Second United Nations
International Conference
on the Peaceful Uses
of Atomic Energy

A/CONF.15/P/1097
AUSTRALIA
20 May 1958

ORIGINAL: ENGLISH

URANIUM ALLOY POWDERS BY DIRECT REDUCTION OF OXIDES.

by

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ABSTRACT

A process is outlined for the production of uranium alloy powders by co-reduction of mixtures of uranium dioxide and alloy element oxide with calcium in a sealed reaction vessel. The process is shown to produce powder with a wide variation in particle to particle composition although of consistent composition over various sized fractions. The particle size and shape is also described. Reduction of compound oxides with calcium is shown to be unsuitable.

The particular alloy systems considered are uranium with nickel, chromium, molybdenum, and niobium. The uranium-molybdenum and uranium-niobium powders are single phase metastable gamma, which is of consequence in the production of dimensionally stable nuclear fuels. Likely applications of the alloy powders are discussed.

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DISCLAIMER

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I. INTRODUCTION

1. The production of uranium powder by the calcium reduction of uranium dioxide has been described by Myers <u>et al.</u>[1], Buddery[2], and Myers and Robins[3]. The improvement in dimensional stability and in corrosion resistance of certain uranium alloys together with the known advantages of the powder metallurgical techniques for the fabrication of uranium fuel elements, prompted the authors to study the feasibility of producing uranium alloy powders by a direct reduction process similar to that used for uranium.

2. The alloy systems which were chosen included ones likely to be of interest as fuels as well as ones in which the determination of composition variation was made possible by the application of metallographic techniques. The results given in this paper were selected to show the general trend in composition variation, purity, and particle size and shape of the powders. During the reduction work both compound, and mechanically mixed oxides were tried; the latter gave a more suitable product.

II. PROCEDURE AND RESULTS

3. Details of the equipment and procedures used in this work have already been described[3]. Briefly the procedure was to charge either the compound oxides or the mechanically mixed oxides with calcium metal granules into a calcium oxide lined, heat-resisting steel reaction vessel or "bomb" under an atmosphere of argon. The bomb was heated slowly enough to maintain a uniform temperature in the charge until reaction occurred - usually at about 630°C - after which the bomb temperature was raised rapidly to a selected value above the

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liquidus of the particular alloy (except in the case of 20 at.-% niobium and 30 at.-% molybdenum).

4. When cold the reaction products were crushed, and leached in cold dilute acetic acid to remove the calcium oxide and excess calcium surrounding the uranium alloy particles, which were then washed and dried.

(a) Reduction of Compound Oxides

5. Initially reduction experiments were carried out on compound oxides because it was thought that these would be most likely to yield a homogeneous product. Two stable and readily prepared compound oxides, $UO_3.MoO_3$ and $UO_3.NiO$ were studied. The heats of reaction for the reduction of these oxides were much greater than for UO_2 and even on a 50g scale the reactions were mildly explosive.

6. In the case of $UO_3.MoO_3$ the reaction was so exothermic that the products of reaction were completely fused, and a metal button was recovered having a composition of 58 at.-% molybdenum. This button represented a yield of 57%.

7. In the reduction of $UO_3.NiO$, the products were thrown upwards in the bomb and so were rapidly cooled. The metal recovered represented only 65% of that charged and had an overall composition of 48 at.-% nickel. The distribution of composition was estimated by examining individual particles metallographically. Because of the existence of several easily identified intermediate phases, these particles could be classified into one of three composition ranges, namely 28.0-33.5, 33.5-48.0, and 48.0-63.0 at.-% nickel respectively. The range of composition was found to be approximately from 28 to 63 at.-% nickel. The particles, which were of irregular shape, ranged in size up to only 30 micron due probably to the rapid cooling following the explosive reaction.

(b) Reduction of Mixed Oxides

8. The systems chosen for this work were alloys of uranium with nickel, chromium, molybdenum, and niobium. The particular alloy compositions were based on literature reports of alloys which had been found to reduce the dimensional instability and/or susceptibility to corrosion of pure uranium.

