made in Figures 35 and 36.

In Figures 35 and 36 about 20% of the particles are larger than 600 Å and it was believed that these could be another phase. An electron diffraction analysis was run on the extracted particles and the data is shown in Table 9. The patterns appear to index with the standard ThO_2 pattern except that one point (2.54 Å) is not accounted for. From this data one might make the following assumptions:

1. The non-indexing of one point in the electron diffraction is significant and some of the particles are of unknown phase.

2. The non-indexing of one point is not significant and all the particles are ThO_2.

If assumption 1 is made, then one may further assume that the unknown phase is either a mixed oxide of the matrix alloy metals or a hard to reduce oxide picked up in one of the processing steps. In the former case, it would be advantageous to sinter the pressed billets in a can under very dry hydrogen to remove any matrix oxides still not reduced. In the latter case, care should be taken not to pick up any oxides in the processing equipment.

If one is to assume that all the large particles are ThO_2, then one should compare the particle size distributions of this alloy with those of other dispersion-strengthened alloys having improved properties. Inman and Smith (10) plotted the dispersoid size distributions of a Ni-2^v/o ThO_2 alloy and found about 6% of the particles larger than 600 Å. Raymond and Neumann (11) plotted the dispersoid size distribution in two Ni-20Cr-2^v/o ThO_2 alloys made by two manufacturers and found that each alloy had at least 16% of the particles larger than 500 Å and that some of the particles were up to 2000 Å. It may therefore be inferred that in all oxide dispersoid strengthened materials there is some growth of some of the particles so that a stable size distribution results and this may be the reason for the size distribution of the particles in this alloy.

Raymond and Neumann (11) also found that one of the two Ni-20Cr-2^{v}/o ThO_2 alloys had better high temperature stability and they attributed this to the difference in the average particle diameter of the two products; the more stable material had an average dispersoid diameter of 550 Å compared to 820 Å for the less stable product. The average particle diameter of Extrusions 19 and 20 were calculated to be 349 and 455 Å respectively indicating that both these extrusions had sufficient fine particles to be effective in strengthening the alloy at high temperatures.

VII. CONCLUSIONS

1. A Co-18Cr-20Ni-4^{v}/o ThO_2 alloy powder with acceptable microstructural parameters can be produced using the Flash Drying Selective Reduction Process. Furthermore, this alloy powder can be processed into rod of substantially 100% of theoretical density and having acceptable microstructural parameters. The following process parameters should be followed:

A. The starting solutions should consist of a colloidal suspension of 50-150 Å ThO_2 of a concentration of 30-100g/dm^3 and a 35% (by weight) solution of Co, Cr, Ni, nitrate solutions.

B. The colloidal ThO_2 suspension and metal nitrate solution should be mixed at a point just before both solutions enter the Flash Dryer.

C. The flash drying should be done at 200 °C.

D. The flash dried material should be calcined at 400 °C for 15 minutes.

E. The calcined oxides should be ground to minus 50 mesh.

F. The ground oxides should be first reduced at 925 °C for 20 minutes under hydrogen.

G. The first reduced material should be blended with sufficient high purity graphite to combine with the non ThO_2 oxygen.

H. The blended material should be second reduced at 1095 °C for 2 hours under hydrogen.

I. The second reduced material should be third reduced at 1205 °C for 2 hours under hydrogen.

J. The third reduced material should be ground to minus 50 mesh.

K. The resulting powder should be pressed into a billet at 10 TSI (140 N/mm^2).

L. The resulting billet should be sintered under -68 °C hydrogen for 2 hours at 1205 °C.

M. The sintered billet should be canned in mild steel and evacuated to 1 micron absolute pressure.

N. The canned billet should be extruded at a ratio of 10:1 at 1095 °C.

O. The extruded rod should be decanned in 50% nitric acid.

2. The alloy produced by this method contains ThO_2 as a fine dispersion while the median size of the dispersoid is 210 Å, (the ThO_2 is present in a range of sizes from 40 Å to 1500 Å). It is not certain at the present time whether the large particles are ThO_2, unreduced matrix oxides, or some refractory oxide picked up from the processing equipment. It is recommended that precautionary measures be taken to prevent pickup of refractory oxides by making sure all the processing equipment be cleaned prior to use and by discarding the first few pounds of powder going through each machine. It is also recommended that sintering of the pressed billets be done in special close fitting cans under very dry hydrogen so that any unreduced matrix metal oxides may be converted to metal.

3. It has been found that reducing of the metal powders and sintering of the pressed billets under dissociated ammonia (75% H_2, 25% N_2) tends to nitride the alloy due to small amounts of undissociated ammonia left in the gas. Therefore, this gas was found unsuitable for use in the process.

4. The Flash Drying Selective Reduction Process Using Colloidal ThO_2 is suitable for making other dispersion-strengthened materials such as Ni-Cr-ThO_2, Ni-Cr-W-ThO_2, and Co-Cr-Ni-W-ThO_2 alloys.

5. When the starting material for flash drying uses colloidal fine thoria, the particle size of the thoria in the consolidated and extruded alloy approximates that of the colloid. Particle size is thus predetermined. This represents a definite advantage over processes where thoria particles are formed by nucleation and growth as it was attempted in previous work for flash drying from a homogeneous nitrate solution (4).

VIII. RECOMMENDATIONS

1. A program should be initiated to determine fully the properties of the Co-18Cr-20Ni-$4^{v}/o$ ThO_2 alloy produced from powder obtained by the Procedure D reduction method. The alloy should be given suitable thermal and mechanical working to optimize its properties.

2. The following two alloys should be prepared and the properties be determined and optimized by a property improvement program:

(a) Co-20Cr-10Ni-15W-2ThO_2

(b) Ni-18Cr-3Mo-24Fe-4ThO_2

The cobalt base alloy is a modification of alloy L-605. The base alloy combines good formability and excellent high temperature properties and has been used for many years in jet engine parts and industrial furnace applications. The alloy is resistant to oxidation and carburization to 1900 °C. Dispersion strengthening may improve the high temperature strength to the NASA goals.

The nickel base alloy is a modification of Inconel 718. The base alloy exhibits good mechanical and fabrication properties at both high and low temperatures and has excellent resistance to sulfurization. This alloy is normally hardened by precipitation of Ni_3Cb. Substituting ThO_2 for the columbium may improve the high temperature strength to NASA goals.

REFERENCES

(1) R. C. Nelson and R. Widmer, "Development of Dispersion-Strengthened, Nickel-Molybdenum, Nonoxidation-Resistant Alloys." NASA Report CR-54502, April, 1967.

(2) R. Grierson, L. J. Bonis, R. Rogers and H. L. Livingston, "The Development of Dispersion-Strengthened Nickel Chromium Oxidatiion Resistant Alloys." NASA Report CR 54523, July, 1966.

(3) H. M. McCullough and M. Ortner, "Development of a Dispersion Strengthened Nickel Base Alloy Using the High Intensity Arc Process." NASA Report CR-54520.

(4) B. H. Triffleman, "Development of Procedures for Producing Dispersion-Strengthened Cobalt Base Alloys by the Flash Drying Selective Reduction Process." NASA Report CR-54516, December, 1967.

(5) R. F. Cheney and W. Scheithauer, "Development of Cobalt Base Dispersion-Strengthened Alloys." NASA Report CR-54599, December, 1968.

(6) M. Gensamer, W. S. Pellini and J. R. Low, "Tensile Properties of Pearlite, Bainite and Spheroidite," Trans. Am. Soc. Metals, 30, 983 (1942).

(7) M. Gensamer, "Strength and Ductility," Trans. Am. Soc. Metals, 36, 30 (1946).

(8) F. V. Lenel and G. S. Ansell, "Powder Metallurgy." Edited by Werner Leszynski, Interscience Publishers.

(9) A. L. Mincher, "Research on Dispersion Strengthened Cobalt Base Alloys." Air Force Materials Laboratory Technical Report AFML-TR 65-442, Part 2, March, 1967.

(10) M. C. Inman and P. J. Smith, "Oxide Dispersion Strengthening", G. S. Ansell et al, editors, Gordon and Breach Science Publishers, New York, 1968, p. 291.

(11) L. Raymond and J. P. Neumann, International Journal of Powder Metallurgy, 5, No. 2, 97, (1969).

TABLE 1

RESULTS OF X-RAY AND TOPOGRAPHICAL ANALYSES OF COLLOIDAL ThO_2 SAMPLES

Manufacturer's Designation	Topographical Analyses	X-Ray Diffraction Analyses
50 - 150 Å	100 Å	117 Å
100 - 300 Å	200 Å	149 Å
300 - 600 Å	N. D.	745 Å
400 - 800 Å	425 Å	218 Å

N. D. = Not Determined

TABLE 2

ThO_2 CRYSTALLITE SIZE AND PHASES PRESENT IN VARIOUS STAGES OF POWDER PRODUCTION

Stage	Ave. Crystallite Size - Å	Phases Present
Starting ThO_2 Sol.	117	
Flash Dried	78	$CoO.Co_2O_3$ ThO_2
Calcined	96	$CoO.Co_2O_3$ ThO_2
1st Reduced (Procedure A)	186	Co (f.c.c.) $CoO.Cr_2O_3$ ThO_2
2nd Reduced (Procedure A)	228	Co (f.c.c.) ThO_2
Reduced (Procedure B)	576	Co (f.c.c.) ThO_2

TABLE 3

RESULTS OF REDUCING GROUND OXIDES UNDER HYDROGEN AT 1205°C FOR VARIOUS TIME PERIODS

TIME - HOURS	NON-THO$_2$ O$_2$	REMARKS
2	2.62	Powder Pyrophoric
4	2.13	Powder Pyrophoric
8	0.87	Powder Stable
12	0.03	Powder Stable

TABLE 4

CHEMICAL ANALYSES OF POWDERS MADE BY FOUR PROCEDURES

Reduction Procedure	A	B	C	D
Powder Lot No.	13B-28	12A-38	12A-42	12A-43
Element				
Co	61.03			
Cr	16.31			
Ni	18.19			
ThO_2	4.41			
C	0.04	< 0.01	0.04	< 0.02
O**	0.40	0.04	0.04	0.00
N	0.039		0.004	0.003
P	0.006			
S	0.004			
Ag	*	*	*	*
Al	0.01	0.01	0.01	0.01
As	*	*	*	*
B	*	*	*	*
Ba	*	*	*	*
Bi	*	*	*	*
Ca	0.02	0.02	0.05	0.05
Cb	*	*	*	*
Cd	*	*	*	*
Cu	< 0.01	< 0.01	< 0.01	< 0.01
Fe	0.2	0.2	0.02	0.02
K	*	*	*	*
Li	*	*	*	*
Mg	< 0.01	< 0.01	< 0.01	< 0.01
Mn	< 0.01	< 0.01	0.01	< 0.01
Mo	< 0.01	< 0.01	< 0.01	< 0.01
Na	*	*	< 0.01	< 0.01
Pb	*	*	*	*
Sb	*	*	*	*
Si	< 0.01	< 0.01	0.05	0.05
Sn	*	*	*	*
Sr	*	*	*	*
Ti	*	*	< 0.01	< 0.01
V	*	*	*	*
W	*	*	*	*
Zn	*	*	*	*
Zr	*	*	*	*

* Not Detected

** Non-ThO_2

TABLE 5

ELECTRON DIFFRACTION DATA FOR THO$_2$ PARTICLES EXTRACTED FROM THE COMPACTED AND DENSIFIED PROCEDURE A POWDER

No. 1	No. 2	ThO$_2$
3.26 Å	3.25 Å	3.23 Å
3.10	3.10	
		2.80
2.65	2.63	
1.97	1.96	1.98
1.86	1.87	
	1.68	1.69
1.59	1.59	1.61
1.51	1.50	
1.49		
	1.38	1.40
1.34		
1.30	1.29	1.28
		1.25
1.19	1.19	
1.16	1.15	1.14
1.10		
1.05	1.05	1.07
0.99	0.99	0.99
		0.95
		0.93
0.89	0.90	0.89
		0.85
		0.84

TABLE 6

RESULTS OF PRESSING, SINTERING, AND EXTRUSION EXPERIMENTS ON Co-18Cr-20Ni-4^{v}/oThO$_2$ POWDERS

Sintering Run No.	1	2	3	8	9	10	12	19	20
Extrusion No.	---	---	---	8	---	---	12	19	20
Powder Reduced by Procedure	A	A	A	A	A	A	B	C	D
Powder Lot No.	13A-22	13A-22	13A-22	13B-28	13B-28	13B-28	12A-38	12A-42	12A-43
Pressed at N/mm^2	560	560	560	560	560	560	140	140	140
Green Density -% T.D.	66.6	66.3	66.4	65.4	65.3	65.4	49.4	50.6	51.6
Sintering Temp. - ^{o}C	1095	1205	1095	1095	1095	1095	1205	1095	1205
Sintering Times - Hrs.	2	2	8	8	12	2	4	2	2
Sintering Atmosphere	Vac.	Vac.	Vac.	75H$_2$, 25N$_2$	Vac.	Vac.	H$_2$	H$_2$	H$_2$
Sintered Density - % T.D.	71.6	83.6	71.3	66.6	82.1	71.6	49.1	53.6	51.4
Carbon - %	0.09	0.03	0.05	0.04	0.03	0.03	$<$0.01	0.04	$<$0.02
Non-ThO$_2$ O$_2$ %	0.08	0.00	0.03	0.01	0.07	0.11	0.00	0.04	0.00
ThO$_2$ Crystallite Size - Å	259	259	231	---	---	---	---	---	---
Extrusion Temp. - ^{o}C	---	---	---	1095	---	---	1205	1095	1095
Extrusion Ratio	---	---	---	20:1	---	---	10:1	15:1	15:1

TABLE 7

EVALUATION OF EXTRUDED AND HEAT TREATED RODS OF Co-18Cr-20Ni-4^{v}/o ThO$_2$

Extrusion No.	8	12	19	20
Powder Reduced by Procedure	A	B	C	D
Extrusion Temp. - °C	1095	1205	1095	1095
Extrusion Ratio	20:1	10:1	15:1	15:1
Carbon - %	0.04	<0.01	0.04	<0.02
Non-ThO$_2$ O$_2$ - %	0.01	0.00	0.04	0.00
Extruded Properties:				
Hardness - Rc	39	37	41	39
Density - g/cc	8.57	8.55	8.59	8.58
Particle Volume Fraction - %	8.15	5.00	4.12	4.53
Average Particle Diameter - Å	1170	2020	1130	1410
Mean Free Path - microns	0.88	2.55	1.56	1.98
Median Particle Diameter* - Å	207	207	---	---
Heat Treated Properties:				
Hardness - Rc	33	35	34	35
Density - g/cc	8.55	8.58	8.57	8.58
Particle Volume Fraction - %	7.78	6.60	7.09	6.26
Average Particle Diameter - Å	1600	2200	1200	1470
Mean Free Path - microns	1.26	2.09	1.05	1.40
Median Particle Diameter* - Å	---	---	157	210

*From Extracted Particles Micrograph

TABLE 8

COMPARISON OF SPECTOGRAPHIC ANALYSES OF POWDER AND EXTRUDED ROD NO. 8

METAL	POWDER (Lot No. 13B-28)	EXTRUDED ROD (No. 8)
Ag	*	*
Al	< 0.01	0.2
As	*	*
B	*	*
Ba	*	*
Bi	*	*
Ca	0.02	0.02
Cb	*	*
Cd	*	*
Cu	< 0.01	< 0.01
Fe	0.2	0.2
K	*	*
Li	*	< 0.01
Mg	< 0.01	< 0.01
Mn	< 0.01	< 0.01
Mo	< 0.01	0.2
Na	*	*
Pb	*	*
Sb	*	*
Si	< 0.01	0.05
Sn	*	*
Sr	*	*
Ta	*	*
Ti	*	0.05
V	*	*
W	*	*
Zn	*	*
Zr	*	*

* Not Detected

TABLE 9

ELECTRON DIFFRACTION DATA ON ThO_2 PARTICLES EXTRACTED FROM PROCEDURE C AND D EXTRUSIONS

Ext. No. 19	Ext. No. 20	ASTM Std. ThO_2
3.21 Å	3.26 Å	3.23 Å
2.77	2.78	2.80
-	2.54	-
1.99	1.98	1.98
1.67	1.71	1.69
1.60	1.62	1.62
1.39	1.39	1.40
1.28	1.29	1.28
1.25	-	1.25
1.14	1.14	1.14
1.08	1.08	1.08
0.98	0.98	0.99
0.93	0.93	0.94

FIGURE 1

STEP CHART SHOWING MANUFACTURE OF ALLOY-OXIDE POWDERS AND CONVERSION INTO EXTRUDED ROD

Step Number

1A. Dissolve
1B. Filter
1C. Stock Solutions
1D. Mix Solutions
2. Flash Dry
3. Calcine
4. Grind
5. Reduce
6. Crush
7. Grind
8. Analyze
9. Blend

Step Number

10. Press
11. Sinter
12. Evaluate Billet
13. Can Billet
14. Extrude to Rod
15. Decan
16. Evaluate Extruded Rod
17. Heat Treat Extruded Rod
18. Evaluate Heat Treated Rod

