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(54) Titre : AGGLOMERES DE METAUX AU COBALT, LEUR PROCEDE DE PRODUCTION ET LEUR UTILISATION
(54) Title: COBALT METAL AGGLOMERATES, PROCESS FOR PRODUCING THE SAME AND THEIR USE

(57) **Abrégé/Abstract:**

The present invention relates to cobalt metal agglomerates consisting of peanut-shaped primary particles with average particle sizes in the range from 0.5 to 2 µm, to a process for the production thereof and to the use thereof.



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A b s t r a c t

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Cobalt metal agglomerates, process for producing the same and their use

5 The present invention relates to cobalt metal agglomerates consisting of peanut-shaped primary particles with average particle sizes in the range from 0.5 to 2 μm , to a process for the production thereof and to the use thereof.

10 Finely divided cobalt metal is mainly used as a binder in the production of hard metal and cutting tools based on various hard materials, such as for example WC, diamond, SiC and CBN. The cobalt metals used, for example, in the production of diamond tools must fulfil specific requirements. These include, in the first instance, that impurities such as Al, Ca, Mg, S and Si should be avoided as these elements readily form stable oxides with the residual oxygen of the cobalt metal powder, so causing unwanted porosity in the segments.

15 It is also necessary, especially when producing segments with synthetic diamonds, to use only cobalt metal powders with very active sintering properties, as minimum densities of 8.5 g/cm^3 are required in this case. These densities should be achieved at a sintering temperatures of as low as $< 900^\circ\text{C}$ because the diamond may be converted into graphite at higher temperatures. If the sintering activity of the cobalt metal is inadequate, sufficient hardness is not achieved. Under the
20 extreme stresses to which annular drilling bits or cutting tools are exposed, the abrasive action of stone dust leads to deep erosion and unwanted detachment of the diamonds or other hard materials and consequently a loss of cutting performance.

25 According to the prior art, cobalt metals are used, on the one hand, in the form of mixtures of atomised cobalt metal powders with hydrogen-reduced powders, as are disclosed in DE-A 4 343 594, on the other hand as ultra-fine and extra-fine grade cobalt metal powders.

Ultra-fine powders are differentiated by their FSSS value of $< 1.0 \mu\text{m}$ from extra-fine powders which have FSSS values of between 1.2 and 1.4 μm .

30 The small particle size and the resultant large surface areas of the described cobalt metal powders promote the absorption of atmospheric oxygen and moisture, which frequently leads to degradation of the flowability of the powders.

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The present invention provides a sintering active cobalt metal which does not exhibit or at least mitigates the stated disadvantages, but does allow the production of segments with elevated density and hardness.

5 It has now proved possible to provide a cobalt metal powder which exhibits these required properties. These are cobalt metal agglomerates consisting of peanut-shaped primary particles with average particle size in the range from 0.5 to 2 μm , characterised in that they have a
10 spherical secondary structure with average agglomerate diameters of 3 to 50 μm . These cobalt agglomerates are the subject matter of this invention. The agglomerate diameter of the cobalt metal agglomerates according to the invention is preferably 5 to 20 μm . By virtue of their spherical
15 secondary structure they are distinguished by good flow properties.

The irregularly shaped elongated primary particles preferably have an average particle length of 0.5 to 2 μm and, generally, a diameter of $< 0.5 \mu\text{m}$.

20 Figure 1 show the hardness values of a sintered article produced from the cobalt metal powder agglomerate of the invention from example 3 in comparison with sintered articles produced from commercially available ultra- and extra-fine cobalt metal powders as a function of sintering
25 temperatures.

Figure 2 show the densities of a sintered article produced from the cobalt metal powder agglomerate of the invention from example 3 in comparison with sintered articles produced from commercially available ultra- and
30 extra-fine cobalt metal powders as a function of sintering temperatures.

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Figures 3a and 3b show 1000 and 5000 times magnification scanning electron micrographs of the cobalt metal powder agglomerates of the invention produced according to example 3.

5 Figures 4a and 4b show 500 and 5000 times magnification scanning electron micrographs of the cobalt metal powder agglomerates of the invention produced according to example 4.

 The specific surface areas of the cobalt metal
10 agglomerates according to the invention (determined using the nitrogen single point method to DIN 66 131) are preferably 2 to 3.5 m²/g. These surface areas and the small particle sizes of the primary particles are responsible for the elevated sintering activity of the cobalt metal
15 agglomerates according to the invention, from which sintered articles having densities of 8.5 g/cm³ may be produced at temperatures of as low as 700°C.