9. The existence of the metastable gamma phase in uranium-molybdenum, and uranium-niobium, over a wide composition range, indicated that the powders produced should be single phase. In the uranium-nickel and uranium-chromium systems the estimation of composition variations by metallographic techniques was possible. The uranium-nickel alloys were most

easily located in a particular composition range by the identification of the several intermediate phases present. Although uranium-chromium was a simple eutectic system, the accuracy of the determination of particle composition was reduced due to eutectic degeneration.

10. All of the alloy powders prepared from mixed oxides were reacted in a bomb of sufficient size to produce 1 kg of metal powder (10 cm diameter and 30 cm high). The mixing of the component oxides was carried out in a stainless steel ball mill, which was overloaded with oxide and underloaded with stainless steel balls, to promote mixing rather than size reduction and to reduce contamination by attrition of the mill and balls.

(i) Uranium-nickel

11. The results for two compositions involving uranium and nickel are presented; one of composition U_6Ni (14.3 at.-% Ni) and the other of eutectic composition (33.5 at.-% Ni). Both batches were prepared from mixtures of UO_2 and NiO, and after the reaction with calcium had occurred the nominally U_6Ni batch was held at 1230°C, and the nominally eutectic batch at 800°C for approximately forty minutes (i.e. 300°C and 60°C above the respective liquidus temperatures). The particle size distributions for these powders, shown in Table 1. indicated a mean mass diameter of 90 micron for "U_6Ni" and 200 micron for "eutectic" material.

TABLE 1.

PARTICLE SIZE DISTRIBUTION OF URANIUM-NICKEL POWDERS

Size Range (micron)	Cumulative Mass Percentage	
	"U_6Ni" Alloy	"Eutectic" Alloy
-10	7	6
-20	12	7
-40	21	11
-74	45	18
-104	52	27
-147	55	36
-208	56	51
-295	59	66
Yield-%	80	71

12. To estimate the variation in composition of particles in the powder, samples from each size range were mounted, polished, and etched to reveal the different phases. The estimation of the distribution in composition was carried out by the metallographic identification of the composition of individual particles in five fields of 100 particles for each of the size fractions. The "U_6Ni" powder had a variation in particle composition of 4 - 48 at.-% nickel, with 50% by weight of the particles falling between 14.3 - 33.5 at.-%. The "eutectic" powder had a variation of 14.3 - 63 at.-%, the details of which are shown in Table 2.

TABLE 2.

DISTRIBUTION OF COMPOSITION IN U-Ni "EUTECTIC" POWDERS

Composition Range (at.-%)	Mass Percentage in Various Size Ranges (micron)			
	74-104	104-147	147-208	208-295
0 - 14.3	-	1	-	-
14.3 - 28.0	4	5	4	2
28.0 - 33.5	16	18	17	20
33.5 - 48	65	58	60	56
48 - 63	10	12	16	19
Oxide particles	3	3	2	1
Unidentified particles	2	3	1	2

A typical photomicrograph of the U-Ni "eutectic" powder is shown in Plate 1. The regular shape of the particles can be seen. Chemical analysis of each of the sized fractions above 74 micron and of the minus 74 micron fraction for both alloys showed 16.0 ± 0.6 at.-% nickel for the "U_6Ni" powders and 34.5 ± 0.8 at.-% nickel for the "eutectic" powders.

(ii) Uranium-Chromium

13. To show the reproducibility of yields and particle size distribution of the powders, the results obtained from three batches of uranium-chromium powder of nominally eutectic composition (20 at.-% chromium) are presented. In each case a mixture of UO_2 and Cr_2O_3 was reacted with calcium and then the temperature held at 960°C for 30 minutes (i.e., 100°C above the eutectic melting point). The similar distribution of particle sizes for each batch can be seen from Table 3. The mean mass diameter was approximately 90 micron.

TABLE 3

PARTICLE SIZE DISTRIBUTION OF URANIUM-CHROMIUM POWDER OF NOMINALLY EUTECTIC COMPOSITION

Size Range (micron)	Cumulative Mass Percentage		
	Batch 1	Batch 2	Batch 3
-10	14	17	19
-20	27	22	27
-40	30	29	36
-74	46	40	50
-104	56	51	59
-147	64	68	70
-208	77	86	82
-295	95	98	96
Yield-%	86	85	88

14. A typical photomicrograph of the polished and etched powder is shown in Plate 2, in which the regular particle shape can be seen. The range of particle composition was found metallographically to be 10 - 80 at.-% chromium, with approximately 70% by weight between 20 and 30 at.-%. The composition of individual fractions was found by chemical analysis to be 20.9 ± 0.9 at.-% chromium.