FIGURE 2

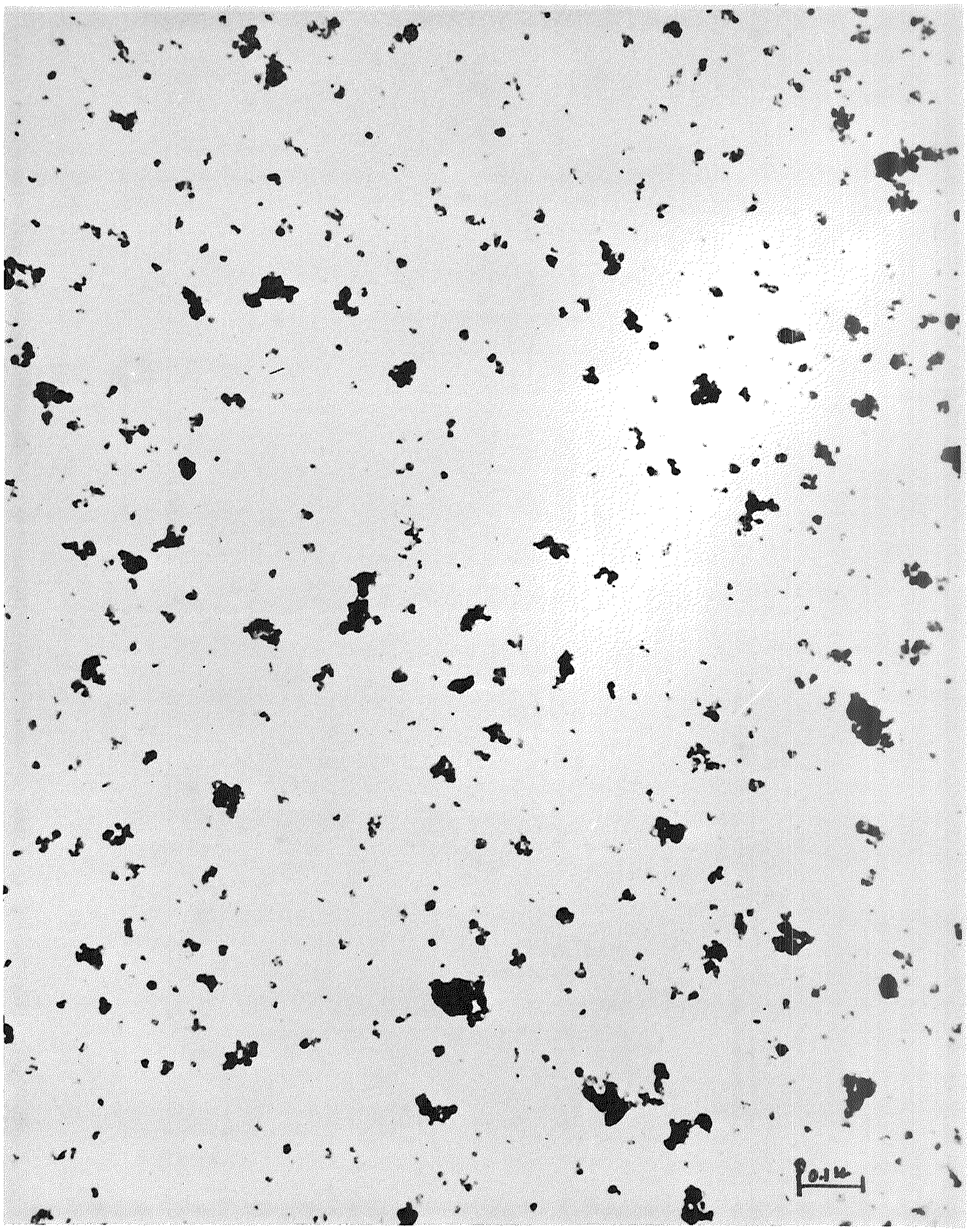


Photo No. 2375
Henley & Co.
G-403

Colloidal ThO_2
50 - 150 Å

Mag. 100,000X

FIGURE 3

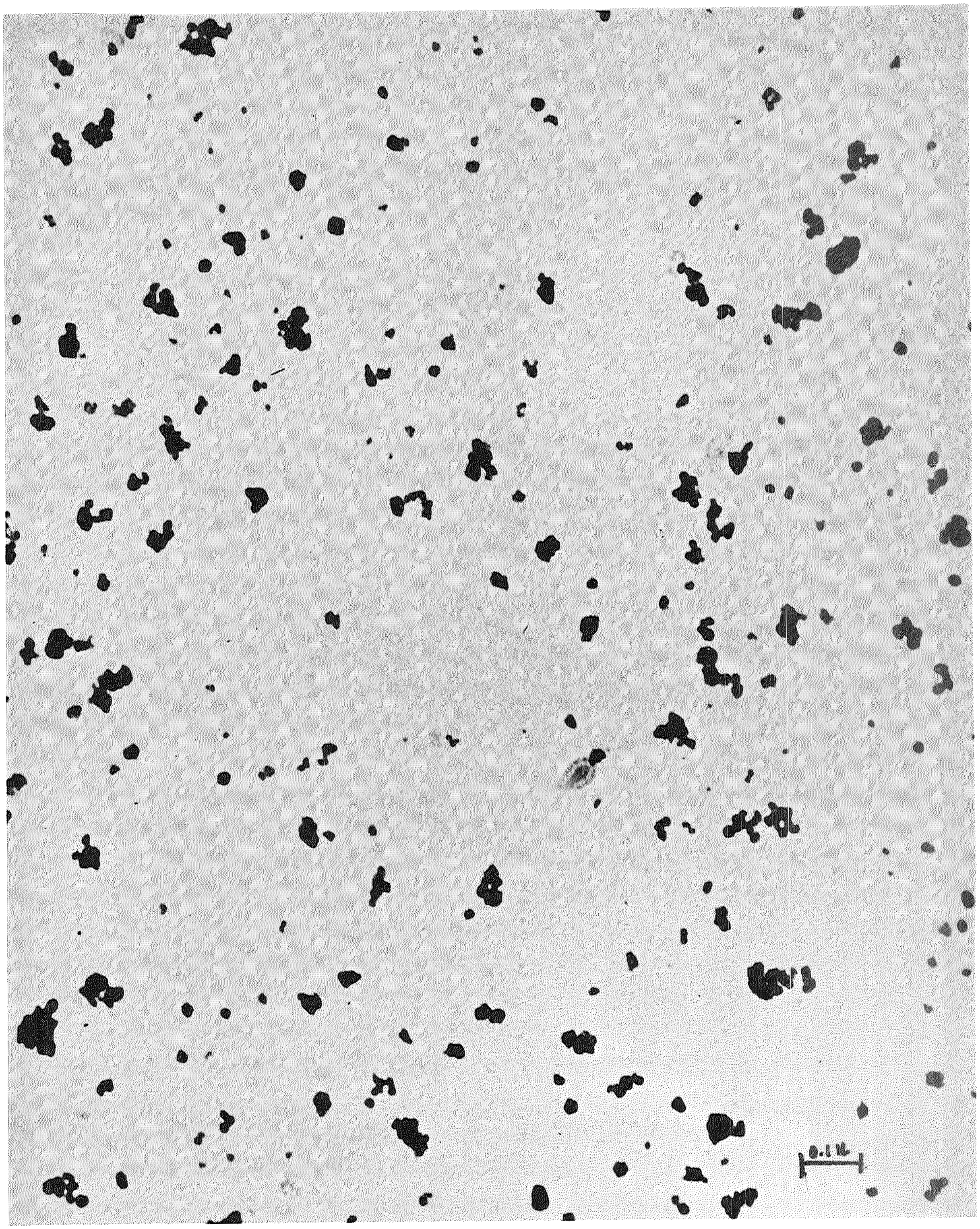


Photo No. 2376
Henley & Co.
G-401

Colloidal ThO_2
100 - 300 Å

Mag. 100,000X

FIGURE 4

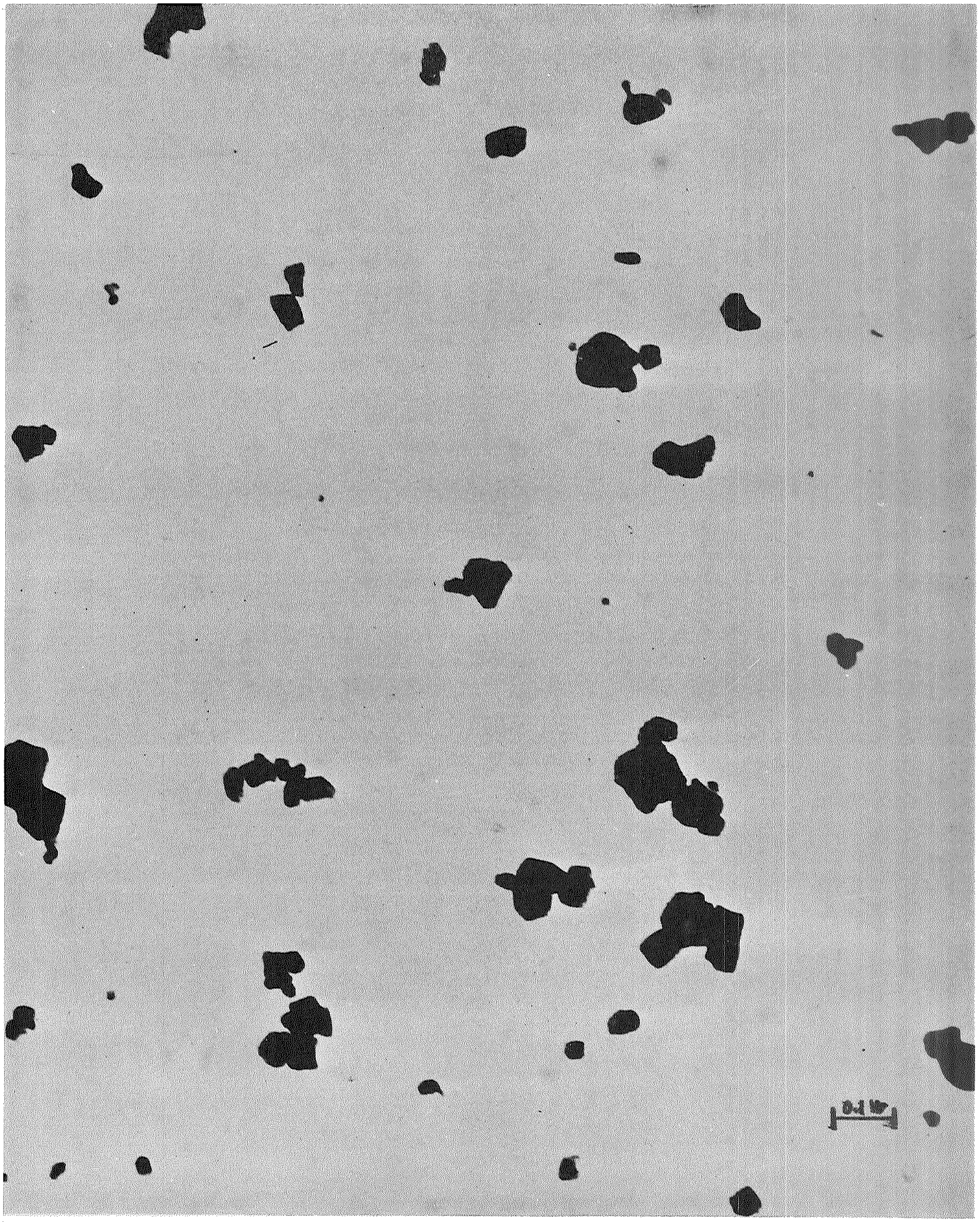


Photo No. 2373
Henley & Co.
G-402

Colloidal ThO_2
400-800Å

Mag. 100,000X

FIGURE 5

REDUCTION PROCEDURES FOR ALLOY-OXIDE POWDERS

A TWO STEP DISSOCIATED AMMONIA REDUCTION PROCEDURE

1. First Reduction ← $75H_2$, $25N_2$ to 6% O_2
2. Grinding
3. Blending ← Graphite
4. Second Reduction ← $75H_2$, $25N_2$ to 0.03% O_2

B ONE STEP HYDROGEN REDUCTION PROCEDURE

Reduce to ← H_2
0.03% O_2

C TWO STEP HYDROGEN REDUCTION PROCEDURE

1. First Reduction ← H_2 to 6% O_2
2. Grinding
3. Blending ← Graphite
4. Second Reduction ← H_2 to 0.05% O_2

D THREE STEP HYDROGEN REDUCTION PROCEDURE

1. First Reduction ← H_2 to 6% O_2
2. Grinding
3. Blending ← Graphite
4. Second Reduction ← H_2 to 0.05% O_2
5. Third Reduction ← H_2 to 0.00% O_2

FIGURE 6

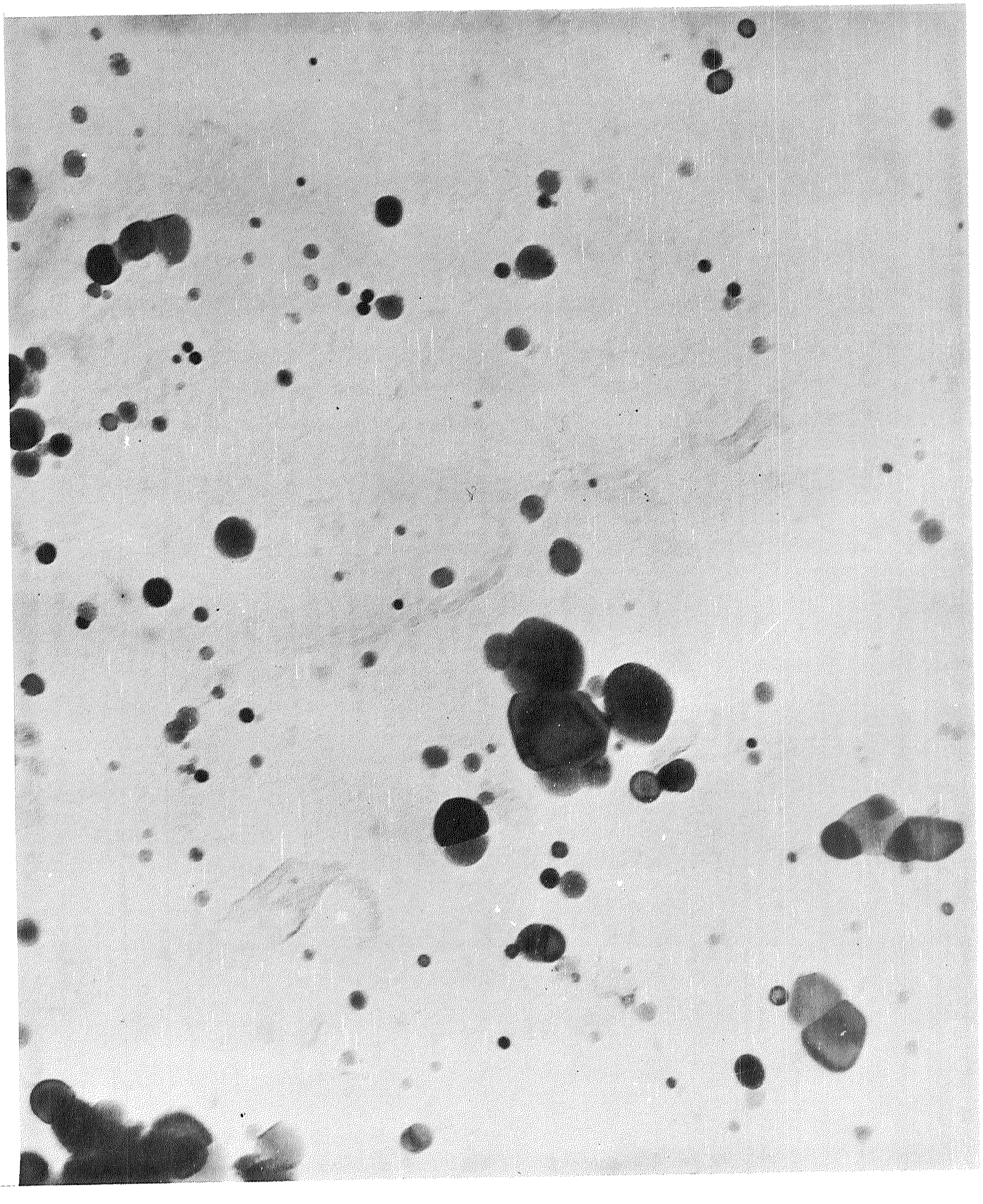


Photo No. 8958 C-W Co-18Cr-20Ni-4.6ThO_2 Mag. 150,000X
Batt. No. EH2172 Explosively Compacted and Hot Rolled
PP2-12A-29 Extracted Particles

FIGURE 7

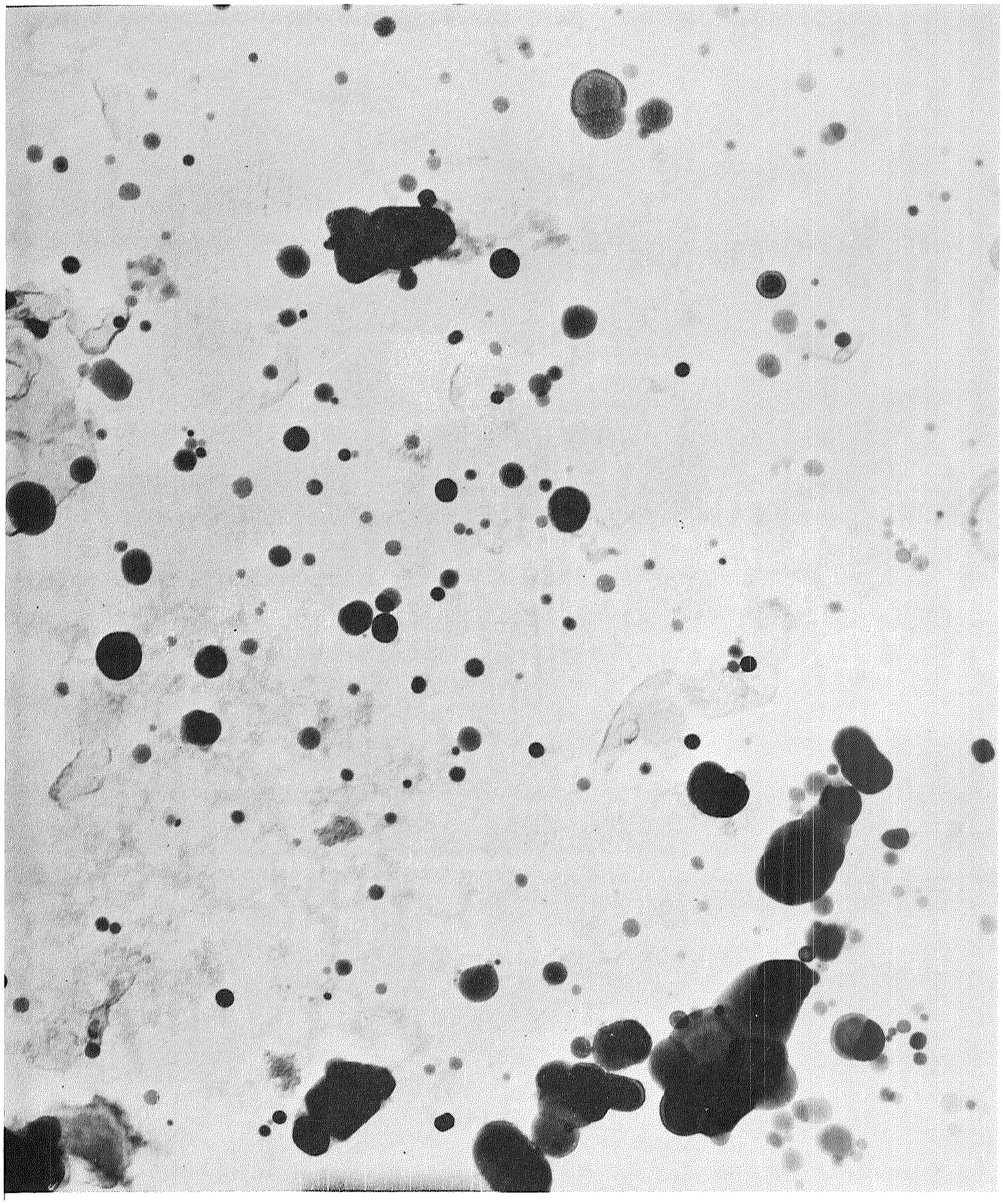
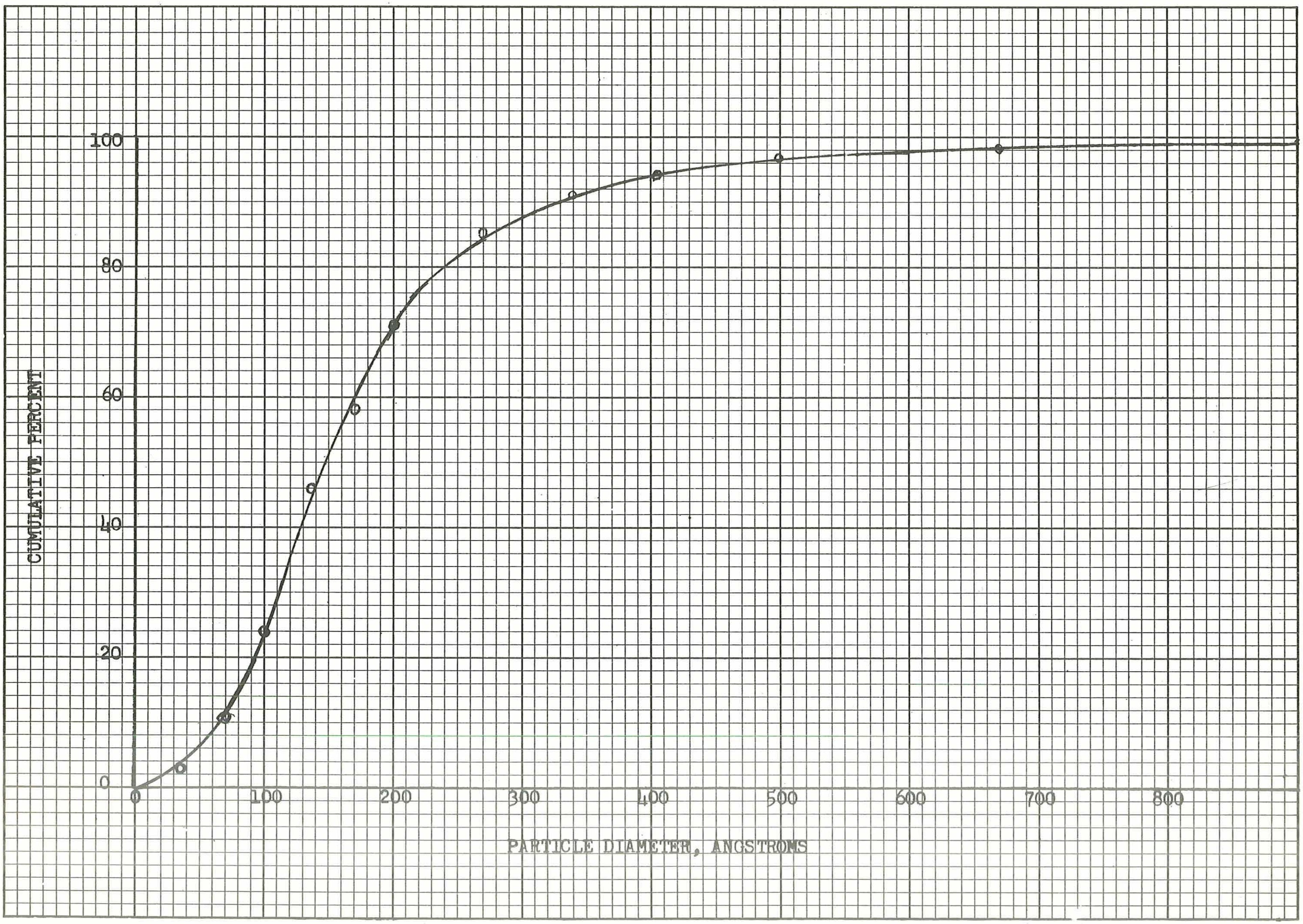


Photo No. 8957
Batt. No. EH2173
PP2-12A-29

C-W Co-18Cr-20Ni4.6ThO$_2$
Explosively Compacted and Hot Rolled
Extracted Particles

Mag. 150,000X

FIGURE 8



Particle size distribution of the ThO_2 particles extracted from the compacted and densified powder sample.