 The present invention also provides a process for the production of the cobalt metal agglomerates according to
20 the invention. This process is characterized in that in a first stage an aqueous cobalt(II) salt solution of the general formula CoX₂, wherein X⁻ = Cl⁻, NO₃⁻ and/or ½ SO₄²⁻ is reacted in a continuously operated tubular flow reactor with vigorous stirring with aqueous solutions or suspensions of
25 alkali metal and/or ammonium carbonates and/or hydrogen carbonates. The temperature range for the reaction is here between 40 and 100°C, preferably between 60 and 90°C. In this process, in contrast with the conventional precipitation process, a rod-shaped crystallised cobalt
30 carbonate is not formed, but instead a spherical basic cobalt

carbonate. This is filtered and washed until free of neutral salt. In order to minimise the content of impurities which are critical for subsequent use, the resultant basic cobalt carbonate may be converted in a further processing stage into spherical cobalt(II) hydroxide by adding alkali and/or ammonia liquors. This processing stage is superfluous if suitably pure solutions are used during formation of the cobalt carbonate.

Cobalt(II) hydroxide or basic cobalt carbonate obtained in this manner is then subjected to reduction. To this end, the reaction is performed with a gaseous reducing agent, such as preferably hydrogen, methane, dinitrogen oxide and/or carbon monoxide, at furnace temperatures of 300 to 800°C, preferably of 350 to 650°C.

Unlike conventional known extra-fine and ultra-fine cobalt powders, the cobalt metal agglomerates according to the invention have very good flow properties by virtue of their spherical secondary structure.

By virtue of the described properties, the cobalt metal powders according to the invention are particularly suitable as binders in the production of hard metal and/or diamond tools. It should be noted that the cobalt metal powder agglomerates may here advantageously be used both alone and combined with other binder metals.

The present invention accordingly provides the use of the cobalt metal agglomerates according to the invention for the production of sintered cobalt articles and for the production of composite sintered articles based on cobalt metal and hard materials from the group comprising diamond, CBN, WC, SiC and Al_2O_3 .

By virtue of the good flow properties and the fine primary structure of the cobalt metal powder agglomerates according to the invention, they are also particularly suitable for incorporation into the positive electrode composition containing nickel hydroxide in rechargeable batteries based on nickel/cadmium or nickel/metal hydride technologies.

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- During the so-called forming cycles, the cobalt metal is initially oxidised in accordance with its potential to cobalt(II). In the alkaline electrolyte (30% KOH solution), this forms soluble cobaltates(II) and is thus uniformly distributed within the electrode composition. On further charging, it is ultimately deposited as an electrically conductive $\text{CoO}(\text{OH})$ layer on the nickel hydroxide particles, so allowing the desired full utilisation to be made of the nickel hydroxide in the storage battery. The described anodic dissolution of the cobalt metal powder naturally proceeds all the faster and more effectively, the finer is the primary structure or the greater is the surface area of the metal powder.
- 10 The present invention thus also provides the use of the cobalt metal agglomerates according to the invention as a component in the production of positive electrodes in alkaline secondary batteries based on nickel/cadmium or nickel/metal hydride technologies.
- 15 The invention is illustrated in examples below, without this constituting any limitation.

Examples

Example 1

20 l of water were introduced into a stirred flow reactor and heated to 80°C. 5 l/h of a 1.7 molar CoCl_2 and 19 l/h of a 0.9 molar NaHCO_3 solution were continuously metered into the reactor with vigorous stirring. Once the steady state had been reached, the resultant product was discharged from the reactor overflow, filtered and washed with water until free of neutral salt. The product was then dried to constant weight at $T = 80^\circ\text{C}$.

Chemical analysis of the basic cobalt carbonate obtained in this manner revealed a Co content of 54.3% and carbonate content was determined at 32.3%.

Example 2

500 g of basic cobalt carbonate, produced according to example 1, were suspended in 1.5 l of water. This suspension was combined, with vigorous stirring, with 200 g of NaOH dissolved in 500 ml of water. The temperature was then raised to 60°C and the mixture stirred for 1 hour. The product was filtered, washed and dried to constant weight at $T = 90^\circ\text{C}$.

The yield was 426 g of spherically agglomerated, pure phase cobalt(II) hydroxide with a Co content of 63.3%.

Example 3

200 g of spherical cobalt(II) hydroxide, produced according to example 2, were weighed into a quartz boat and reduced in a stream of hydrogen for 1 hour at $T = 700^\circ\text{C}$. 126 g of spherically agglomerated cobalt metal were obtained. Figure 3 shows 1000 and 5000 times magnification scanning electron micrographs.