(iii) Uranium-molybdenum

15. Batches of uranium-molybdenum powder having nominal compositions of 11, 22 and 30 at.-% were prepared from mixtures of UO_2 and MoO_2. After the reaction had occurred in each case the temperature was raised to the maximum operating temperature of the bomb - 1300°C - and held for one hour. The distribution of particle size of the powder for each batch is given in Table 4. The mean mass diameter decreased from 180 micron for the 11 at.-% alloy, to 90 and 60 micron for the 22 and 30 at.-% alloys respectively.

16. Metallographic examination of the powders revealed that the 11 and 22 at.-% alloys were single phase and that the 30 at.-% alloy, while being predominantly single phase, included some particles with the molybdenum rich phase which existed above 32 at.-% molybdenum. An accurate composition range could not be established but in the two lower alloys it was within 0 to 32 at.-% and in the richest alloy, 0 to approximately 40 at.-% molybdenum. In contrast to the two lower alloys the 30 at.-% alloy consisted of irregular, porous particles.

TABLE 4

PARTICLE SIZE DISTRIBUTION OF URANIUM-MOLYBDENUM POWDERS

Size Range (micron)	Cumulative Mass Percentage		
	11 at.-% Alloy	22 at.-% Alloy	30 at.-% Alloy
-10	10	12	13
-20	11	22	24
-40	14	28	31
-74	22	41	67
-104	27	55	73
-147	45	61	87
-208	53	72	91
-295	61	78	94
Yield-%	74	81	81

17. The molybdenum content of the various fractions from each batch was found to be (nominal composition in brackets): 11.5 ± 0.7 (11 at.-% Mo), 22.6 ± 0.6 (22 at.-% Mo), and 30.6 ± 0.6 (30 at.-% Mo).

(iv) Uranium-niobium

18. Although the liquidus temperature of a 20 at.-% niobium alloy was higher than the safe working temperature of the reaction vessel the results obtained were similar to those for the other alloys, except for the irregular particle shape. After the reaction of a mixture of UO_2 and Nb_2O_5, the temperature was raised to 1300°C and held for one hour. The distribution of particle size for the uranium-niobium powder produced is given in Table 5 which indicates a mean mass diameter of approximately 130 micron.

TABLE 5

PARTICLE SIZE DISTRIBUTION OF URANIUM-20 at.-% NIOBIUM POWDER

Size Range (micron)	Cumulative Mass Percentage
-10	22
-20	23
-40	32
-74	40
-104	46
-147	53
-208	60
-295	71
Yield-%	88

Metallographic examination of the powders could not be used to estimate individual particle composition as the product was single phase. Chemical analysis of the various fractions of uranium-niobium powder showed their niobium content to be 20.6 ± 1.4 at.-%.

(v) Impurities in the powders

19. All powders were spectrographically analysed to determine whether there was any contamination by iron, nickel, chromium or calcium. The total Fe + Ni + Cr pick up seldom exceeded 0.006% in the plus 74 micron fractions although in the minus 74 micron fraction it rose to 0.02% in the nickel, chromium and molybdenum alloys and 0.06% in the niobium alloy. The calcium content of the minus 74 micron fractions of the powders was usually less than 0.01%. However, in the coarser fractions of the molybdenum and niobium alloys it rose to 0.2% due probably to entrapment of lime in the pores of the particles (See Plate 4).

IV. DISCUSSION

20. The compound oxide reduction process limited the choice of alloy compositions, and resulted in extremely high heats of reaction, low yields, irregular particle shape and a wide variation in particle to particle composition. As the process based on mixed oxides led to variation in particle composition of the same order and did not suffer from the disadvantages mentioned above, it was considered more likely to be of use. The following discussion deals only with the mixed oxide process.