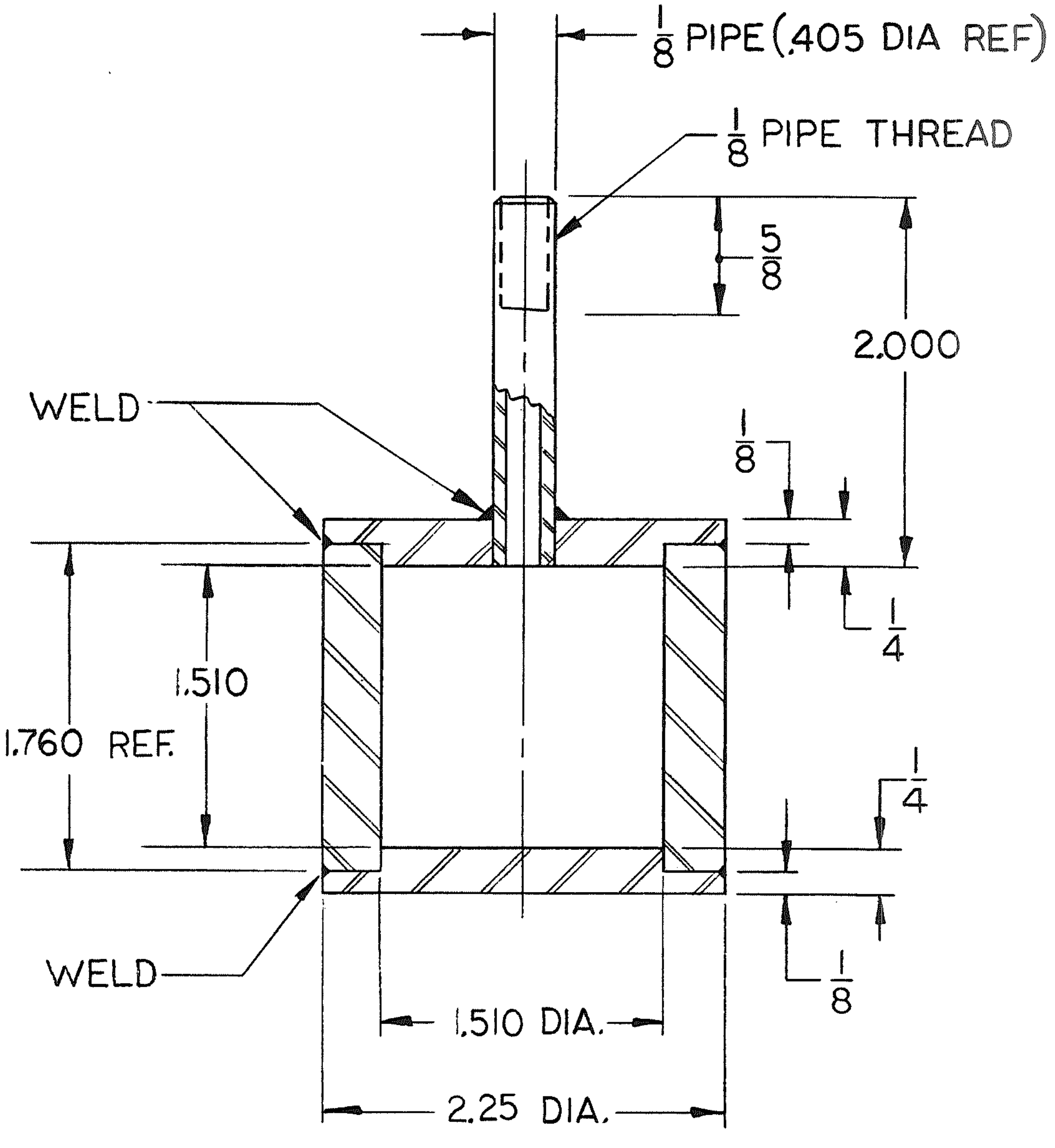
FIGURE 9

PROCEDURES FOR CONSOLIDATION OF ALLOY-OXIDE POWDERS

I. High O_2 Content Powder	II. Low O_2 Content Powder
1. Blend Graphite	1. ---
2. Press at 40 TSI (560 N/mm^2)	2. Press at 10 TSI (140 N/mm^2)
3. Sinter Under Vacuum and Dissociated Ammonia (75% H_2, 25% N_2)	3. Sinter Under H_2

4. Evaluate Billets
5. Can Billets
6. Extrude to Rod
7. Decan Rod
8. Evaluate Rod
9. Heat Treat Rod
10. Evaluate Heat Treated Rod

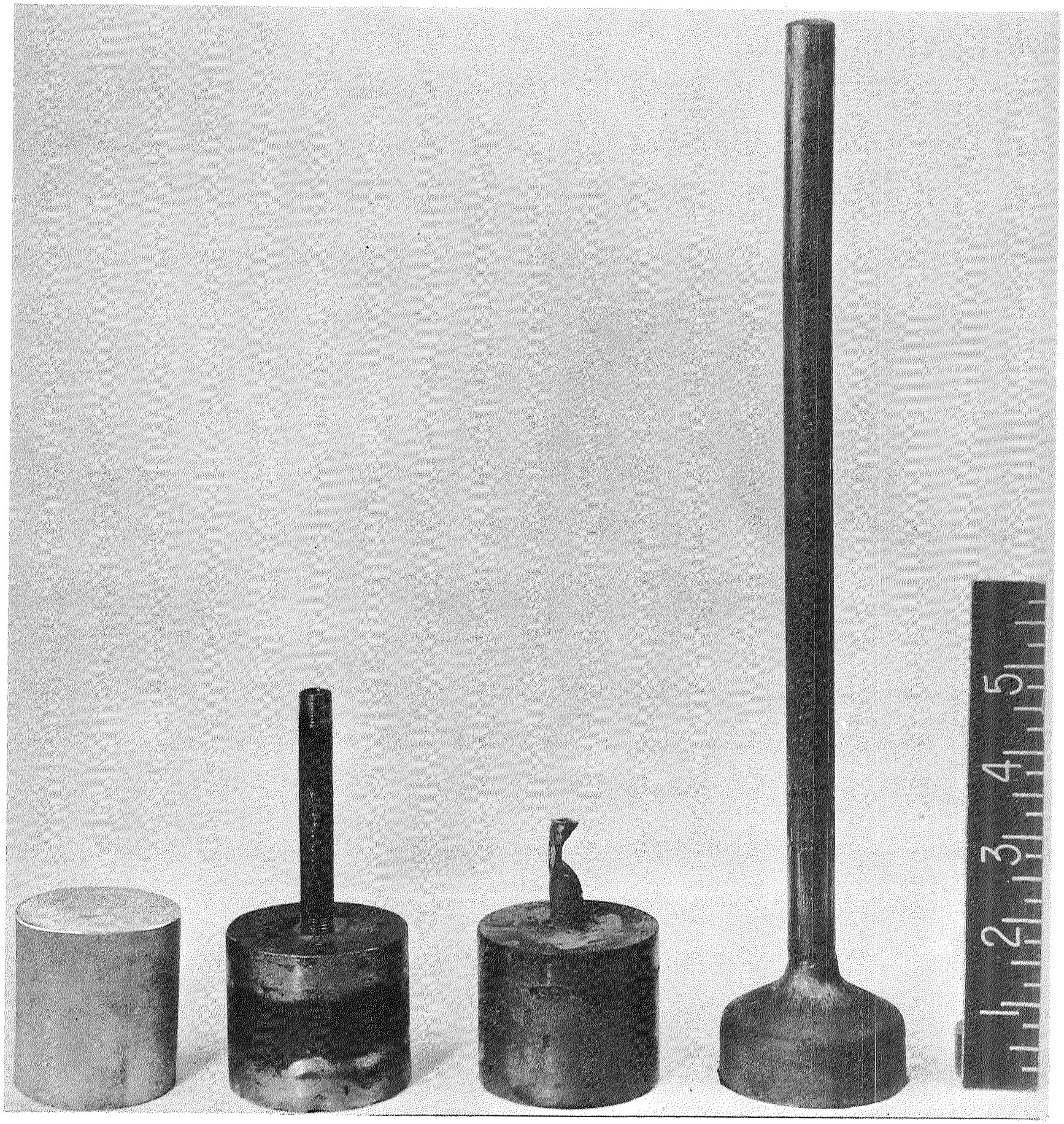
FIGURE 10
CANS FOR TEST EXTRUSIONS



MATERIAL :
LOW CARBON COLD DRAWN
SEAMLESS MECHANICAL
TUBING
COLD ROLL STEEL FOR
END PLATES

FIGURE 11

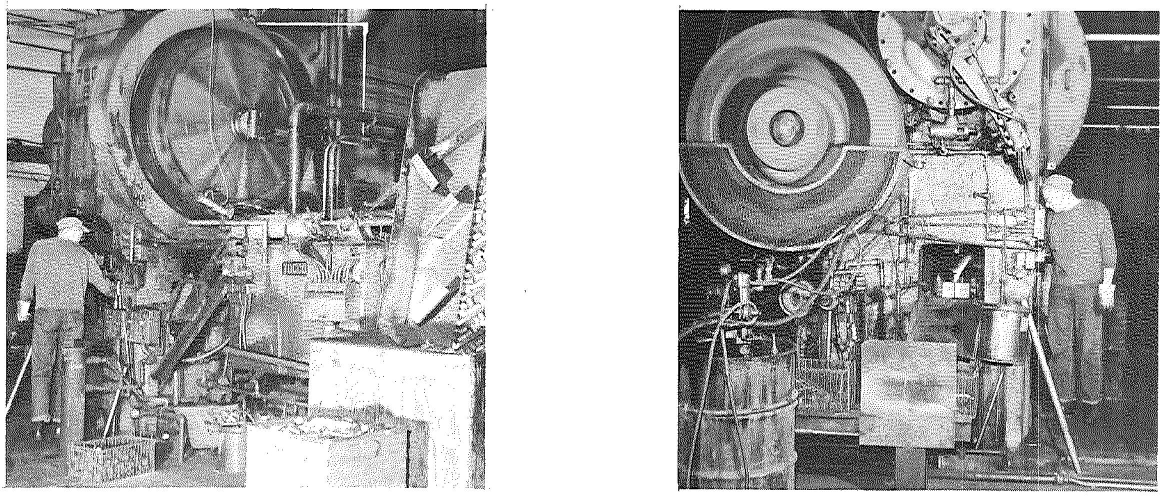
CURTISS-WRIGHT EXPERIMENTAL EXTRUSION STEPS



(1) Sintered Billet
(2) Canned Billet Section
(3) Canned and Degassed Billet
(4) Extruded Sample

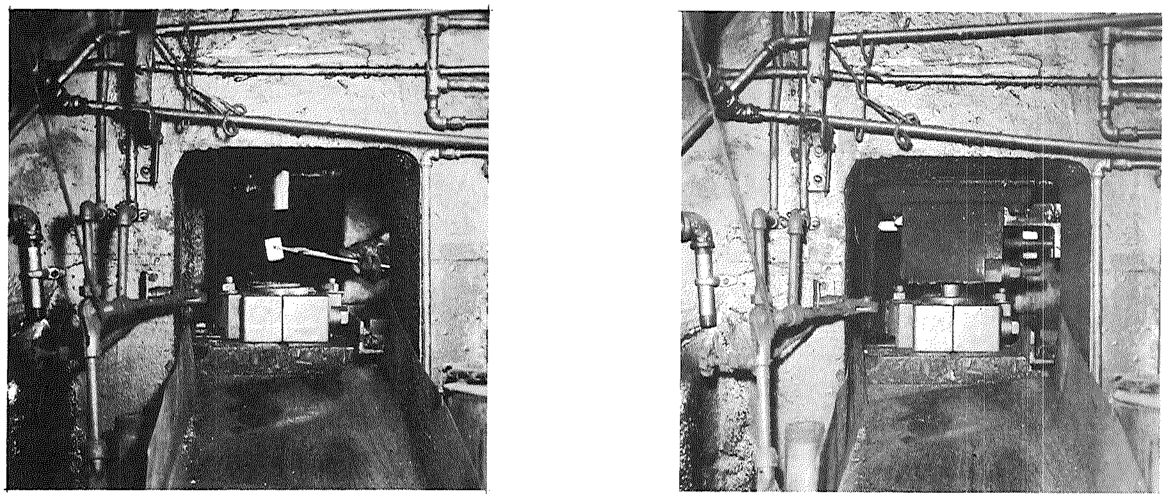
FIGURE 12

CURTISS-WRIGHT VERTICAL EXTRUSION SET-UP



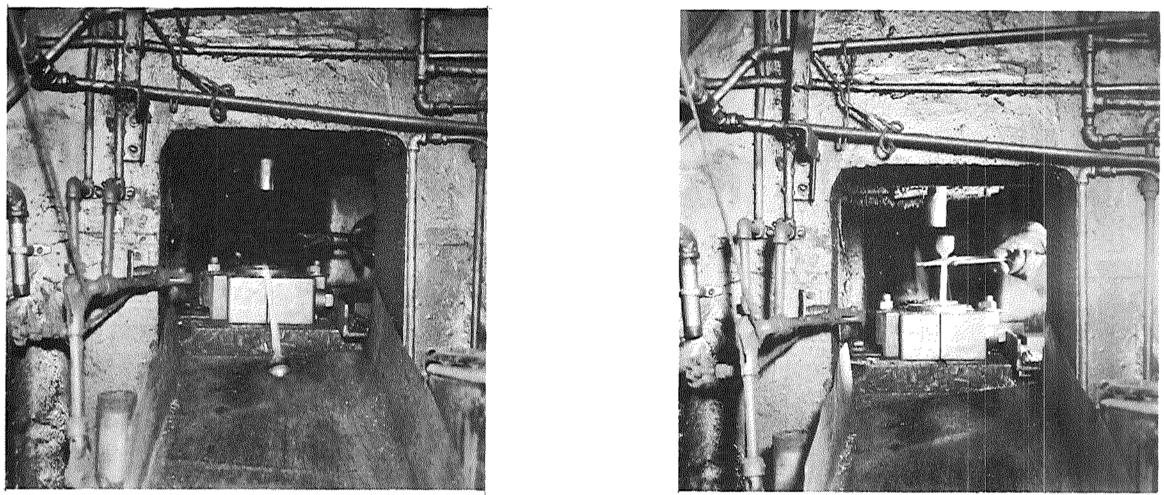
OVER ALL VIEW

SIDE VIEW



HOT BILLET

EXTRUSION



EJECTION

SAMPLE PART

FIGURE 13A

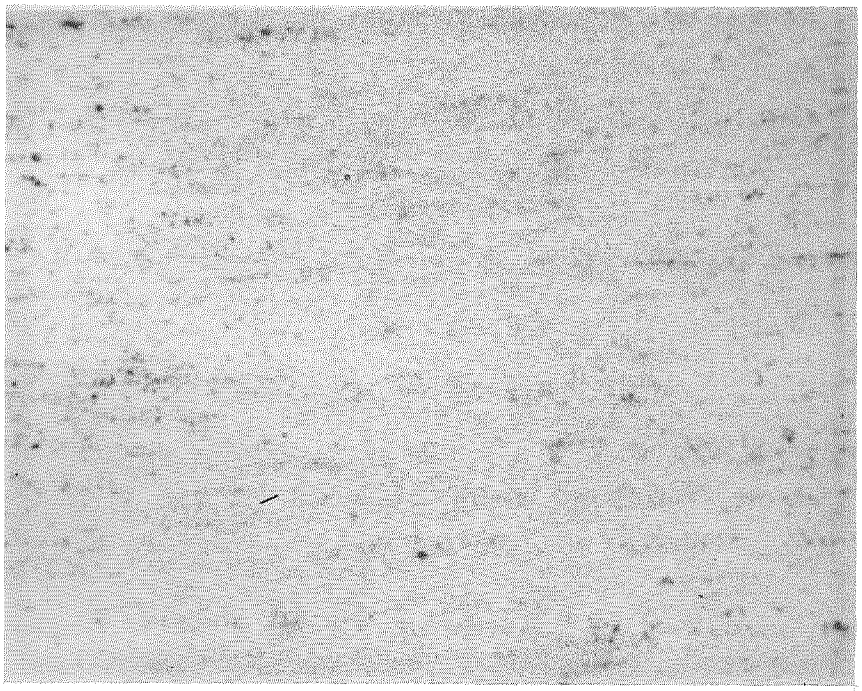


Photo No. P2739
PP2-13B-28
Bl 1-1, Ext. #8

CW Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 20:1 Ratio
8.57g/cc or 99.64% of T.D.
Rc 39

Mag. 2000X
Unetched

FIGURE 13B

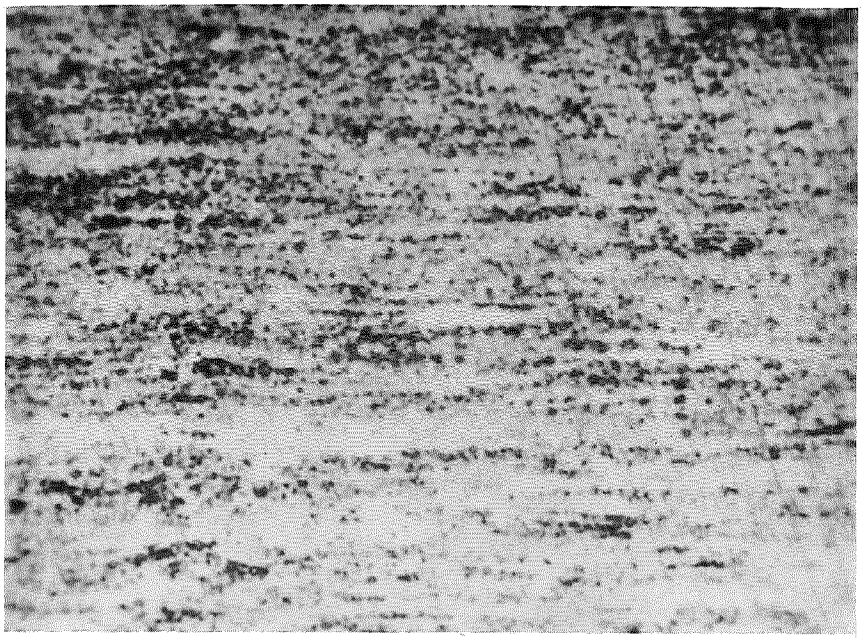


Photo No. P2741
PP2-13B-28
Bl 1-1, Ext. #8

CW Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 20:1 Ratio
8.57g/cc or 99.64% of T.D.
Rc 39

Mag. 2000X
Etchant:
Marbles

FIGURE 14

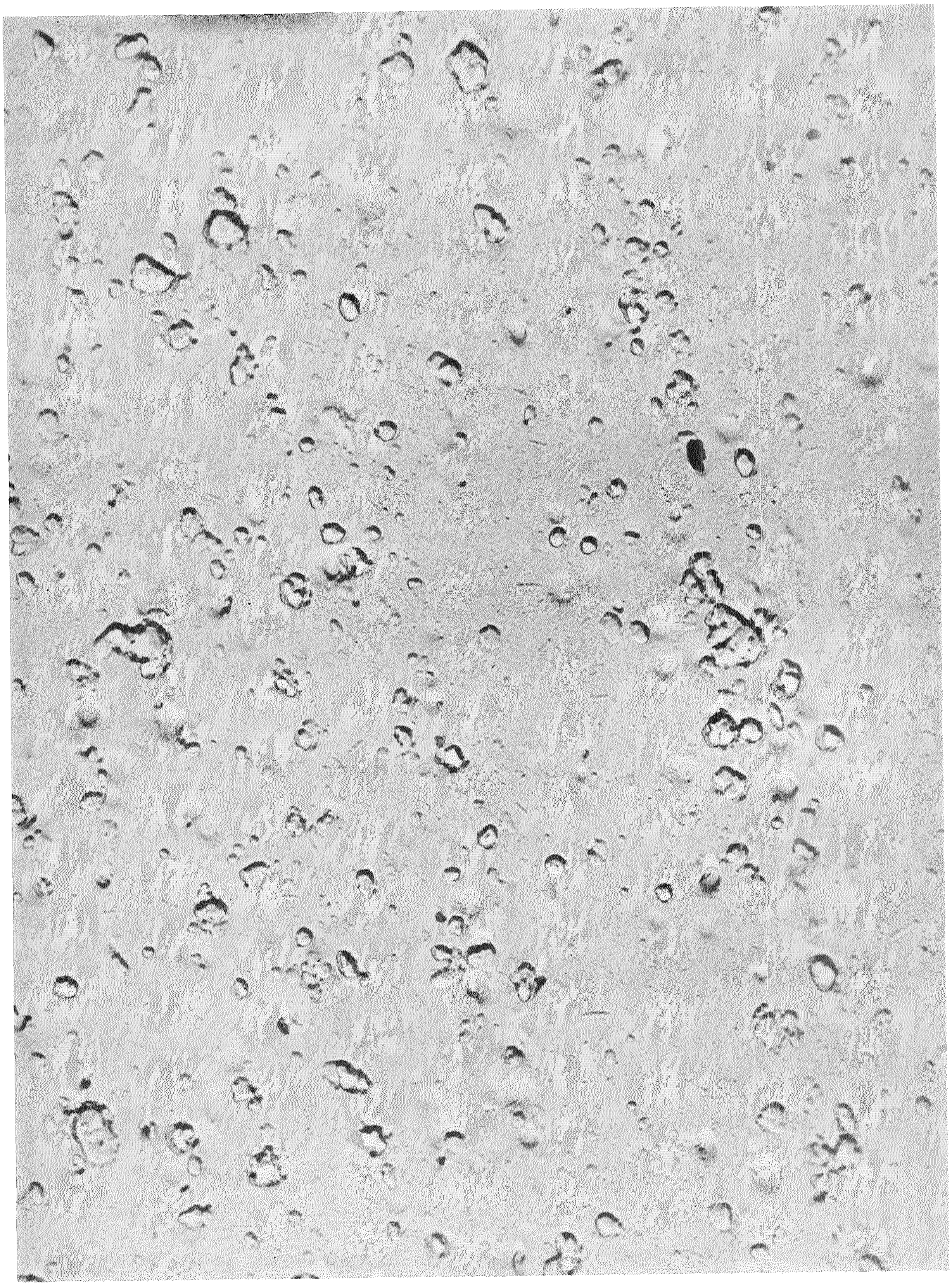


Photo No. 8907
Batt. No. G3443G
PP2-13B-28
Bl 1-1, Ext. #8

C-W Co-18Cr-20Ni4.6ThO_2
Extruded at 1095°C at Ratio of 20:1
8.57g/cc or 99.64% of T.D.
Rc 39

Mag. 20,000X

FIGURE 15A

Photo No. P2756
PP2-12A-38 Ext. #12

Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 10:1 @ 1205°C
99.4% of T.D. (8.60g/cc=100%)
Rc 37

Mag. 100X
Etchant:
Marbles

FIGURE 15B

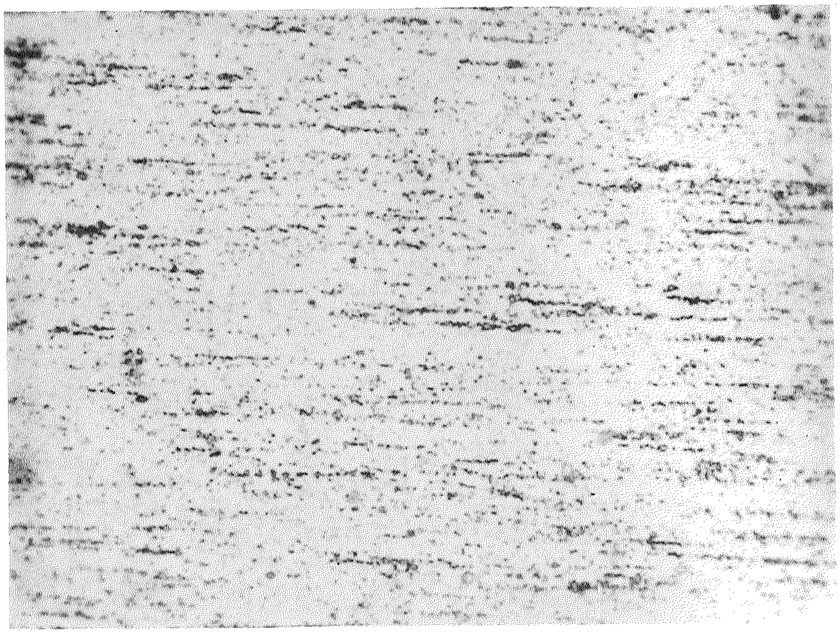


Photo No. P2757
PP2-12A-38
Ext. #12

Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 10:1 @ 1205°C
99.4% of T.D. (8.60g/cc=100%)
Rc 37

Mag. 1000X
Etchant:
Marbles

FIGURE 16

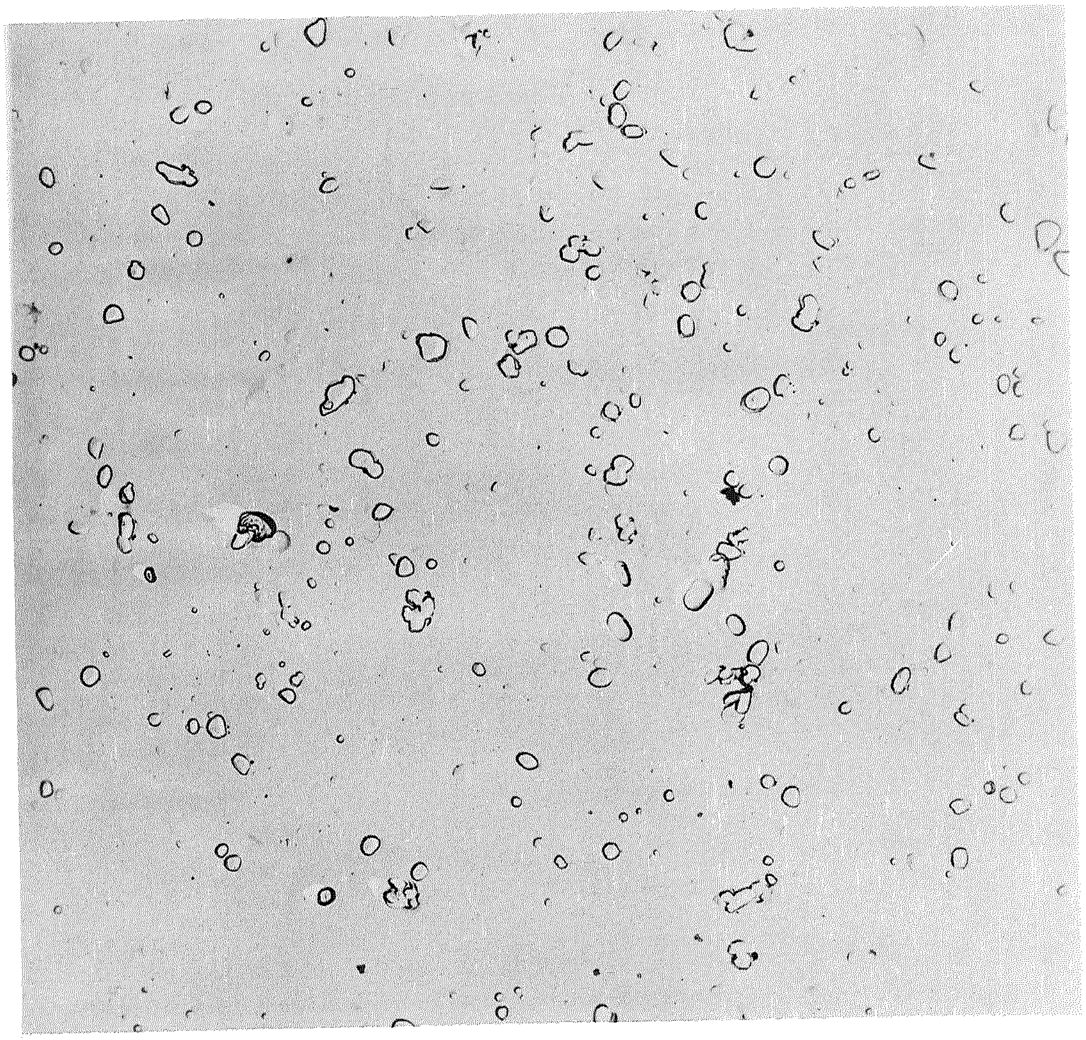


Photo No. 8956
Batt. No. E3465A
PP2-12A-38
Ext. #12

C-W Co-18Cr-20Ni-4.6ThO_2
Extruded @ 1205°C @ Ratio of 10:1
8.54g/cc or 99.4% of T.D.