Example 4

100 g of spherical basic cobalt carbonate produced according to example 1 were treated in a similar manner to example 3. The yield was 54 g of spherical cobalt metal powder agglomerates. Figure 4 shows 500 and 5000
5 times magnification scanning electron micrographs of this powder agglomerates.

Example 5**Sintering test**

The cobalt metal agglomerates obtained according to example 3 were subjected to hot pressing tests under the following conditions:

10	Apparatus used:	DSP 25-ATV (from Dr. Fritsch GmbH)
	Heating time to final temperature:	3 min
	Holding time:	3 min
	Final pressure:	350 N/mm ²
	Final temperature:	see tables 1 and 2
15	Dimensions:	40 × 4 × 10 mm

Table 1 and Figure 1 show the hardness values of a sintered article produced from the cobalt metal powder agglomerate of the invention from example 3 in comparison with sintered articles produced from commercially available ultra- and extra-fine cobalt metal powders as a function of sintering temperatures. It may
20 clearly be seen that elevated hardness values are obtained with the cobalt metal powder according to the invention at temperatures of as low as 700°C, the hardness values moreover remaining constant over the entire temperature range up to 980°C.

Table 1: (Hardness values)

Rockwell hardness values (HR_B)

	700°C	780°C	800°C	900°C	980°C
Co uF ¹⁾	91.5	109.8	-	109.7	107
Co eF ²⁾	102.5	105	-	104.6	97.2
Cobalt metal powder from example 3	107.9	-	109.4	108.8	107.4

¹⁾ Ultra-fine cobalt metal powder supplied by Eurotungstène Grenoble, France

²⁾ Extra-fine cobalt metal powder supplied by Hoboken Overpelt, Belgium

Table 2 and Figure 2 show the densities of a sintered article produced from the cobalt metal powder agglomerate of the invention from example 3 in comparison with sintered articles produced from commercially available ultra- and extra-fine cobalt metal powders as a function of sintering temperatures.

Table 2: (Densities)

Densities [g/cm³]

	700°C	780°C	800°C	900°C	980°C
Co uF ¹⁾	7.72	8.58	-	8.60	8.59
Co eF ²⁾	8.42	8.62	-	8.67	8.61
Cobalt metal powder from example 3	8.51	-	8.69	8.69	8.68

Table 3 compares the particle sizes and BET specific surface areas of the cobalt metal agglomerates (determined using the nitrogen single point method to DIN 66 131) from example 3 with those of commercially available ultra- and extra-fine cobalt powders.

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Table 3: (Particle size and specific surface areas)

	FSSS [μm]	BET [cm^2/g]
Co uF ¹⁾	< 1	1.4
Co eF ²⁾	1.2-1.4	0.8-1.0
Cobalt metal agglomerate from example 3	1	2.5-3.5

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CLAIMS:

1. Cobalt metal agglomerates consisting of peanut-shaped primary particles with average particle sizes in the range from 0.5 to 2 μm , and having a spherical secondary
5 structure with average agglomerate diameters of 3 to 50 μm .
2. The cobalt metal agglomerates according to claim 1, wherein the agglomerate diameters are 5 to 20 μm .
3. The cobalt metal agglomerates according to claim 1 or 2, having a specific surface area in the range
10 from 2 to 3.5 m^2/g .
4. A process for the production of the cobalt metal agglomerates according to any one of claims 1 to 3, wherein a cobalt salt of the general formula: CoX_2 , wherein X^- represents Cl^- , NO_3^- , $\frac{1}{2} \text{SO}_4^{2-}$ or a combination thereof, is
15 continuously reacted with an aqueous solution or suspension of an alkali metal carbonate, ammonium carbonate, hydrogen carbonate or a mixture thereof at a temperature of greater than 40 to 100°C in a tubular flow reactor to form spherical, basic cobalt carbonate, which is separated and washed until
20 free of any neutral salt and then reduced with a reducing agent to yield the cobalt metal agglomerates.
5. The process according to claim 4, wherein the temperature is between 60 and 90°C.
6. The process according to claim 4 or 5, wherein the
25 cobalt carbonate which has been washed until free of neutral salt is converted into spherical cobalt hydroxide with an alkali liquor, an ammonium liquor or a mixture thereof before the subsequent reduction.

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7. The process according to any one of claims 4 to 6, wherein the reaction with a gaseous reducing agent is performed at temperatures of between 300 and 800°C.