(a) Composition variations

21. The alloy element content of the various fractions of any one powder was found to be constant within the limits of accuracy of the analytical methods, and the overall alloy element content of each powder was only slightly above the nominal value. However, this apparent homogeneity did not exist from particle to particle, where a wide variation in composition was found, the worst case being the 10 to 80 at.-% range in the "eutectic" chromium alloy.

22. It had been assumed prior to this work that agglomeration, following the reduction of oxide particles of about 1 micron in diameter, to metal particles with a mean mass diameter of, say, 50 micron, would result in uniform particle composition. When the initial experiments did not show this expected uniformity, a microscopic examination of the mixed oxides was made. This revealed that the constituent oxide particles, all of which were in the size range 0.7 - 2.5 micron, were intimately mixed. This complete mixing was

observed in all subsequent experiments and so far no satisfactory explanation of the variations in composition of the particles in the metal powders can be proposed. The belief that inadequate mixing was not the cause of the variation was reinforced by the results obtained from the experiments using compound oxides in which the uranium and alloying elements would be atomically dispersed.

(b) Particle size

23. Although the individual oxide particles were all less than 2.5 micron in diameter, the metal alloy agglomerates produced from the reduced particles had mean mass diameters ranging up to approximately 200 micron. All powders contained occasional particles up to 3 mm in diameter. In the reduction of uranium oxides with calcium it has been found[1,3,4] that the particle sizes of uranium powders were increased by higher temperatures reached on reaction, higher soaking temperatures above the melting point, and longer soaking times. Although these aspects have not been specifically studied yet for the alloys, the same trend was evident, at least for the first two factors. By comparison with the uranium powders the mean mass diameters of all of the alloy powders were much higher. The approximate value for uranium was 30 micron compared with 60 micron for 30 at.-% Mo, 90 micron for 22 at.-% Mo, the chromium eutectic and U_6Ni, 180 micron for 11 at.-% Mo and 200 micron for the nickel eutectic.

(c) Particle shape

24. The major factor which affected particle shape was the difference between the liquidus temperature of the alloy and the soaking temperature. Regular particles of essentially spherical shape, as illustrated in Plates 1 and 2, were obtained when the temperature of soaking was up to approximately 200°C above the liquidus temperature. With soaking temperatures outside this range irregular particles were produced.

25. When the temperature difference was greater than about 200°C irregular non-porous agglomerates resulted. This type of agglomerate is seen in Plate 3 which shows a section through a fraction of "U_6Ni" powder which was soaked at 300°C above the nominal liquidus temperature. A similar batch of "U6Ni" powder which had been soaked at 100°C above the liquidus temperature had regular particles of the same shape as those in Plate 1.

26. With powders which were soaked at temperatures lower than the liquidus temperature, for example, U-20 at.-% Nb and U-30 at.-% Mo, the particles were irregular and porous. Plate 4 is a photomicrograph of a section through a typical single particle from the U-30 at.-% Mo powder.

(d) Yields

27. The yields of leached alloy powders which were obtained in these experiments were about 80%. The main source of loss was in the metal globules which adhered to the calcium oxide liner. Experiments which had been carried out on a smaller scale gave lower yields due to the greater surface area of the liner in relation to the mass of the products of reaction, so that a significant increase in yield could be expected from reactions carried out on a larger scale. This trend has also been noted in work on the production of pure uranium powder where recoveries of 98.5% have been obtained with batches of 5 kg. The recovery of the adhering material was not attempted as it would have entailed leaching of the greater part of the calcium oxide lining. Apart from increasing the leaching time and acid consumption this would have allowed impurities in the oxide, and scale from the bomb, to mix with the alloy powders. Analyses carried out on the leach liquors and on the parts of the liner with no visible globules adhering accounted for losses amounting to only 0.5%.

(e) Application

28. In the field of nuclear fuel technology the usefulness of the alloy powders produced by the process described in this paper is limited by the wide particle size distribution and particle composition variation. Where a uniform particle composition or size, or a particle size of the order of 1 micron would be desirable, the powders would be unsuitable. They should be suitable for the production by melting or powder metallurgical techniques of bar and special shaped fuel elements and they may have some application in the manufacture of matrix type fuels although it would probably be desirable to use only single phase material, for example, uranium-molybdenum or uranium-niobium alloys.