Mag. 10,000X

FIGURE 17A

Photo No. P2865
PP2-12A-42
Ext. #19
Pc. #3

C-W Co-18Cr-20Ni-4.6ThO_2
Extruded @ 1095°C @ Ratio of 15:1
8.59g/cc or 99.8% of T.D.
Rc 41

Mag. 100X
Etchant:
Marbles

FIGURE 17B

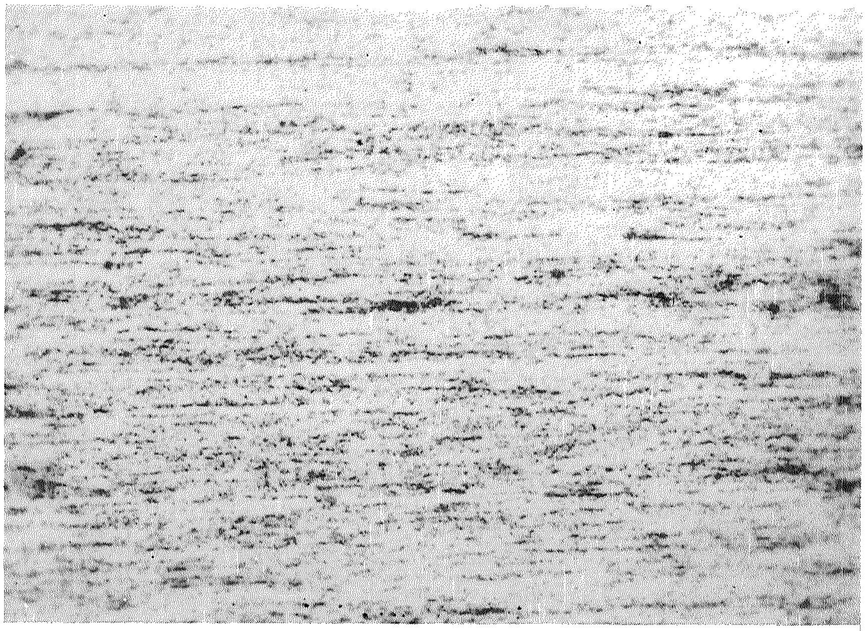


Photo No. P2866
PP2-12A-42
Ext. #19
Pc. #3

C-W Co-18Cr-20Ni-4.6ThO_2
Extruded @ 1095°C @ Ratio of 15:1
8.59g/cc or 99.8% of T.D.
Rc 41

Mag. 1000X
Etchant:
Marbles

FIGURE 18

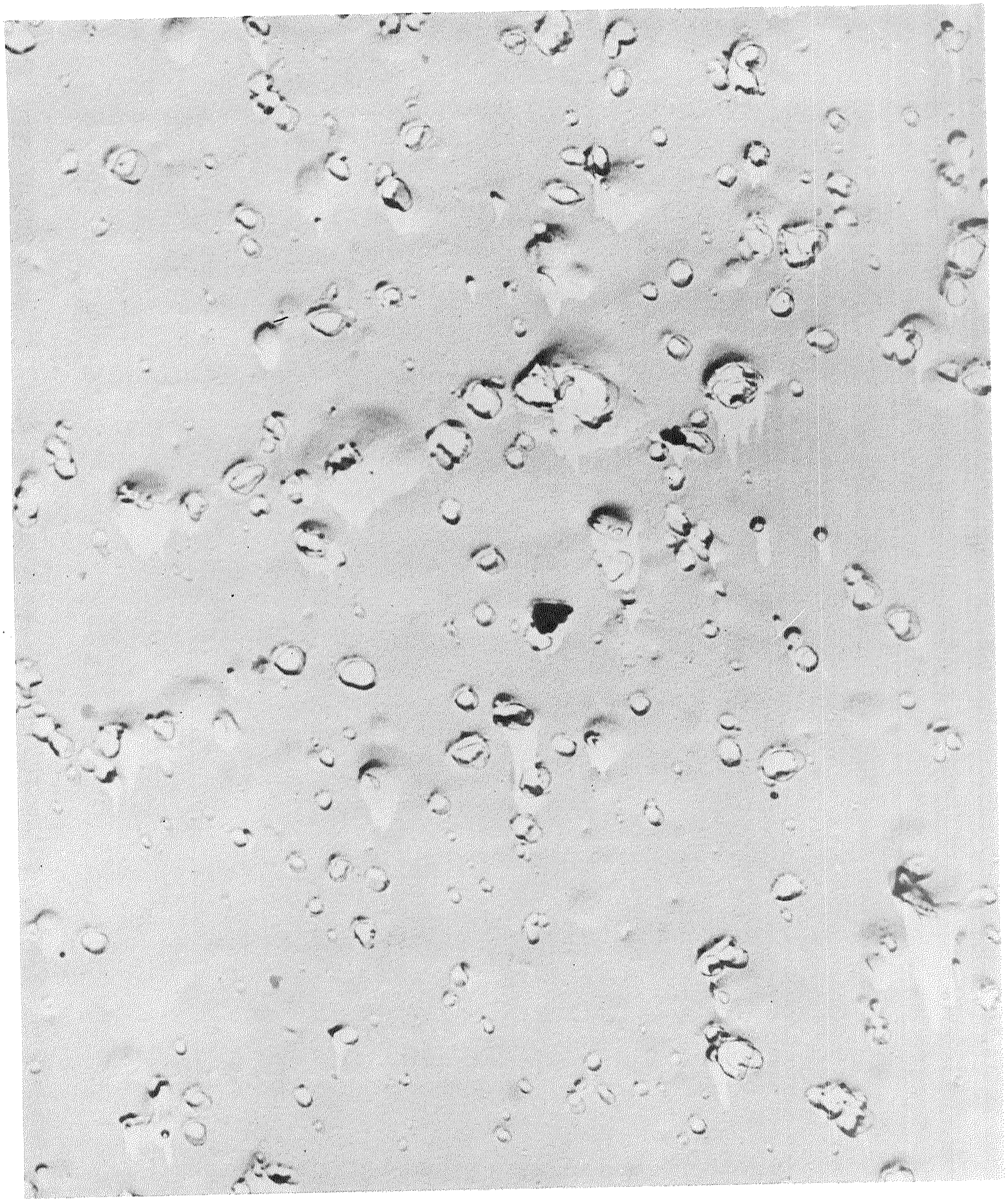


Photo No. 8968
Batt. No. E3473C
PP2-12A-42
Ext. #19

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 15:1
8.59g/cc or 99.8% of T.D.
Rc 41

Mag. 25,000X

FIGURE 19A

Photo No. P2870
PP2-12A-43
Ext. #20
Pc. #5

C-W Co-18Cr-20Ni-4.6ThO_2
Extruded @ 1095°C @ Ratio of 15:1
8.58g/cc or 99.8% of T.D.
Rc 39

Mag. 100X
Etchant:
Marbles

FIGURE 19B

Photo No. P2871
PP2-12A-43
Ext. #20
Pc. #5

C-W Co-18Cr-20Ni-4.6ThO_2
Extruded @ 1095°C @ Ratio of 15:1
8.58g/cc or 99.8% of T.D.
Rc 39

Mag. 1000X
Etchant:
Marbles

FIGURE 20

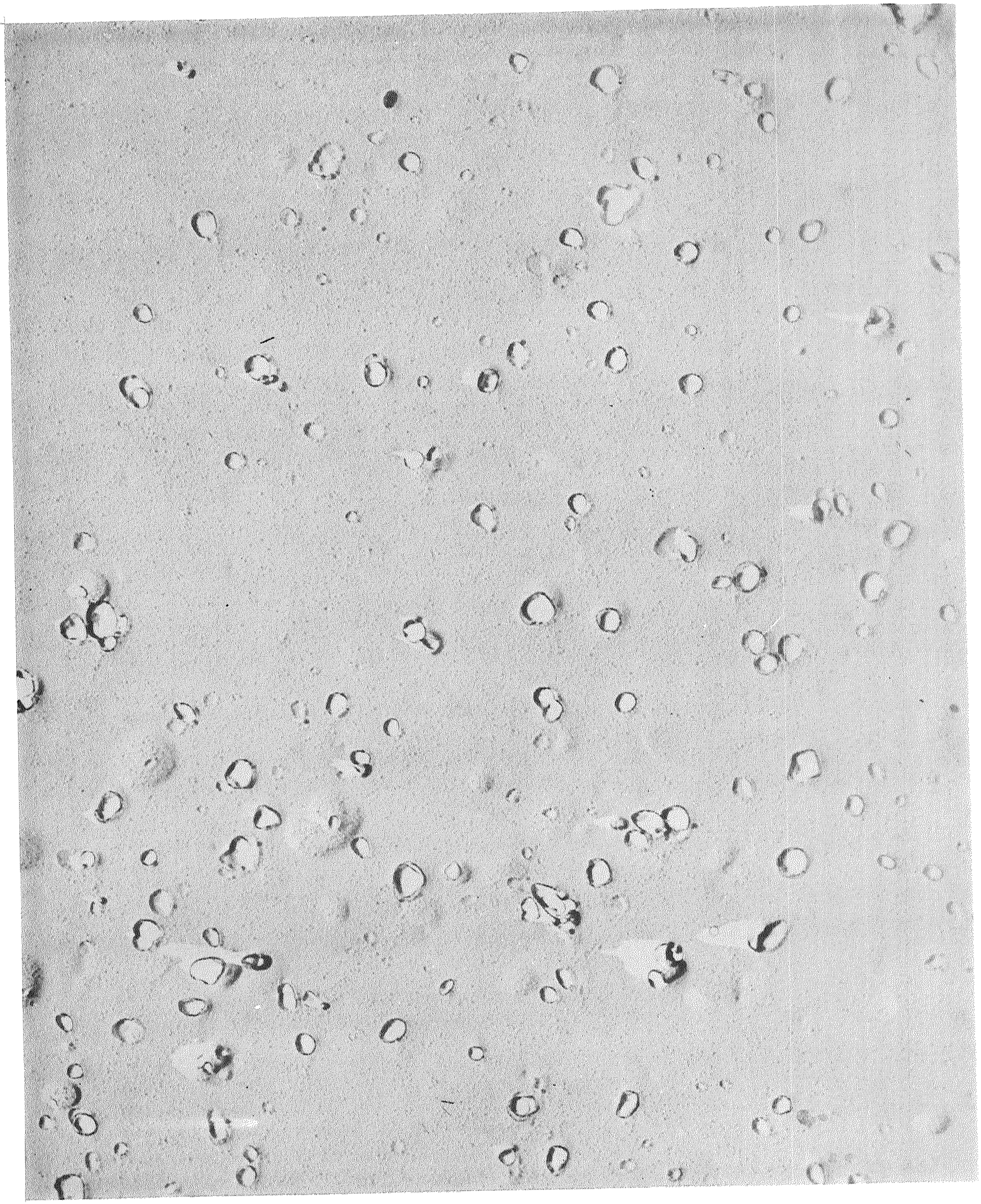


Photo No. 8970
Batt. No. E3474E
PP2-12A-43
Ext. #20

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 15:1
8.58g/cc or 99.8% of T.D.
Rc 39

Mag. 25,000X

FIGURE 21

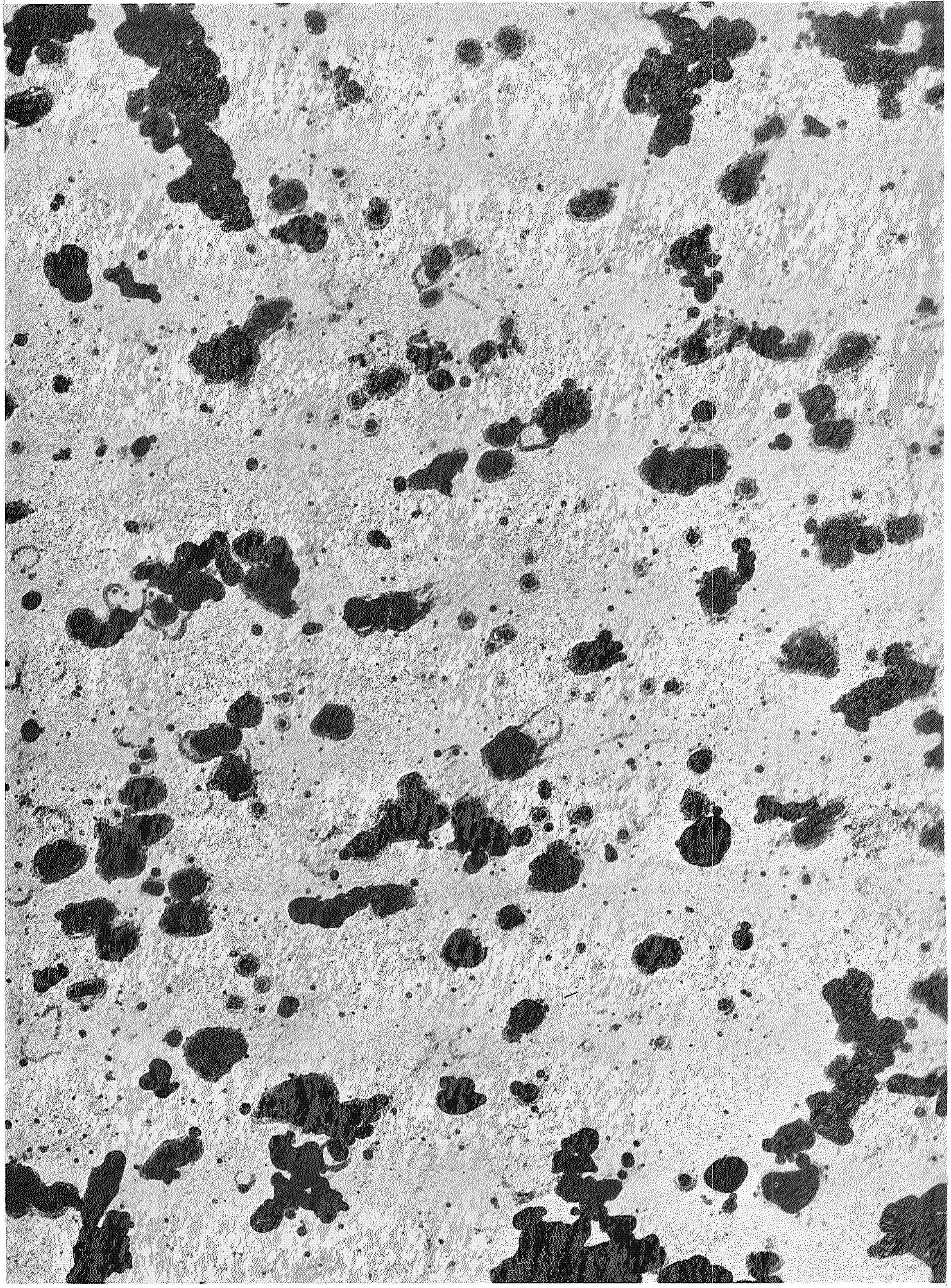
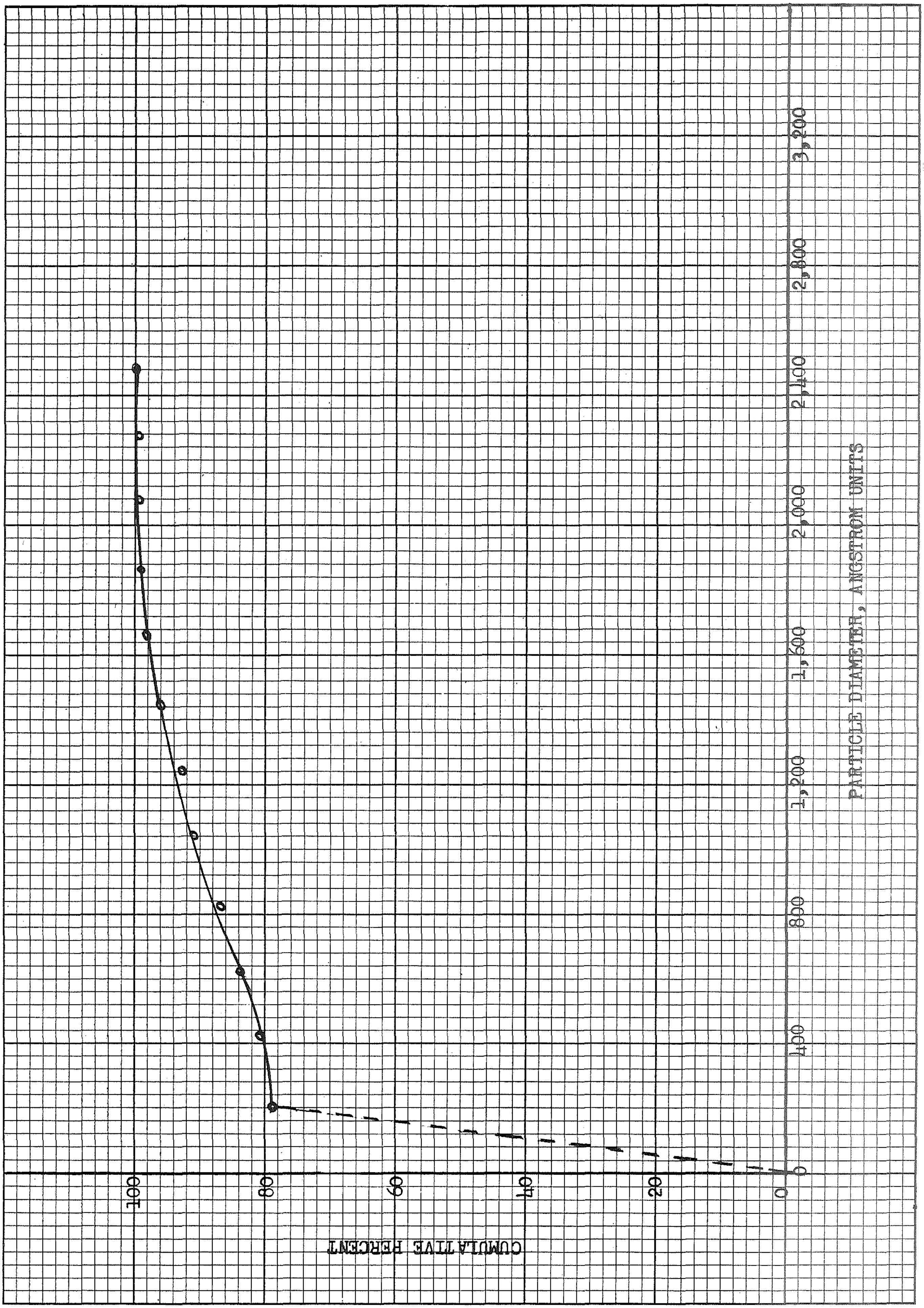


Photo No. 9002
NASA No. 21-69-5
PP2-13B-28
B1 1-1
Ext. No. 8

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 20:1
Extracted Particles

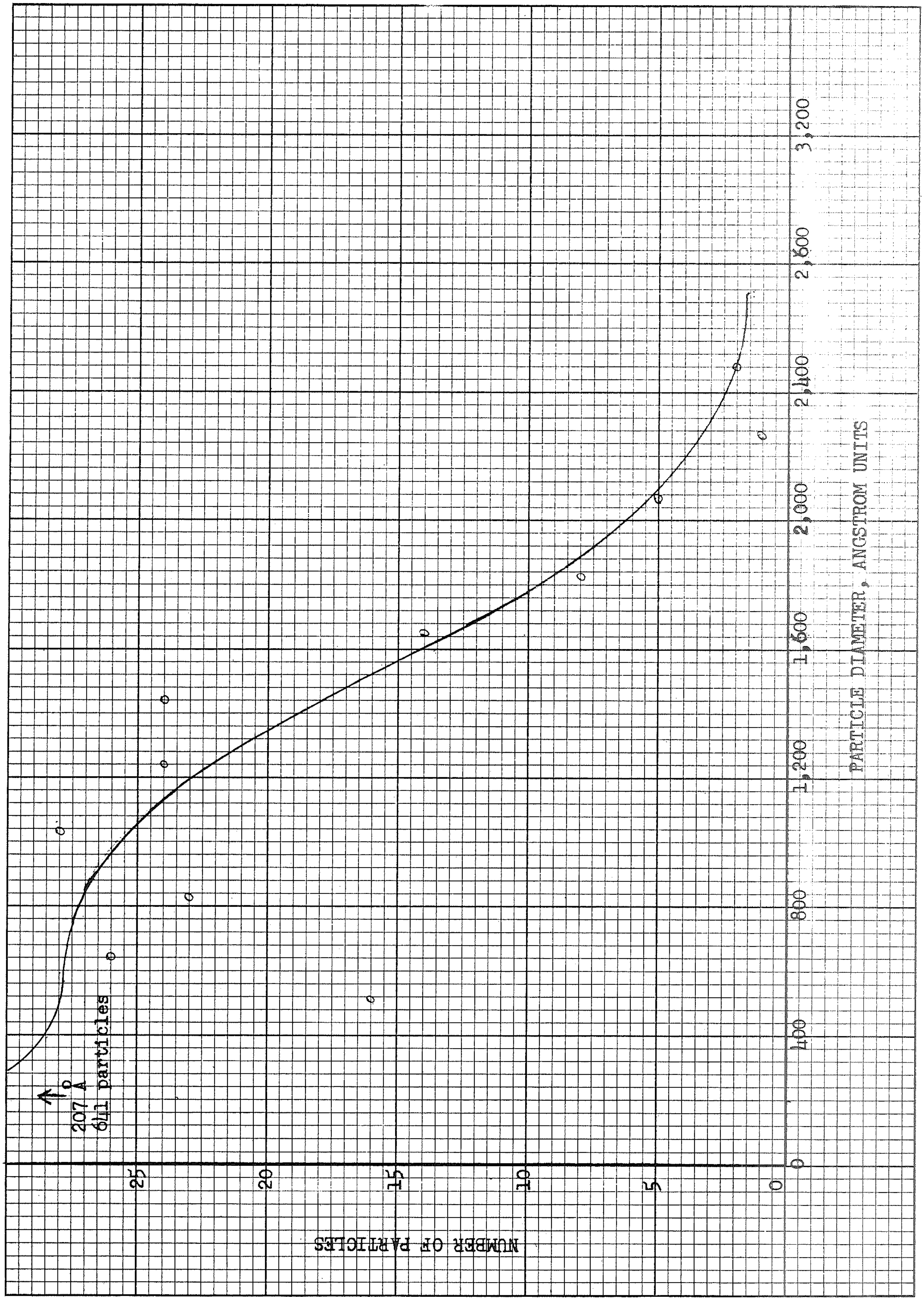
Mag. 48,000X

FIGURE 22



Particle Size Distribution of the ThO_2 particles extracted from Extrusion No. 8

FIGURE 23



Extracted Particle Size Count, Extrusion No. 8

FIGURE 24

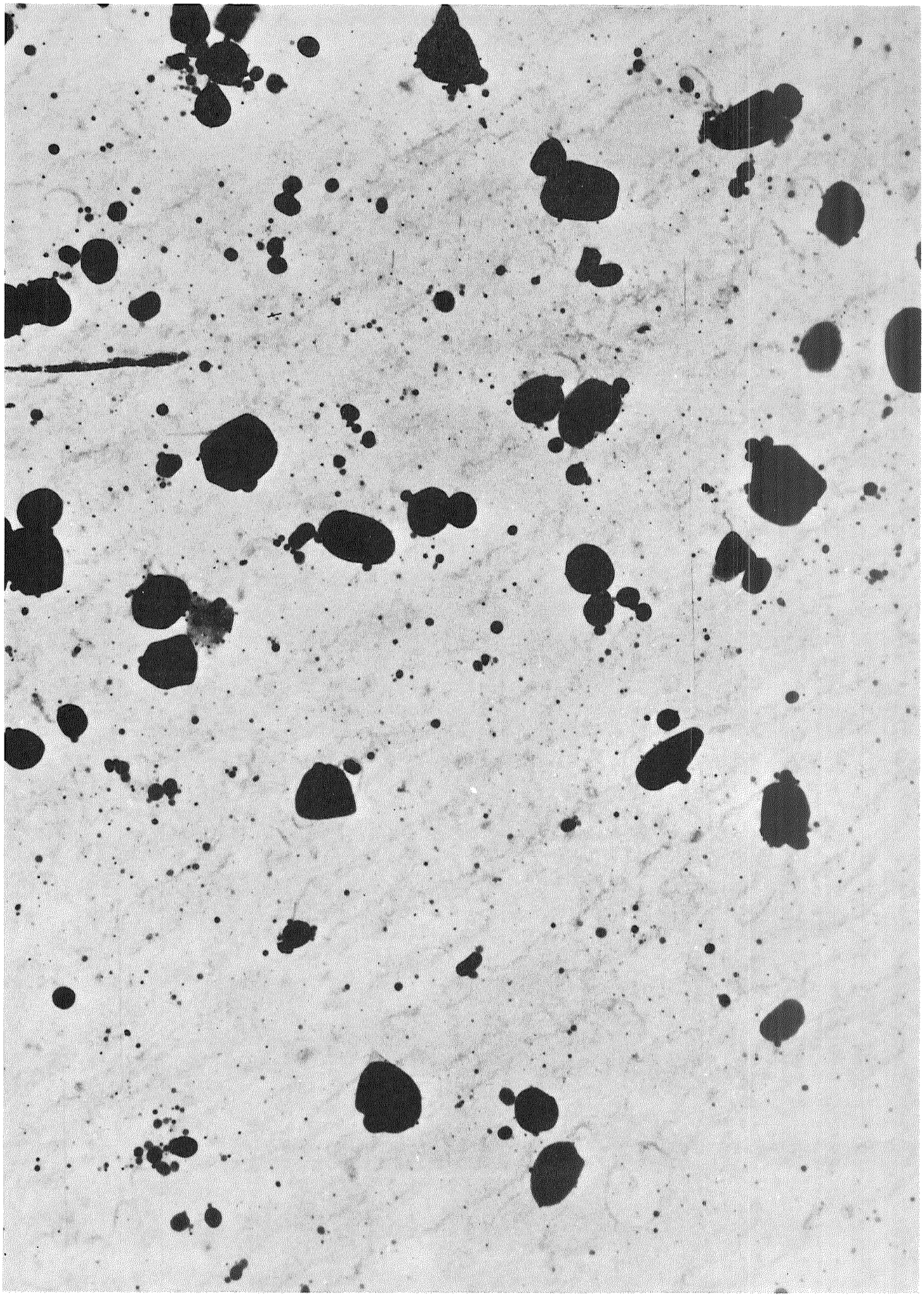
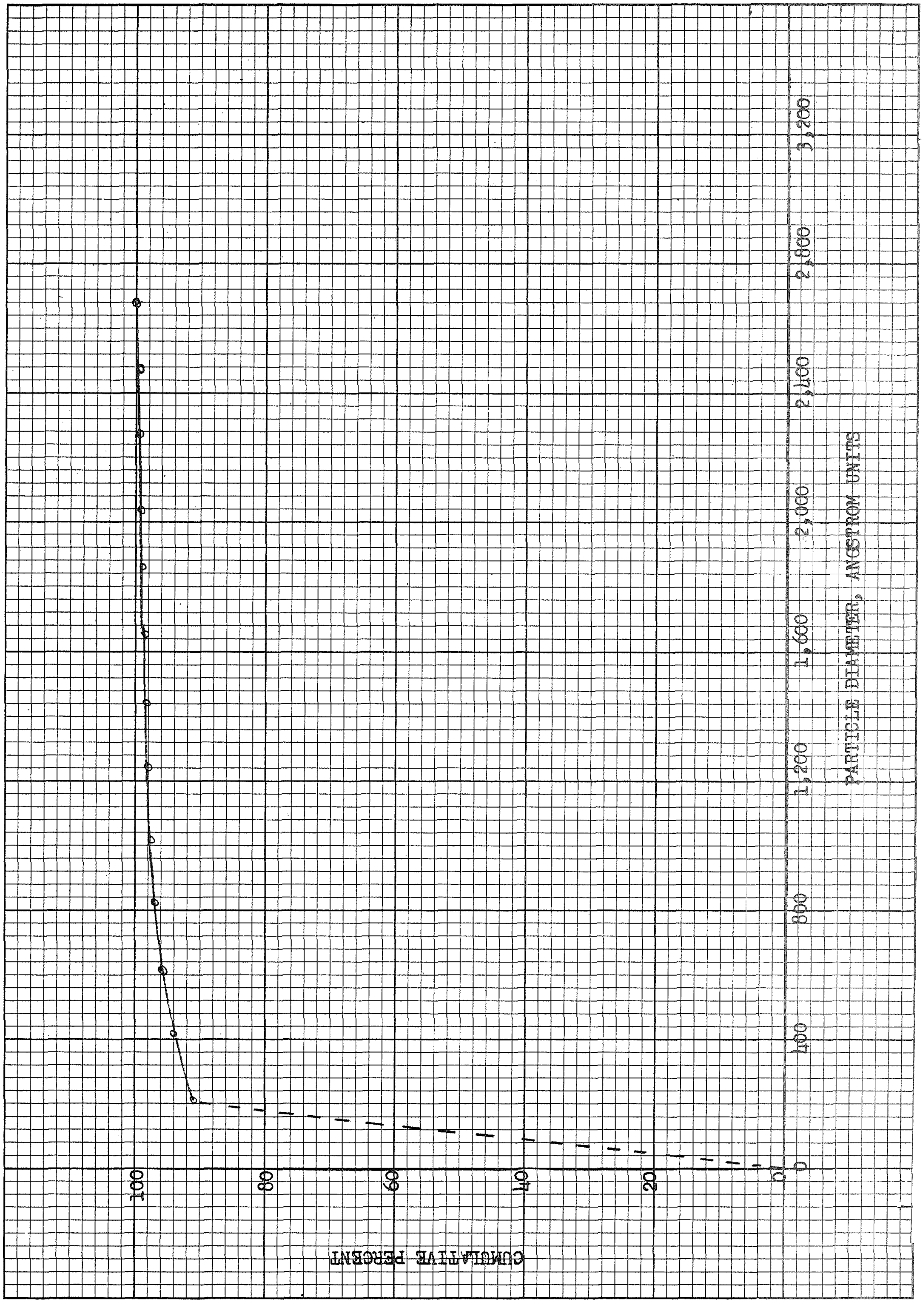


Photo No. 9005
NASA No. 24-69-18
PP2-12A-38
Ext. No. 12

C-W Co-18Cr-20Ni-4.60ThO$_2$
Extruded @ 1205°C @ Ratio of 10:1
Extracted Particles

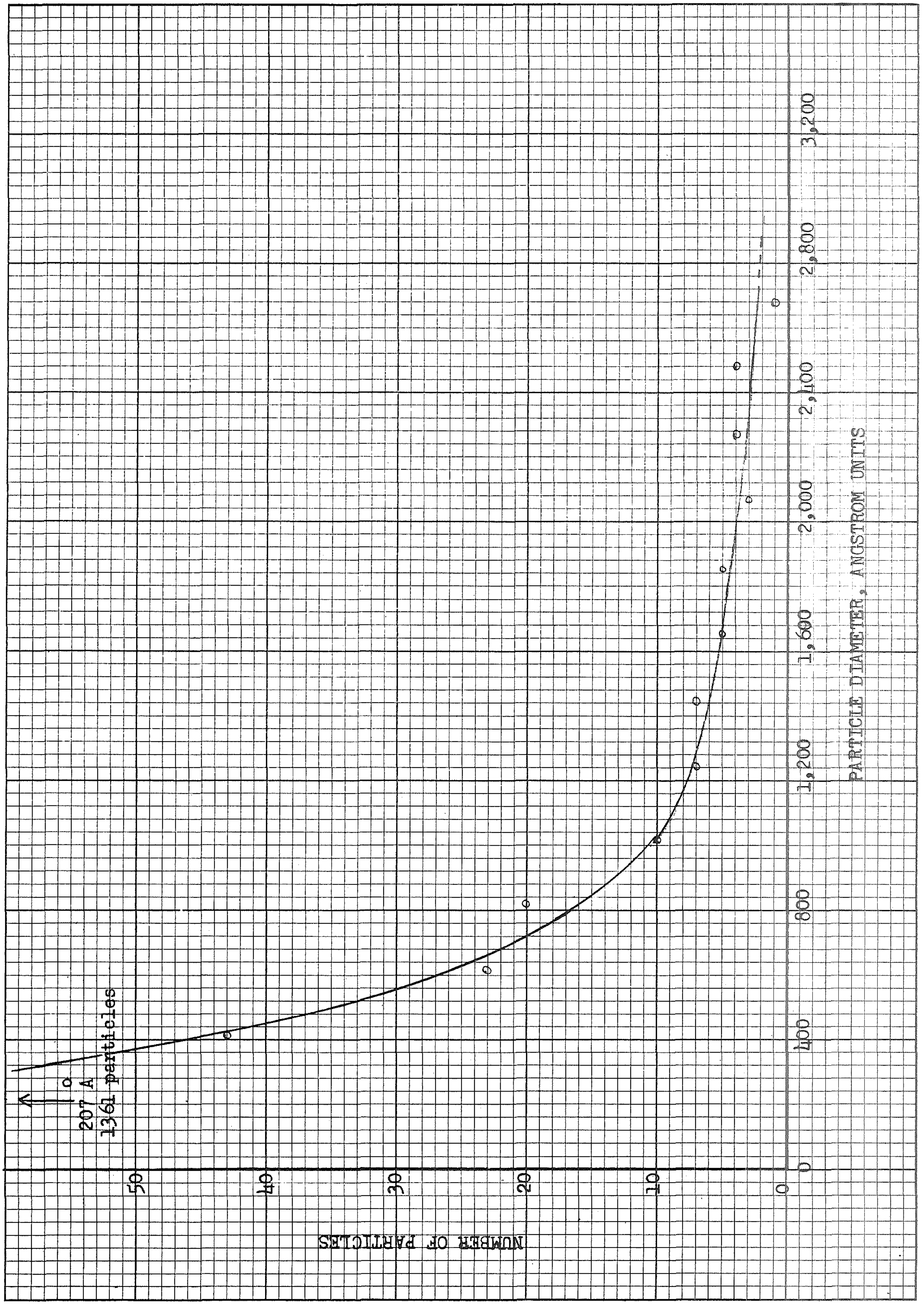
Mag. 48,300X

FIGURE 25



Particle Size Distribution of the ThO_2 Particles Extracted from Extrusion No. 12

FIGURE 26



Extracted Particle Size Count, Extrusion No. 8

FIGURE 27A

Photo No. P2752
PP2-13B-28
Billet 1-1, Ext. #8

Co-18Cr-20Ni-4.6ThO_2
Extruded at 1095 °C @ Ratio of 20:1
Heat Treated 100 Hrs. @ 1205 °C in Vacuum
99.4% of T.D. (8.60g/cc = 100%)
Rc 33

Mag. 100X
Etchant: Marbles

FIGURE 27B

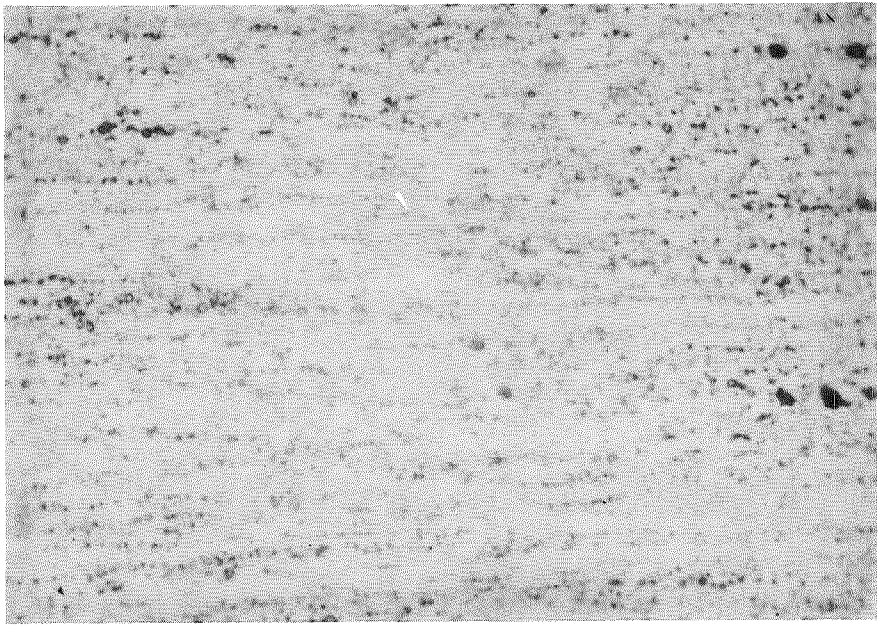


Photo No. P2753
PP2-13B-28
Billet 1-1,
Ext. #8

Co-18Cr-20Ni-4.6ThO_2
Extruded at 1095 °C @ Ratio of 20:1
Heat Treated 100 Hrs. @ 1205 °C in Vacuum
99.4% of T.D. (8.60g/cc = 100%)
Rc 33

Mag. 2000X
Etchant: Marbles

FIGURE 28

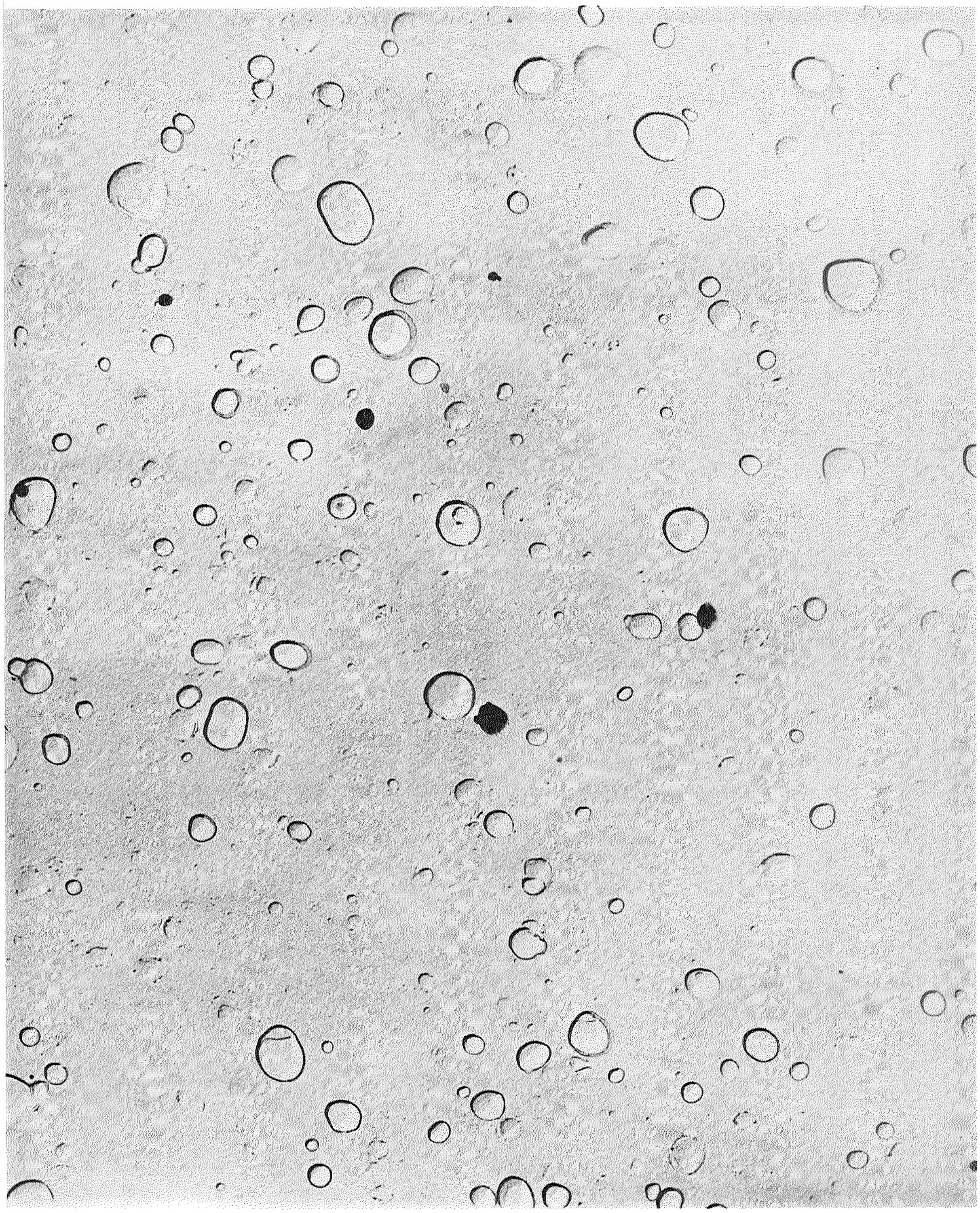


Photo No. 8954 C-W Co-18Cr-20Ni-4.6ThO_2 Mag. 25,000X
Batt. No. E3468C Extruded at 1095°C at Ratio of 20:1
PP2-13B-28, Ext. #8 Heat Treated 100 hrs. at 1205°C
8.55 g/cc or 99.4% of T.D.
Rc 33

FIGURE 29A

Photo No. P2860
PP2-12A-38
Ext. #12

C-W Co-18Cr-20Ni-4.6ThO_2
Extruded at 1205°C at Ratio of 10:1
Heat Treated 100 hrs. in Vacuum
8.58g/cc or 99.76% of T.D.