V. ACKNOWLEDGEMENTS

29. The authors gratefully acknowledge the substantial grant made to the New South Wales University of Technology by the Australian Atomic Energy Commission to support a research programme which includes the work described in this paper. The authors are indebted to Mr.D.A.Sinclair of the Defence Standards Laboratories, Sydney, for the spectrographic analyses.

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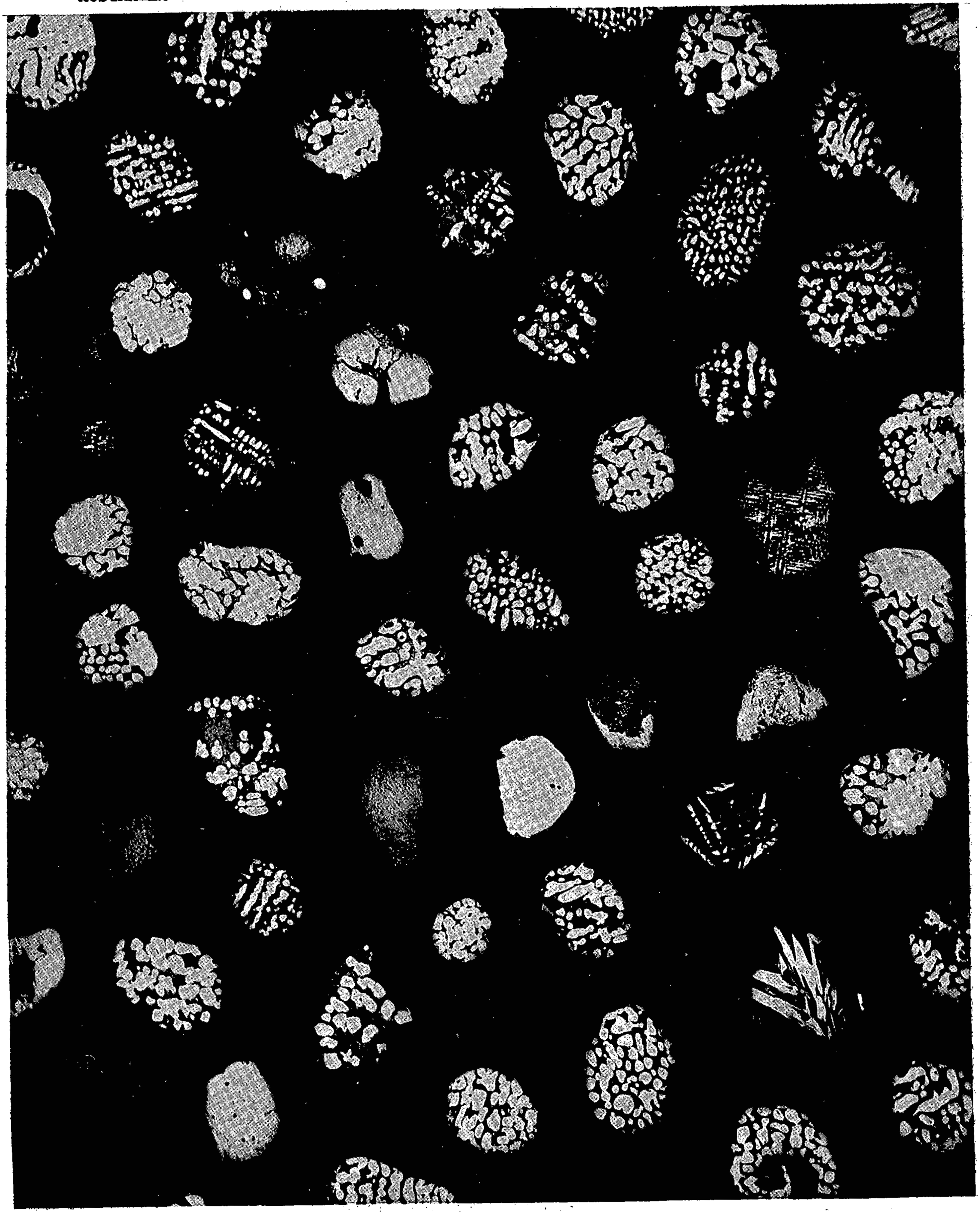
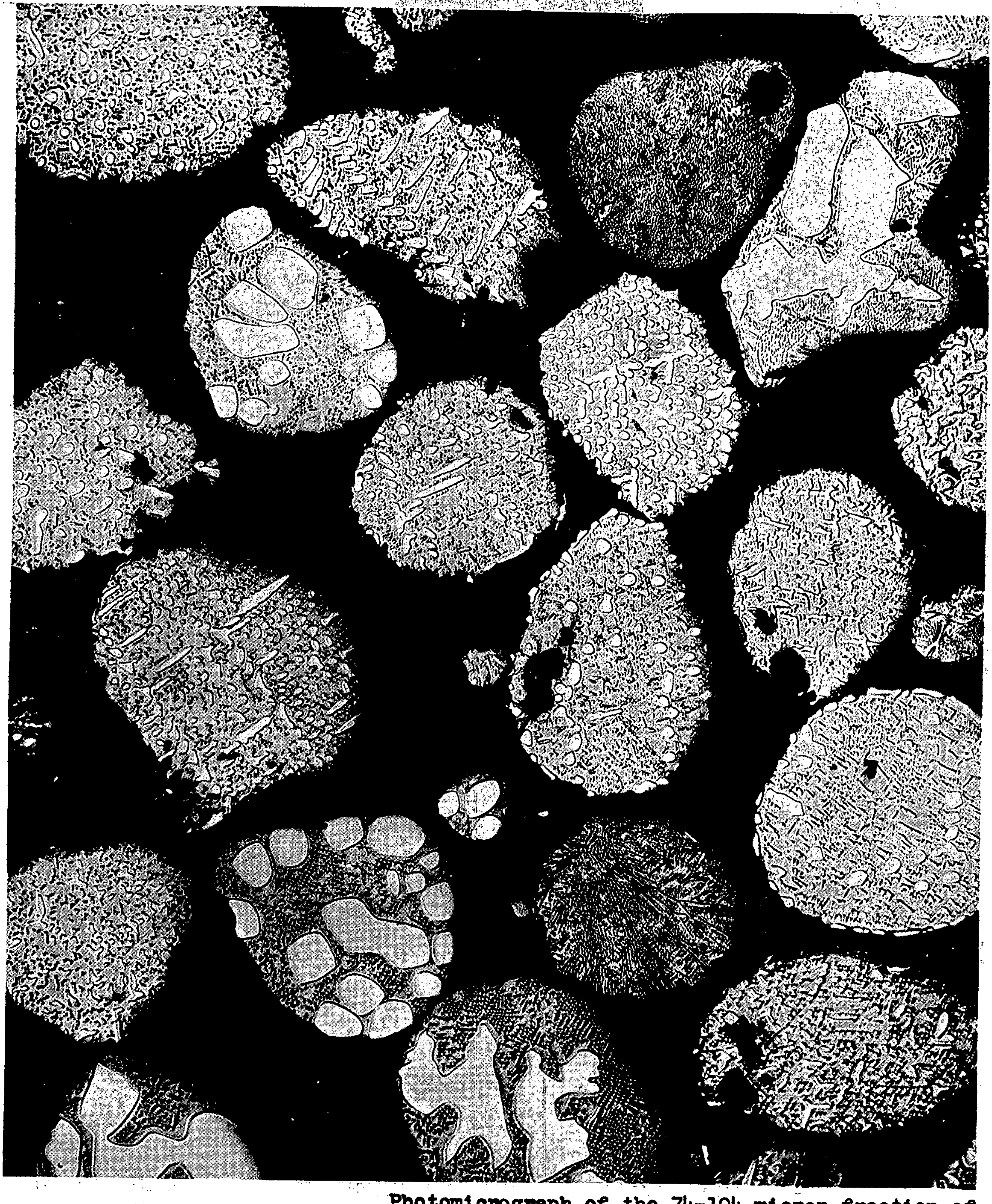


Plate 1

Photomicrograph of the 208-295 micron fraction of the nickel-uranium "eutectic" alloy powder.

Etchant 10% NaOH - H_2O_2



<u>Plate 2</u>

Photomicrograph of the 74-104 micron fraction of the chromium-uranium "eutectic" alloy powder.