Mag. 100X
Etchant:
Marbles

FIGURE 29B

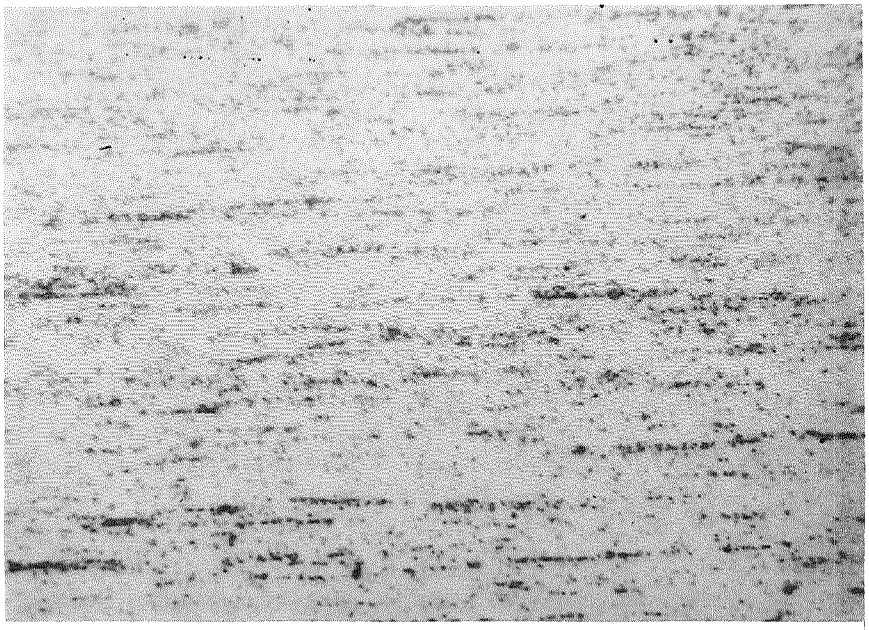


Photo No. P2861
PP2-12A-38
Ext. #12

CW Co-18Cr-20Ni-4.6ThO_2
Extruded at 1205°C at Ratio of 10:1
Heat Treated 100 hrs. in Vacuum
8.58g/cc or 99.76% of T.D.

Mag. 1000X
Etchant:
Marbles

FIGURE 30

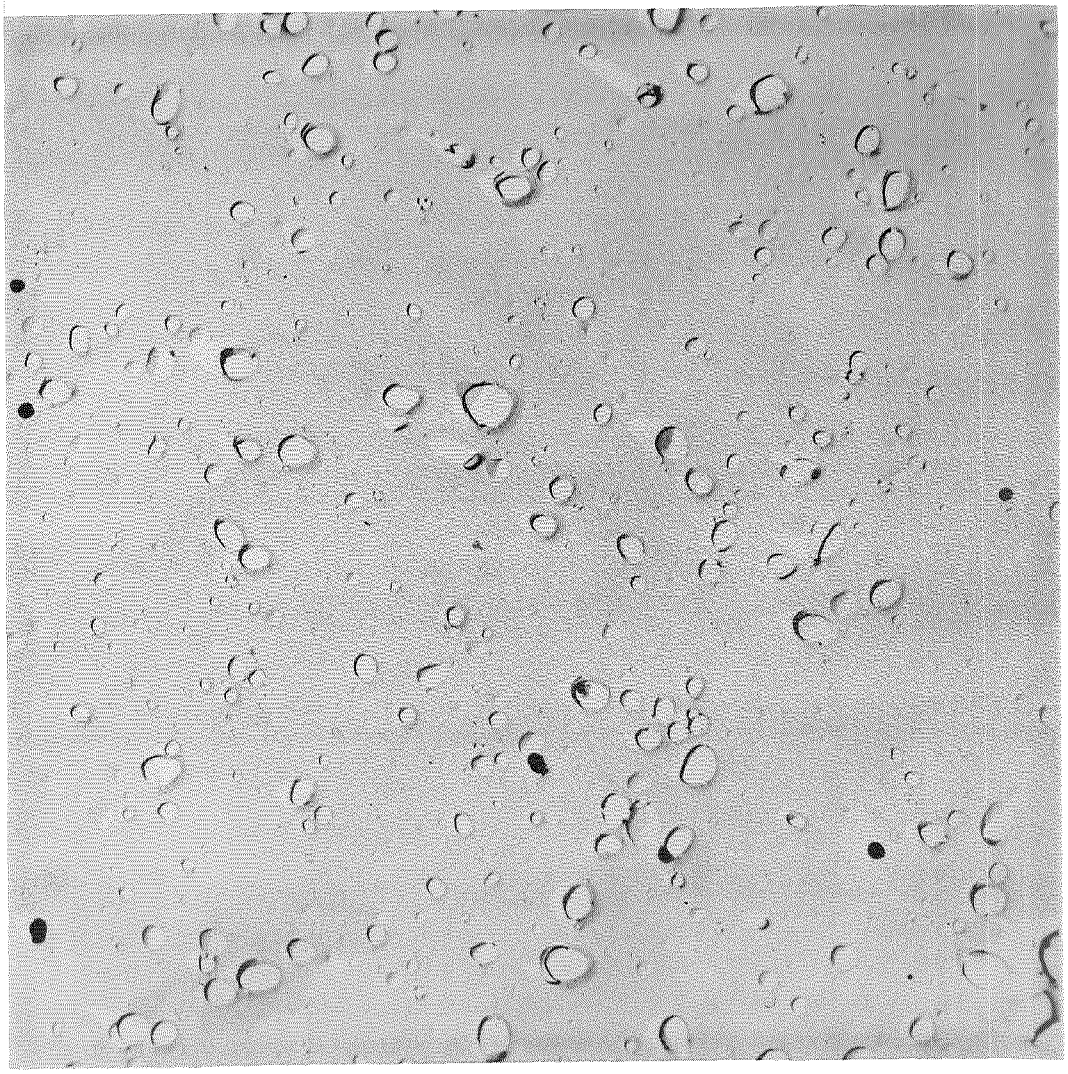


Photo No. 8969
Batt. No. E3472B
PP2-12A-38, Ext. #12

C-W Co-18Cr-20Ni-4.6ThO_2
Extruded @ 1205°C @ Ratio of 10:1
Heat Treated 100 hrs.
@ 1205°C in Vacuum
8.58g/cc or 99.7% of T.D.
Rc 35

Mag. 10,000X

FIGURE 31A

Photo No. P2875
PP2-12A-42
Ext. #19

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 15:1
Heat Treated 100 hrs. @ 1205°C in Vacuum
8.57g/cc or 99.7% of T.D.
Rc 34

Mag. 100X
Etchant:
Marbles

FIGURE 31B

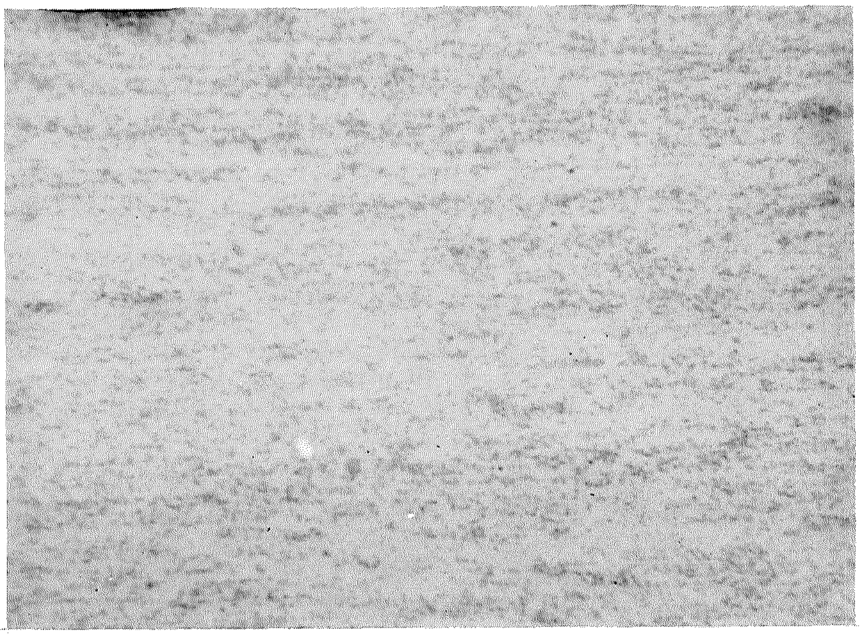


Photo No. P2876
PP2-12A-42
Ext. #19

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 15:1
Heat Treated 100 hrs. @ 1205 C in Vacuum
8.57g/cc or 99.7% of T.D.
RC 34

Mag. 1000X
Etchant:
Marbles

FIGURE 32

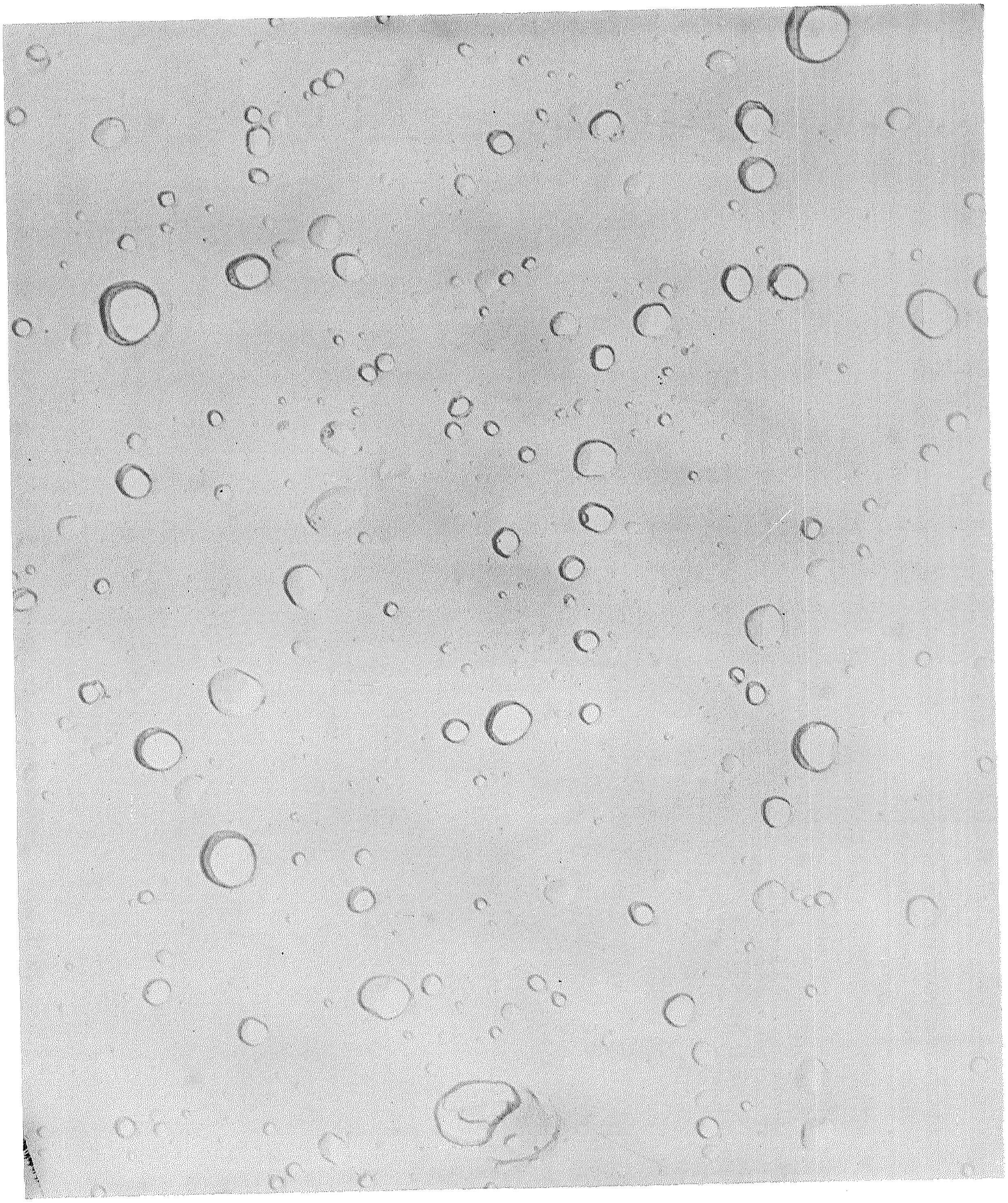


Photo No. 8971 C-W Co-18Cr-20Ni-4.6ThO$_2$ Mag. 25,000X
Batt. No. E3481C Extruded @ 1095°C @ Ratio of 15:1
PP2-12A-42, Ext. #19 Heat Treated 100 hrs. @ 1205°C in Vacuum
8.57g/cc or 99.7% of T.D.
Rc 34

FIGURE 33A

Photo No. P2880
PP2-12A-43
Ext. #20

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 15:1
Heat Treated 100 hrs. @ 1205°C in Vacuum
8.58g/cc or 99.8% of T.D.
Rc 35

Mag. 100X
Etchant:
Marbles

FIGURE 33B

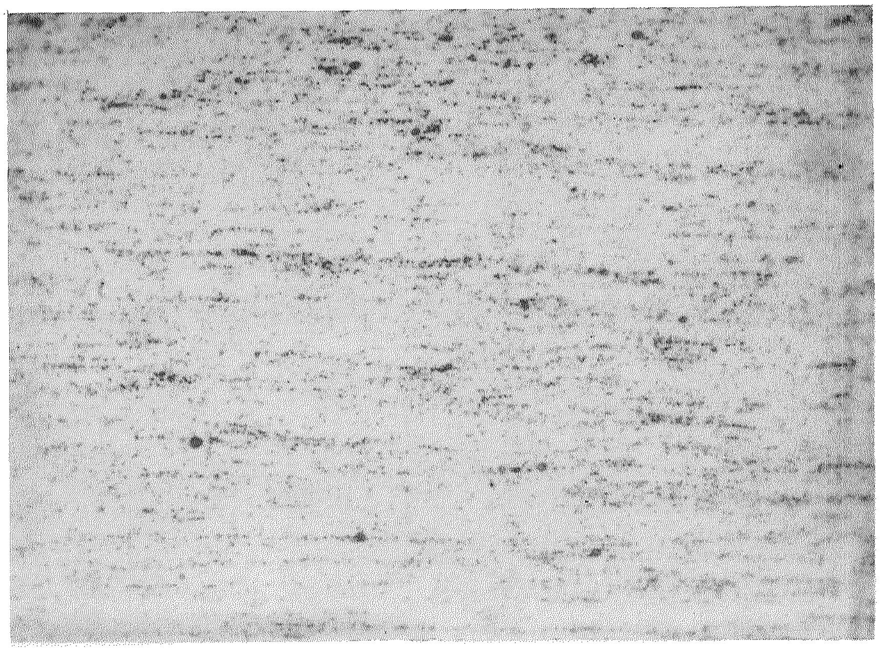


Photo No. P2881
PP2-12A-43
Ext. #20

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 15:1
Heat Treated 100 hrs. @ 1205°C in Vacuum
8.58g/cc or 99.8% of T.D.
Rc 35

Mag. 1000X
Etchant:
Marbles

FIGURE 34

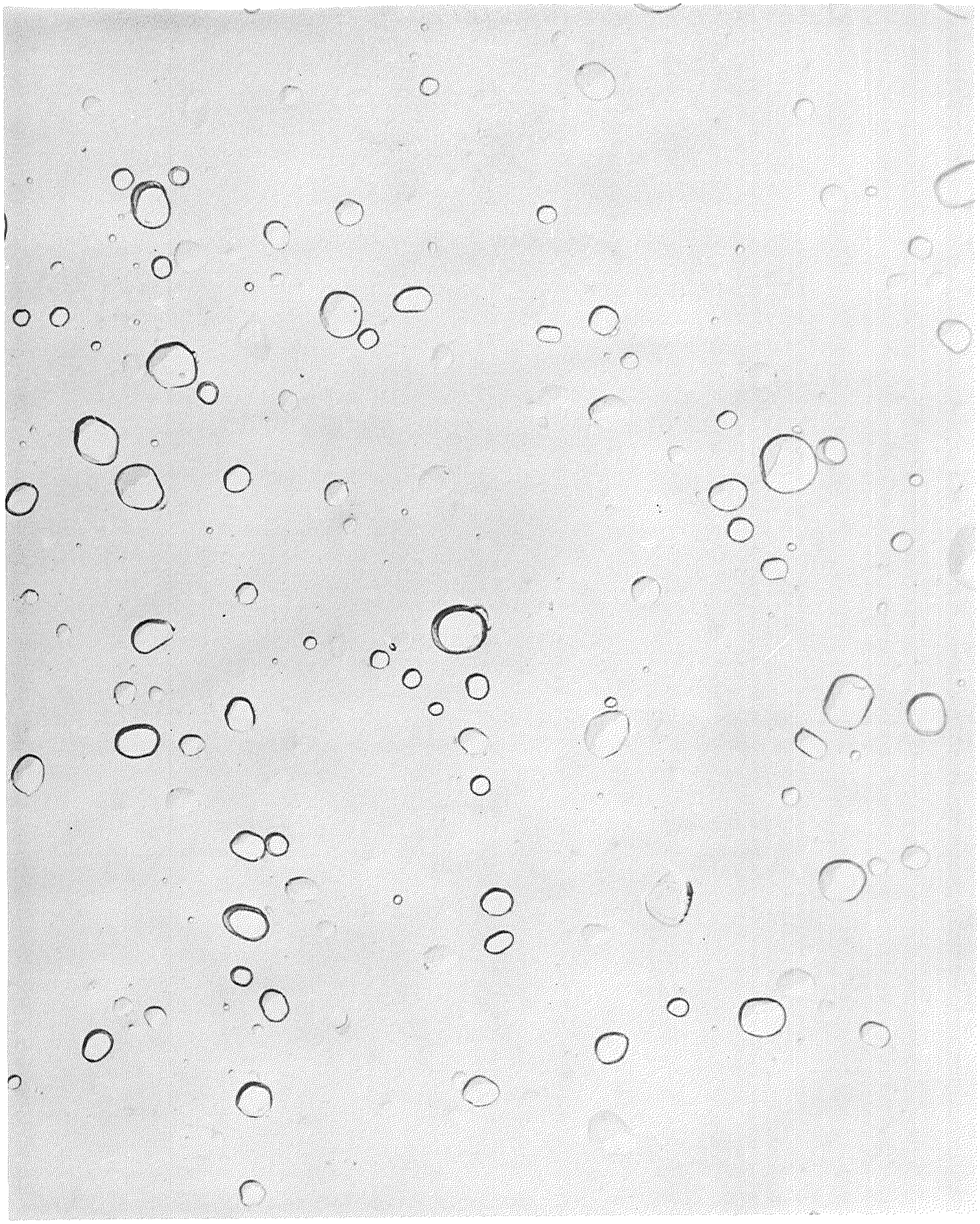


Photo No. 8967
Batt. No. E3482C
PP2-12A-43, Ext. #20

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 15:1
Heat Treated 100 hrs. @ 1205°C in Vacuum
8.58g/cc or 99.8% of T.D.
Rc 35

Mag. 25,000X

FIGURE 35

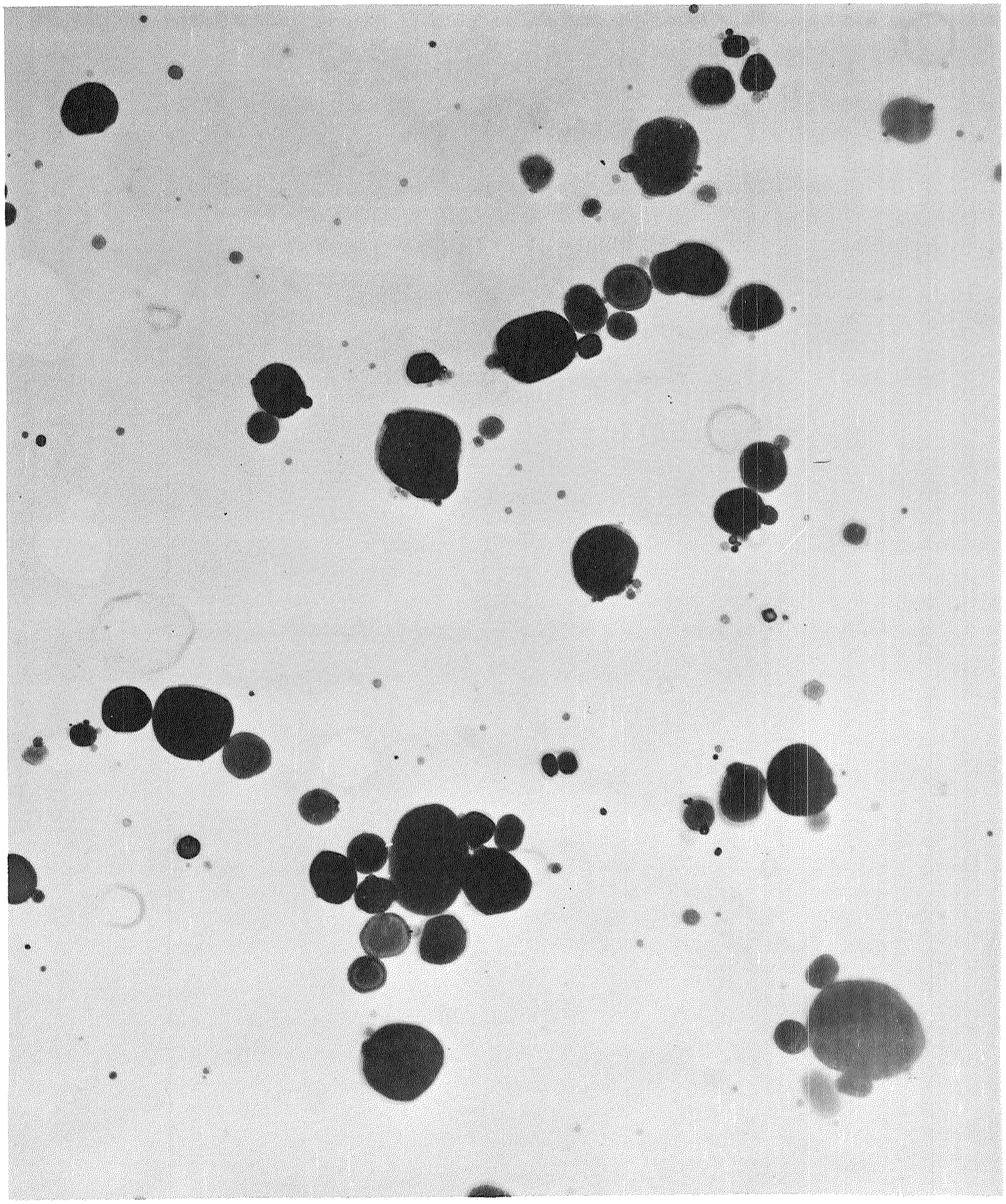


Photo No. 8993 C-W Co-18Cr-20Ni-4.6ThO_2 Mag. 68,500X
Batt. No. EH2330 Extruded @ 1095°C @ Ratio of 15:1
PP2-12A-42, Ext. #19 Heat Treated 100 hrs. @ 1205°C in Vacuum
Extracted Particles

FIGURE 36

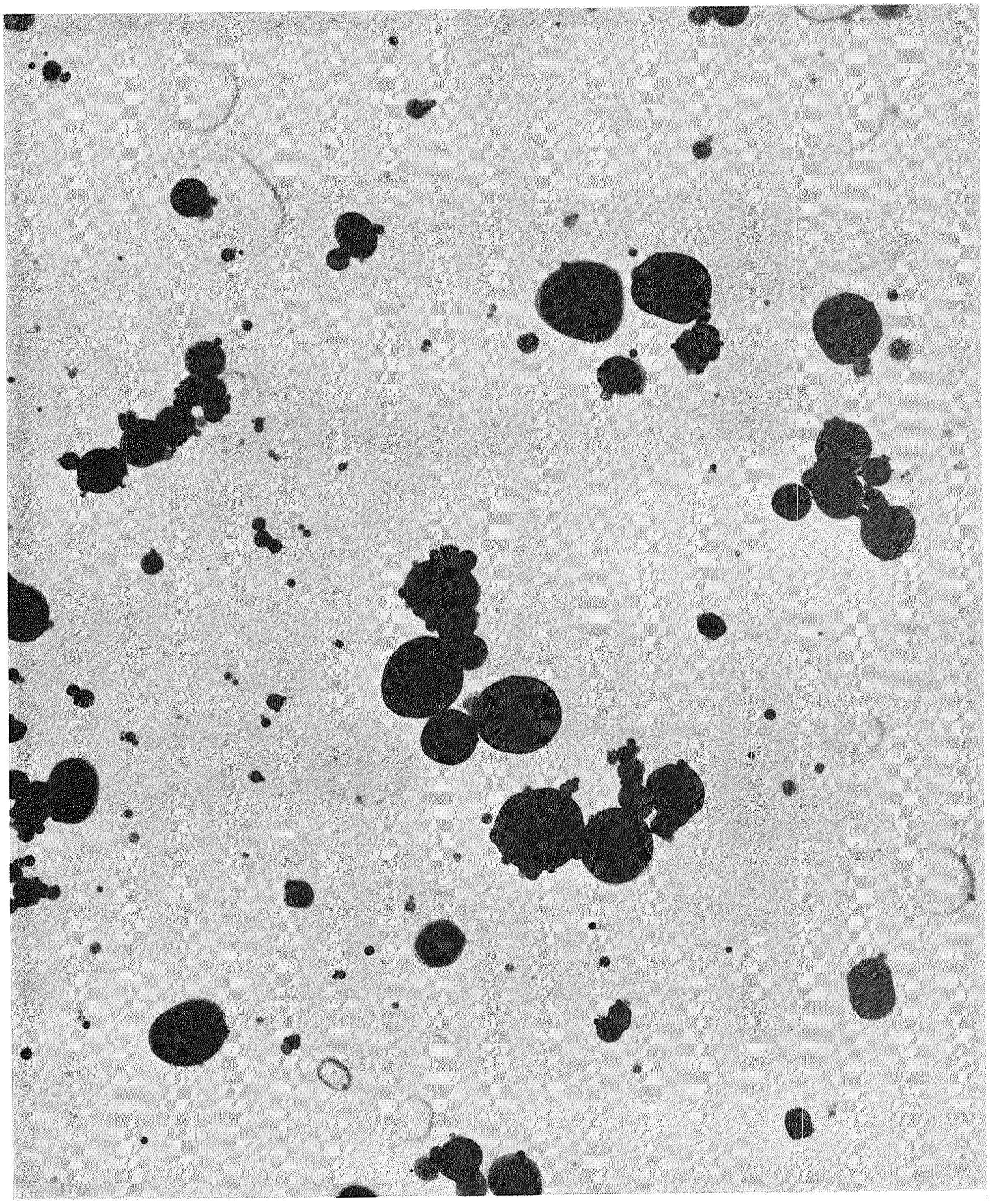
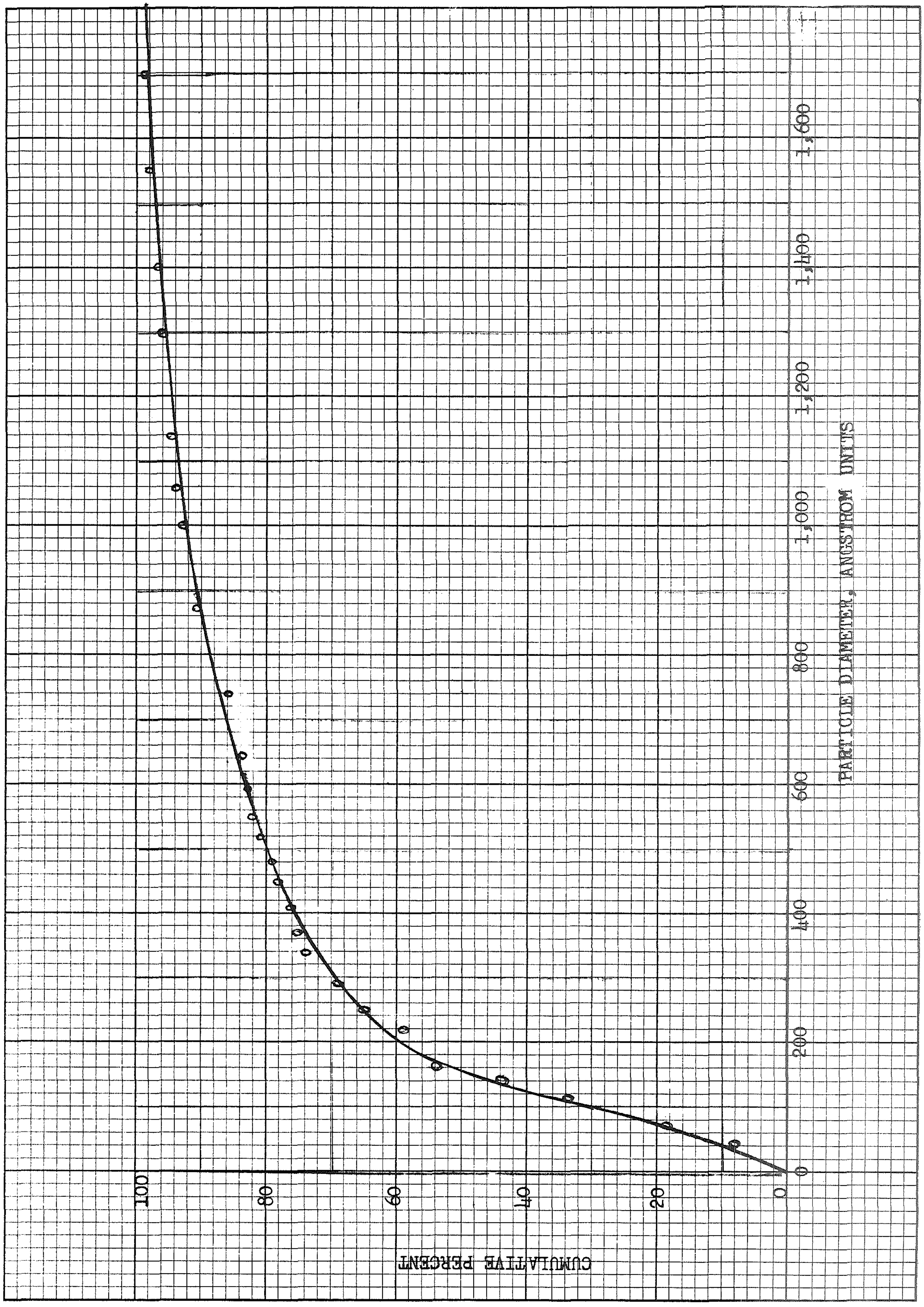


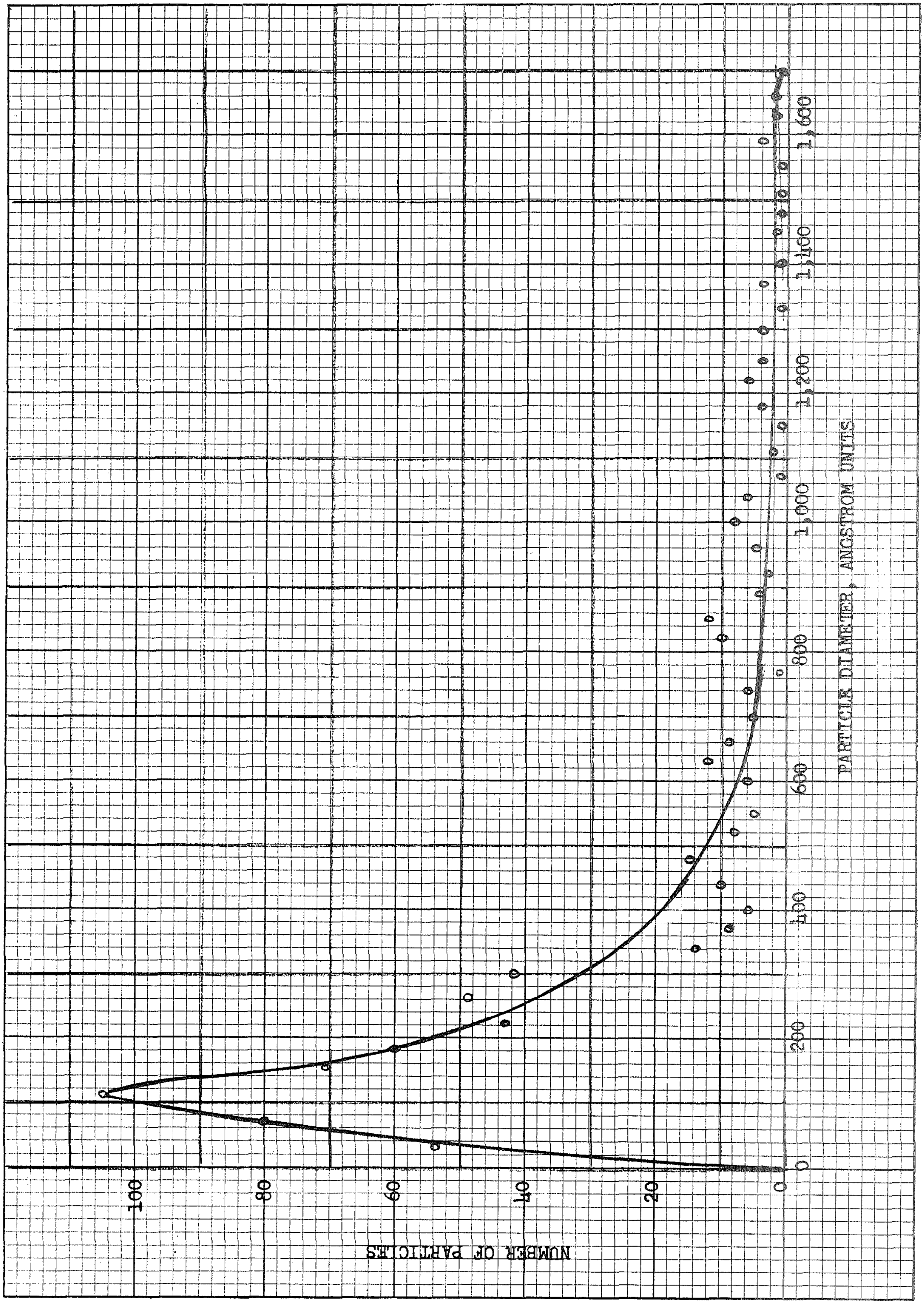
Photo No. 8992 C-W Co-18Cr-20Ni-4.6ThO$_2$ Mag. 68,500X
Batt. No. EH2321 Extruded @ 1095°C @ Ratio of 15:1
PP2-12A-43, Ext. #20 Heat Treated 100 hrs. @ 1205°C in Vacuum
Extracted Particles

FIGURE 37



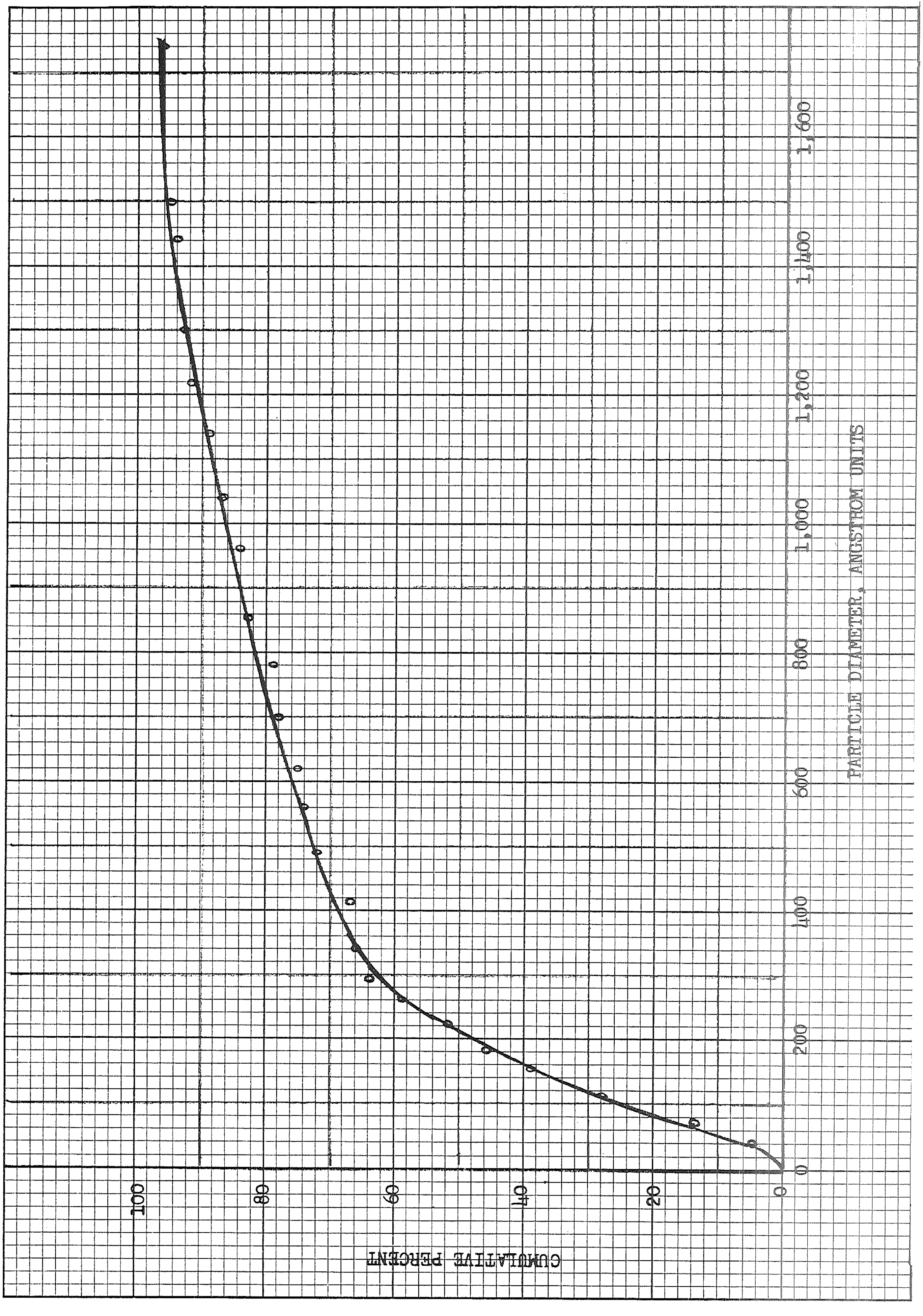
Particle size distribution of the ThO_2 particles extracted from the Heat Treated Extrusion No. 19

FIGURE 38



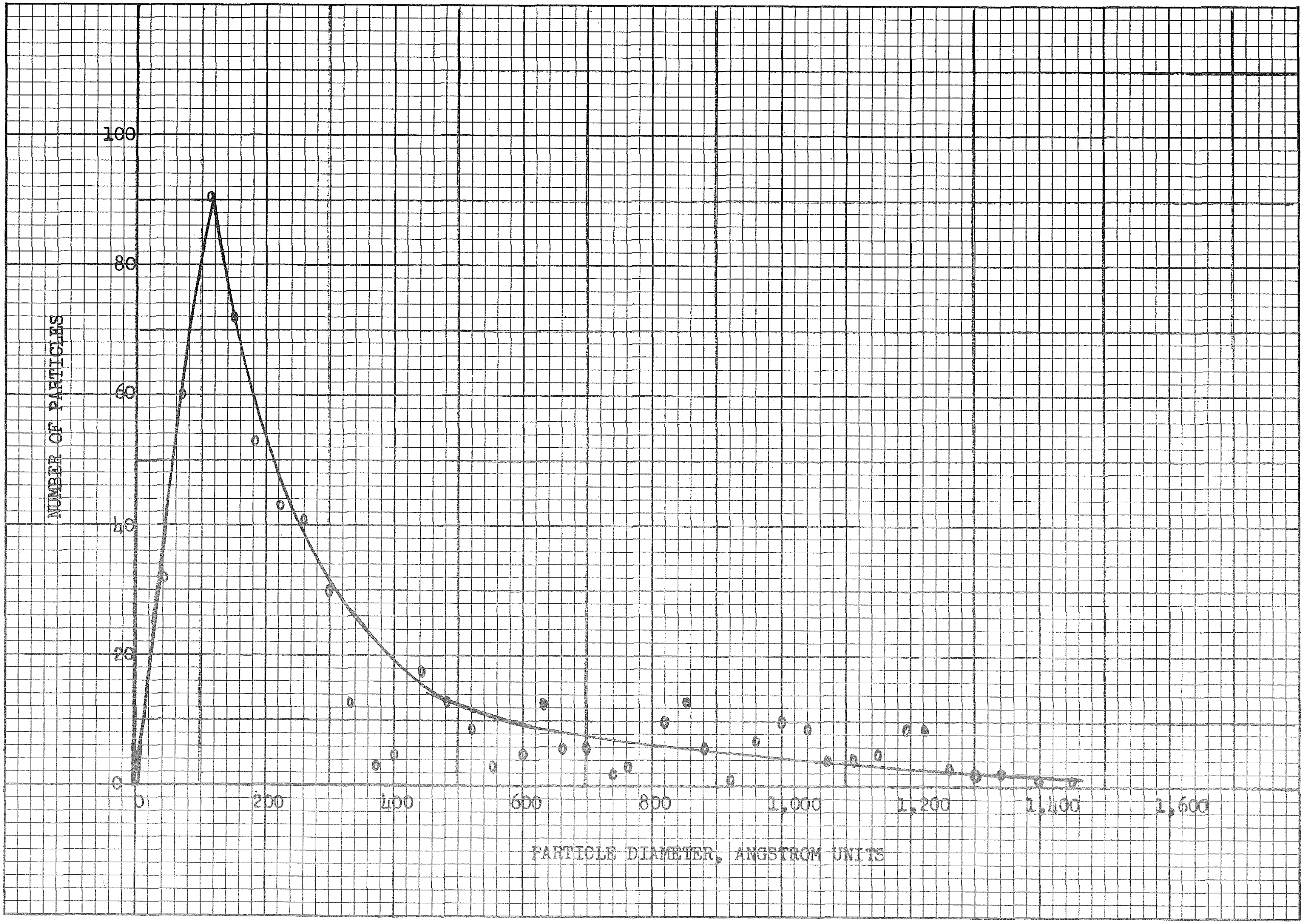
Extracted Particle Size Count, Heat Treated Extrusion No. 19

FIGURE 39



Particle size distribution of the ThO_2 particles extracted from the Heat Treated Extrusion No. 20