Etchant 10% NaOH - H_2O_2

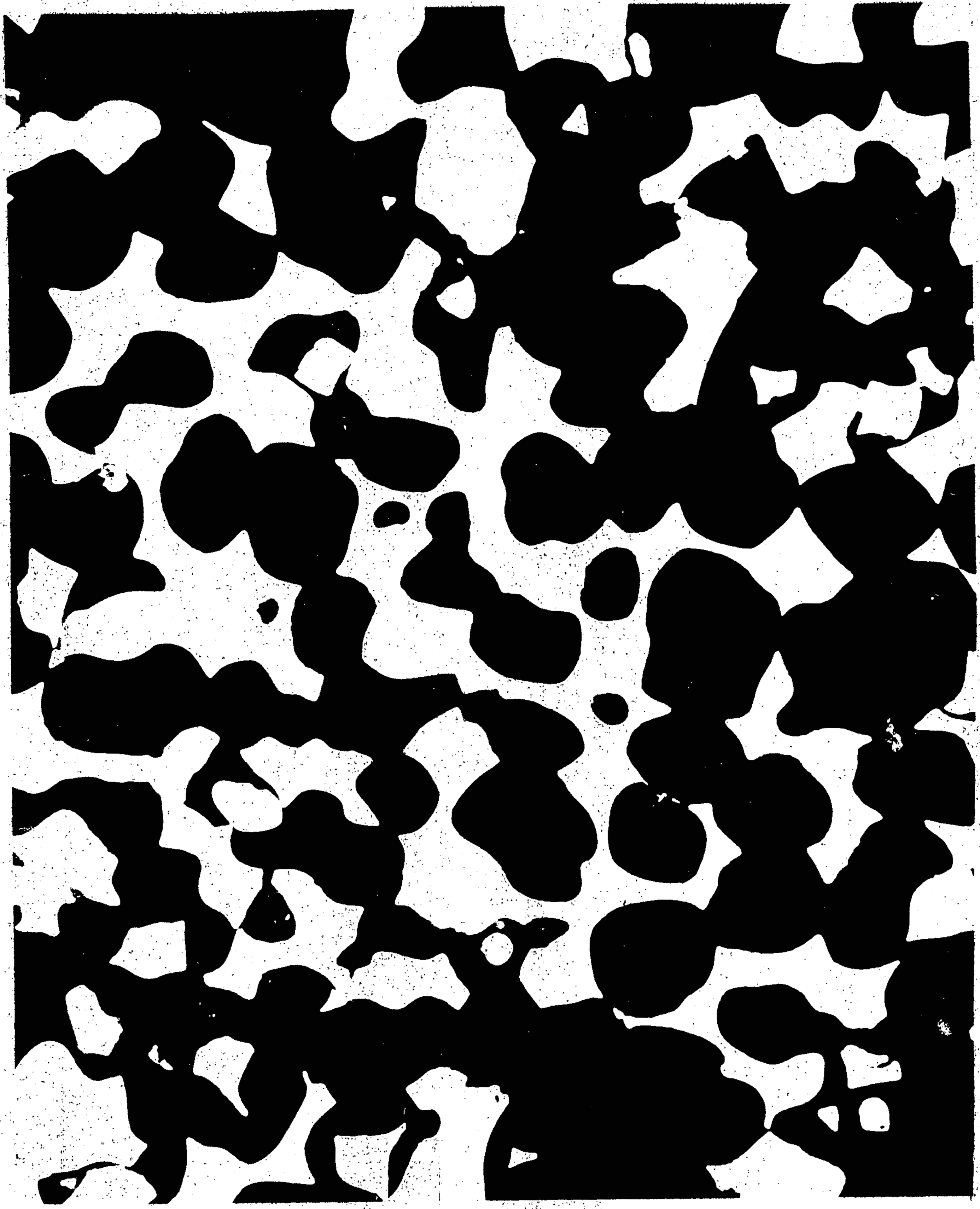


Plate 3 Photomicrograph of the 147-208 micron fraction of "U_6Ni" powder. Polished and unetched.

Plate 4. Photomicrograph of a single particle of 30 at.-% molybdenum alloy - approximately 150 micron diamster.

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