FIGURE 40



Extracted Particle Size Count, Heat Treated Extrusion No. 20

FIGURE 41

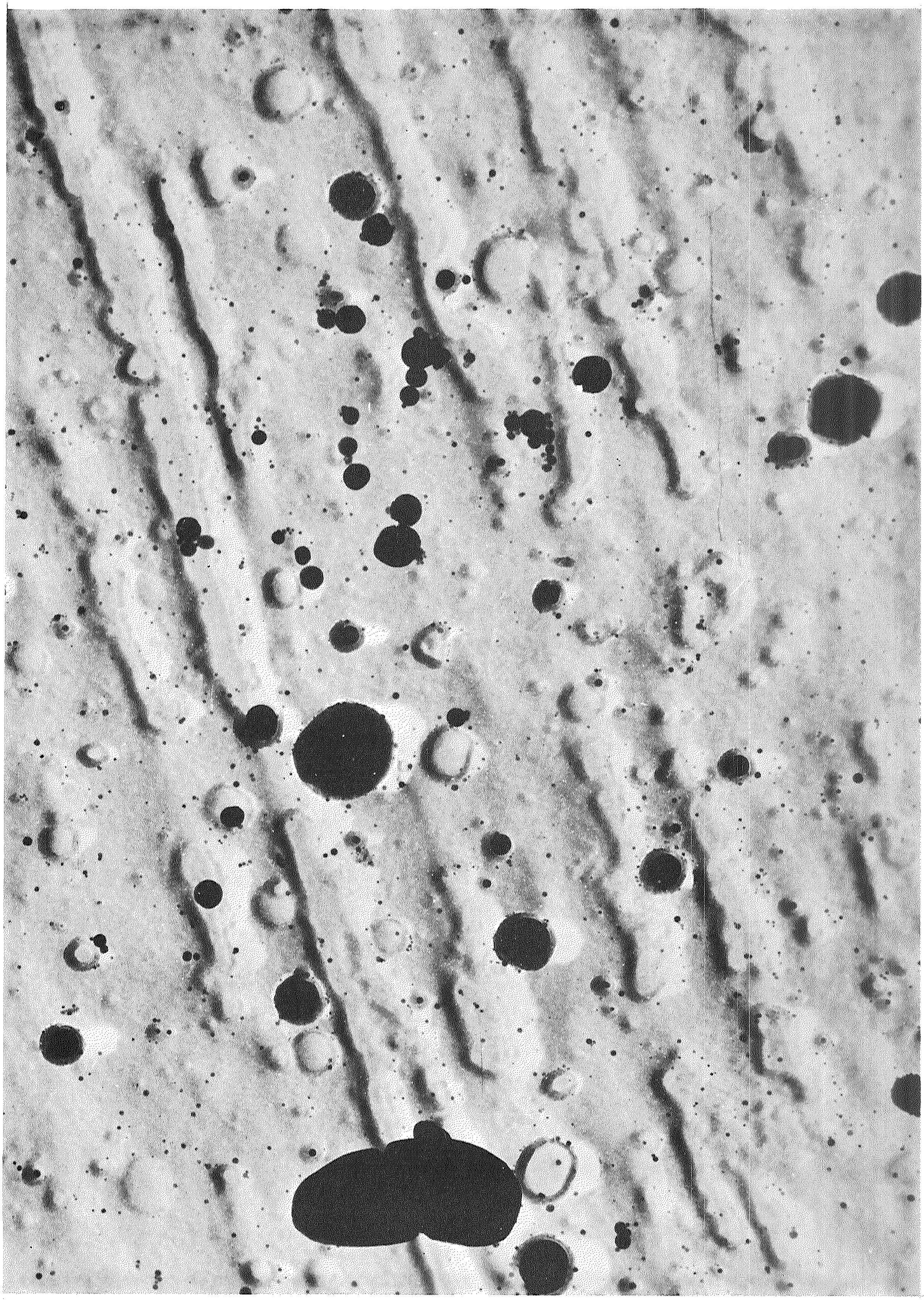


Photo No. 9003 C-W Co-18Cr-20Ni-4.6ThO$_2$ Mag. 46,000X
NASA No. 37-69-23 Extruded @ 1095°C @ Ratio of 15:1
PP2-12A-42 Heat Treated 100 hrs. @ 1205°C in Vacuum
Ext. No. 19 Extracted Particles

FIGURE 42

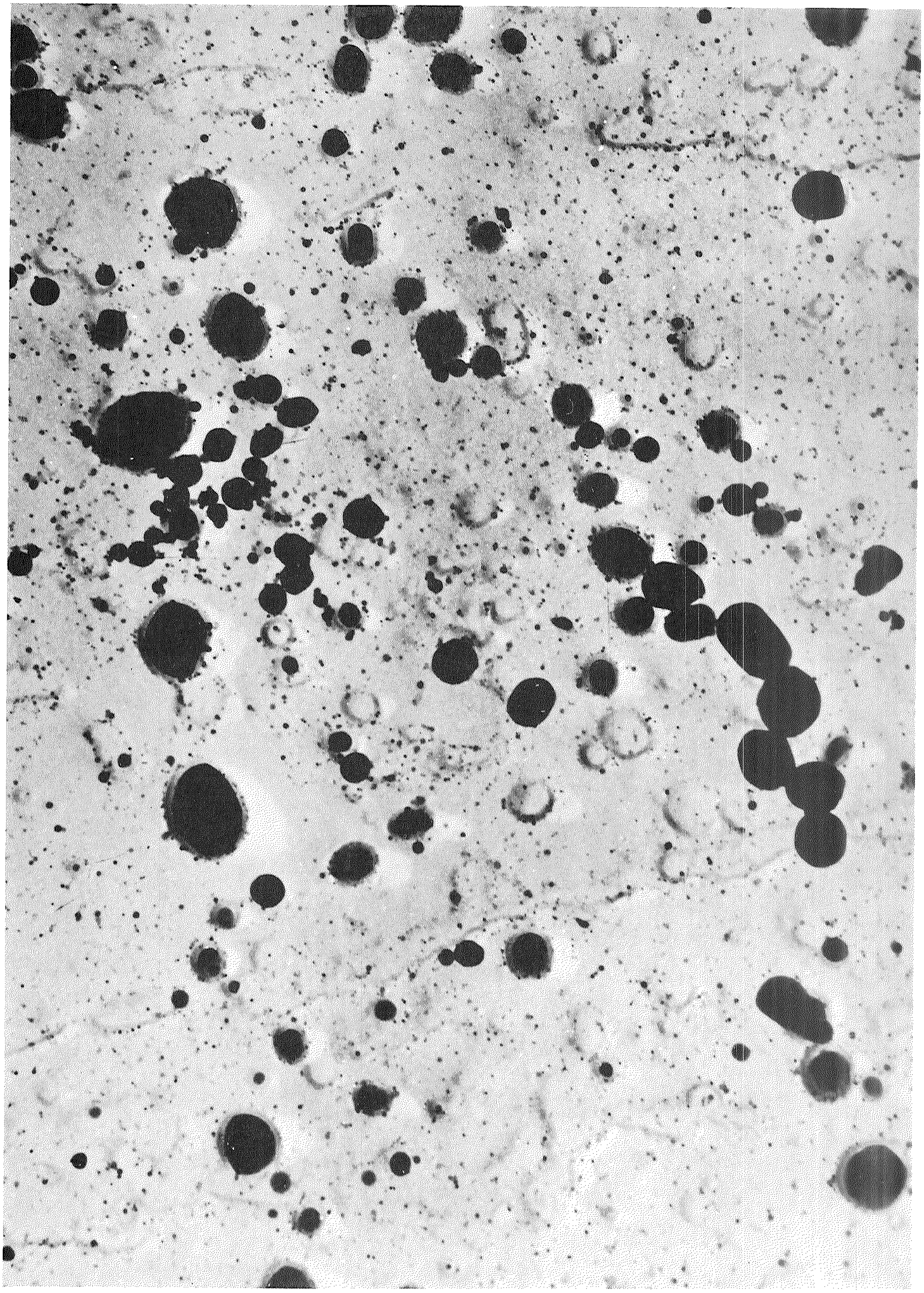


Photo No. 9004
NASA No. 38-69-5
PP2-12A-43
Ext. No. 20

C-W Co-18Cr-20Ni-4.6ThO$_2$
Extruded @ 1095°C @ Ratio of 15:1
Heat Treated 100 hrs. @ 1205°C in Vacuum
Extracted Particles

Mag. 46,000X

APPENDIX 1

FORMULATION OF METAL SALT-COLLOIDAL ThO_2 SOLUTIONS

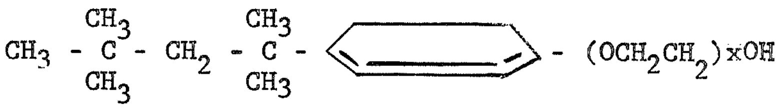
Formulation of Metal Salt-Colloidal ThO_2 Solutions

1. Laboratory amounts of solutions were made up containing salts of Co, Ni, and Cr in the metal content of proportion of 62 Co, 20 Ni, and 18 Cr. The salts used were either nitrates or acetates. At each concentration the salt solutions were adjusted to give variations in pH from 1-14. Each solution was examined and those showing precipitates were discarded. The results are shown in Tables A1 and A2.

2. Two types of colloidal ThO_2 solutions were added to the clear solutions obtained in Step 1 above and the results are shown in Tables A3 and A4.

3. Colloidal ThO_2 of different concentrations were added to a 35% nitrate solution and the results are shown in Table A5. From this work it was concluded that the optimum ThO_2 concentration was in the order of 30-100g/dm^3.

4. Manufacturing companies making colloidalizing agents were contacted and the most promising agents were those of the nonionic octylphenoxyethanol series made by Rohm and Haas. The products are of the type commonly described as aklylarylpolyether alcohols, and have the following structural formula:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_4-(OCH_2CH_2)xOH$$

Two members of this series were used in our experiments and these were as follows:

Triton X-100	(X = 9-10)
Triton X-200	(X = 19-21)

These agents were added to a 35% metal nitrate salt solution, the metals were in proportion of 62Co: 18Cr: 20Ni. The percentage of these surface active agents, their results upon the nitrate solutions, and the results obtained upon addition of the colloidal ThO_2 solution, are shown in Tables A6 and A7.

From the preceding work it was concluded that a 35% nitrate salt solution with colloidal ThO_2 of 30-100g/dm^3 concentration added was the best formulation.

Since it was found that a 35% nitrate solution-colloidal thoria suspension is only stable for a few minutes, it was concluded that the mixing of the two solutions should be performed just prior to the entering of the solutions to the Flash Dryer.

TABLE A1

STABILITY OF VARIOUS NITRATE SOLUTIONS OF A 62 Co, 18Cr, 20 Ni METAL PROPORTION

Solution #	Anhydrous Salt Conc.	Metal Content Wt.	pH	Resultant Solution	Remarks
1	30%	8.89%	1-2	Clear	
2	20%	5.92%	1-2	"	
3	10%	2.96%	2	"	
4	5%	1.48%	3	"	
5	1%	0.30%	3	"	
6	40%	13.38%	3-4	Clear	
7	30%	10.00%	3-4	"	
8	20%	6.68%	4-5	"	
9	10%	3.34%	5	"	
10	5%	1.67%	5	"	
11	1%	0.33%	5	"	
12	40%	7.98%	9	ppt.	Voluminous precipitate. Solution discarded.
13	30%	6.65%	9	"	" "
14	20%	5.00%	9	"	" "
15	10%	2.86%	9	"	" "
16	5%	1.54%	9	"	" "
17	1%	0.32%	9	"	" "
18	40%	3.60%	13	Small ppt.	Ppt. filtered off and found to contain 15% metal content. Filtered solution used for further work.

Note 1: Solutions 1-5 were made of the following salts: $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cr(NO_3)_3$.

2: Solutions 6-18 were made of the following salts: $Co(NO_3)_2$, $Ni(NO_3)_2$, $(NH_4)_2$, Cr_2O_7.

3. Anhydrous salt concentration refers only to metal salts.

4: Solutions 12-17 had 5.1 grams of 30% aqueous NH_3 added for every gram of metal in solution.

5. Solution 18 had 10.1 grams of 30% aqueous NH_3 added for every gram of metal in solution.

TABLE A2

STABILITY OF VARIOUS ACETATE SOLUTIONS OF A 62 Co, 18 Cr, 20 Ni METAL PROPORTION

Solution #	Anhydrous Salt Conc.	Metal Content Wt.	pH	Resultant Solution	Remarks
19	20%	6.10%	6	Clear	Solution unstable due to solubility being exceeded.
20	10%	3.05%	6	Clear	
21	5%	1.50%	6	"	
22	1%	0.30%	6	"	
23	15%	5.56%	5	Clear	
24	10%	3.71%	5	"	
25	5%	1.85%	5-6	"	
26	1%	0.37%	5-6	"	
27	15%	4.32%	9	Ppt.	Voluminous precipitate. Solution discarded.
28	10%	3.10%	9	Ppt.	" "
29	5%	1.69%	9	"	" "
30	1%	0.36%	9	"	" "
31	15%	2.60%	12.5	Small ppt.	Ppt. filtered off and found to contain 2% of metal content. Filtered solution used for further work.

Note 1: Solutions 19-22 were made of the following salts: $Co(C_2H_3O_2)_2$, $Ni(C_2H_3O_2)_2$, $Cr(C_2H_3O_2)_3$.

2: Solutions 23-31 were made of the following salts: $Co(C_2H_3O_2)_2$, $Ni(C_2H_3O_2)_2$, $(NH_4)_2$, Cr_2O_7.

3: Anhydrous salt concentration refers only to metal salts.

4: Solutions 27-30 had 5.1 grams of 30% aqueous NH_3 added for every gram of metal in solution.

5: Solution 31 had 10.1 grams of 30% aqueous NH_3 added for every gram of metal in solution.

TABLE A3

RESULTS OF ADDITION OF COLLOIDAL THO_2 SOLUTIONS TO VARIOUS NITRATE SOLUTIONS OF A 62 Co, 18 Cr, 20 Ni METAL PROPORTION

Solution #	Anhydrous Salt Conc.	Metal Content Wt.	pH	Remarks
1	30%	8.89%	1-2	Small ppt. observed after 5 minutes.
2	20%	5.92%	1-2	" " " " 3 "
3	10%	2.96%	2	" " " " 3 "
4	5%	1.48%	3	" " " " 2 "
5	1%	0.30%	3	No ppt. observed after prolonged standing, (days).
6	40%	13.38%	3-4	Small ppt. observed after 2 minutes.
7	30%	10.00%	3-4	" " " " " "
8	20%	6.68%	4-5	" " " " " "
9	10%	3.34%	5	" " " " 3 "
10	5%	1.67%	5	" " " " " "
11	1%	0.33%	5	" " " " 24 hours.
18	40%	3.60%	13	Small ppt. observed in seconds.
18A	40%	3.60%	13	Small ppt. observed in seconds.

Note 1: Solutions 1-5 were made of the following salts: $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cr(NO_3)_3$.

2: Solutions 6-11, 18, 18A, were made of the following salts: $Co(NO_3)_2$, $Ni(NO_3)_2$, $(NH_4)_2$, Cr_2O_7.

3: Anhydrous salt concentration refers only to metal salts.

4: Solutions 18 and 18A had 10.1 grams of 30% aqueous NH_3 added for every gram of metal in solution.

5: The colloidal ThO_2 solution added to solutions 1-11 and 18 contained 40 grams 50-150 Å ThO_2/Liter.

6: The colloidal ThO_2 solution added to solution 18A contained 8 grams 50-150 Å ThO_2/Liter, 8 grams sucrose/Liter, and 108 grams NH_3/Liter.

TABLE A4

RESULTS OF ADDITION OF COLLOIDAL THO_2 SOLUTIONS TO VARIOUS ACETATE SOLUTIONS OF A 62 Co, 18 Cr, 20 Ni METAL PROPORTION

Solution	Anhydrous Salt Conc.	Metal Content Wt.	pH	Remarks
19	20%	6.10%	6	Small ppt. observed in seconds.
20	10%	3.05%	6	" " " " "
21	5%	1.50%	6	" " " after 1 minute.
22	1%	0.30%	6	No ppt. observed after prolonged standing.
23	15%	5.56%	5	Small ppt. observed in seconds.
24	10%	3.71%	5	" " " " "
25	5%	1.85%	5-6	" " " after 1 minute.
26	1%	0.37%	5-6	" " " " 10 minutes.
31	15%	2.60%	12.5	Small ppt. observed in seconds.
31A	15%	2.60%	12.5	Small ppt. observed in seconds.

Note 1: Solutions 19-22 were made of the following salts: $Co(C_2H_3O_2)_2$, $Ni(C_2H_3O_2)_2$, $Cr(C_2H_3O_2)_3$.

2: Solutions 23-26, 31, 31A, were made of the following salts: $Co(C_2H_3O_2)_2$, $Ni(C_2H_3O_2)_2$, $(NH_4)_2$,Cr_2O_7.

3: Anhydrous salt concentrations refers only to metal salts.

4: Solutions 31 and 31A had 10.1 grams of 30% aqueous NH_3 added for every gram of metal in solution.

5: The colloidal ThO_2 solution added to solutions 19-26 and 31 contained 40 grams 50-150 Å ThO_2/Liter.

6: The colloidal ThO_2 solution added to solution 31A contained 8 grams 50-150 Å ThO_2/ Liter, 8 grams sucrose/Liter, and 108 grams NH_3/Liter.

TABLE A5

RESULTS OF ADDITIONS OF COLLOIDAL THO_2 SUSPENSION OF DIFFERENT CONCENTRATIONS TO A 35% NITRATE SOLUTION HAVING METALS IN PROPORTION OF 62Co:18Cr:20Ni

Colloidal ThO_2 Suspension #	Colloidal ThO_2 Concentration, g/l	Metal Content of Resultant Nitrate Solution Wt. % *	Results Upon Addition of Colloidal ThO_2 Suspension
32	0.0	10.29	- - - - -
33	10.0	7.18	Small precipitate observed after 2 minutes.
34	40.0	9.56	Small precipitate observed after 5 minutes.
35	75.0	9.94	Small precipitate observed after 5 minutes.
36	150	10.39	Small precipitate observed after 4 minutes.

*ThO_2 weight added to metal content.

TABLE A6

RESULTS OF ADDITIONS OF TRITON X-100 AND COLLOIDAL THO_2* TO A 35% NITRATE SOLUTION HAVING METALS IN PROPORTION OF 62Co: 18Cr: 20Ni

Solution #	% X-100 Added	Resultant Solution	Results Upon Addition of Colloidal ThO_2 Suspension**
37	0.5	Clear	Heavy precipitate observed in 2 minutes
38	1.0	Clear	Heavy precipitate observed in 2 minutes
39	2.0	Clear	Heavy precipitate observed in 2 minutes
40	3.0	Clear	Heavy precipitate observed in 2 minutes
41	4.0	Clear	Heavy precipitate observed in 2 minutes
42	8.0	Clear	Heavy precipitate observed in 2 minutes

*Suspension contained 75g/1 of 50-150 Å colloidal ThO_2.

**An amount of ThO_2 was added so that the Co:ThO_2 ratio was 62:4.6.

TABLE A7

RESULTS OF ADDITIONS OF TRITON X-100 AND COLLOIDAL THO_2* TO A 35% NITRATE SOLUTION HAVING METALS IN PROPORTION of 62Co: 18Cr: 20Ni

Solution #	% X-100 Added	Resultant Solution	Results Upon Addition of Colloidal ThO_2 Suspension**
43	0.5	Clear	Heavy precipitate observed after 1 minute
44	1.0	Clear	Heavy precipitate observed after 1 minute
45	2.0	Slight Turbidity	Heavy precipitate observed after 1 minute
46	3.0	Slight Turbidity	Heavy precipitate observed after 1 minute
47	4.0	Heavy Turbidity	Heavy precipitate observed after 1 minute
48	8.0	Heavy Turbidity	Heavy precipitate observed after 1 minute

*Suspension contained 75g/1 of 50-150 Å colloidal ThO_2.

**An amount of ThO_2 was added so that the Co:ThO_2 ratio was 62:4.6.

APPENDIX II

AREAL AND LINEAL ANALYSES PROCEDURES

AREAL ANALYSIS

(Ref. W. Rostoker and J. Dvorak, "Interpretation of Metallographic Structures," 1965, pp. 195-219, Academic Press, N.Y.)

PROCEDURE:

1. Procure photomicrograph of material at a magnification where the average particle size is approximately 0.5 cm.
2. Construct a square or rectangular area so that approximately 100 particles are within that area.
3. Measure the diameter of each of these 100 particles in microns.
4. Total the number of particles (Q1, Q2....) at each diameter size, that is, at .01μ, .02μ, .03μ, etc. (D_1, D_2, D_3, etc.).
5. Calculate the total area (A_p) covered by particles

$$A_p = \frac{\pi D1^2}{4} \times Q_1 + \frac{\pi D2^2}{4} \times Q_2 + \frac{\pi D3^2}{4} \times Q_3 + \ldots$$

6. Calculate area fraction (F)

$F = \frac{A_p}{At}$ where At = Area (in μ^2) encompassed by square or rectangle as per Step #2.

NOTE: F also equals volume fraction [A.B. Wenterbottom in "The Physical Examination of Metals", (B. Chalmess and A. G. Quarrell, editors), Chapter I., Arnold, London, 1960.]

LINEAL ANALYSIS

(Ref. W. Rostoker and J. Dvorak, "Interpretation of Metallographic Structures," 1965, pp. 195-219, Academic Press, N.Y.)

PROCEDURE:

1. Procure photomicrograph of material at a magnification where the average dispersoid size is approximately 0.5 cm.

2. Impose a transparent grid (series of parallel lines 1 cm. apart) over the area to be measured.

3. Measure (in cm.) the portion of each line which is occupied by a dispersoid. Add all portions together to get L_o, the total portion of all lines covered by dispersoids.

4. Calculate volume fraction (F)

   $F = \frac{L_o\ (cm)}{L\ (cm)}$ where = L_o= portion of lines covered by dispersoids (determined in Step 3)
   L = total length of all grid lines imposed on photomicrograph

5. Determine "particles per unit area" (N_a)

   a. Count the number of dispersoid particles in the photomicrograph. If less than half a particle lies in the area, do not count it.

   b. Calculate area represented by the photomicrograph in cm^2 and convert to μ^2 using the following conversion factor:

   $$C.\ F. = \left(\frac{10{,}000}{\text{magnif. of Photomicrographs}}\right)^2$$

   c. Calculate N_A:

   $$N_A = \frac{\text{Total particles counted}}{\text{Area in } \mu^2} = \text{particles}/\mu^2$$

6. Calculate "particles per unit length of line" (N_L)

   $$N_L = \sqrt{F \times \frac{3\pi}{8} \times N_A} = \text{particles}/\mu$$

7. Calculate the radius "r" of the dispersoid

   $$r = \frac{2}{\pi} \times \frac{N_L}{N_A}$$

8. Calculate the "mean free path" or average distance (D) between the peripheries of particles (dispersoids).

   $$D = \frac{1 - F}{N_L}$$

APPENDIX III

EXTRACTION REPLICA MICROSCOPY

EXTRACTION REPLICA MICROSCOPY

The techniques used in making the extraction replicas and in determining the size of the particles were as follows:

The samples were initially mechanically polished by standard metallographic techniques. The ThO_2 particles were then put in relief above the polished surfaces by electropolishing the samples in an electrolyte of 3 parts phosphoric acid and 2 parts sulfuric acid at approximately 30 volts. The polishing time was about 3 to 5 seconds. Approximately 250 Å of carbon was then vapor deposited onto the surfaces of the samples. The carbon layers, with the ThO_2 particles adhering to them, were then freed from the surfaces of the samples by electropolishing further in an electrolyte of 5% perchloric acid in acetic acid at approximately 6 volts. The freed carbon replicas were then picked up on microscopic grids, washed in distilled water, and examined by electron microscopy.

The size of the particles were measured directly from the micrographs by a manual method. Using a 4X magnifying glass the smallest particle that could be measured was 0.25mm. corresponding to 37 Å on a print of 68,750X.

The median particle diameter size is obtained from the 50% point on a cumulative per cent-particle diameter graph.

The average particle diameter is calculated by multiplying the number of particles of each size by the diameter, adding the products together, and dividing by the total number of particles.

APPENDIX IV

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