8. The process according to claim 7, wherein the
5 temperature is between 350 and 650°C.

9. Use of the cobalt metal agglomerates according to any one of claims 1 to 3, for the production of a sintered cobalt article.

10. Use of the cobalt metal agglomerates according to
10 any one of claims 1 to 3, for the production of a composite sintered article based on cobalt metal and a hard material selected from the group consisting of diamond, CBN, WC, SiC and Al₂O₃.

11. Use of the cobalt metal agglomerates according to
15 any one of claims 1 to 3, as a component for the production of a positive electrode in an alkaline secondary battery based on nickel/cadmium or nickel/metal hydride technologies.

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Fig. 1

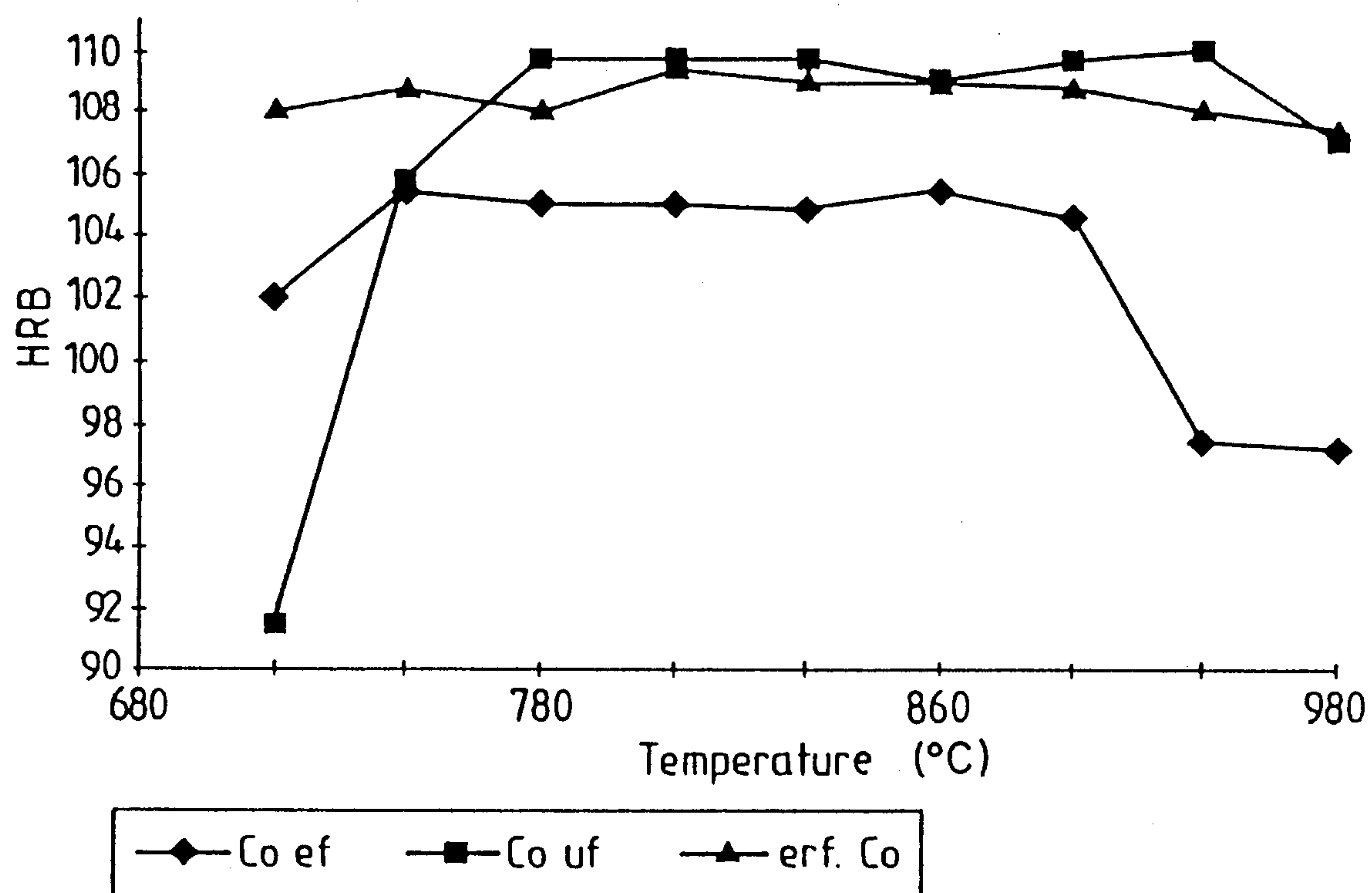
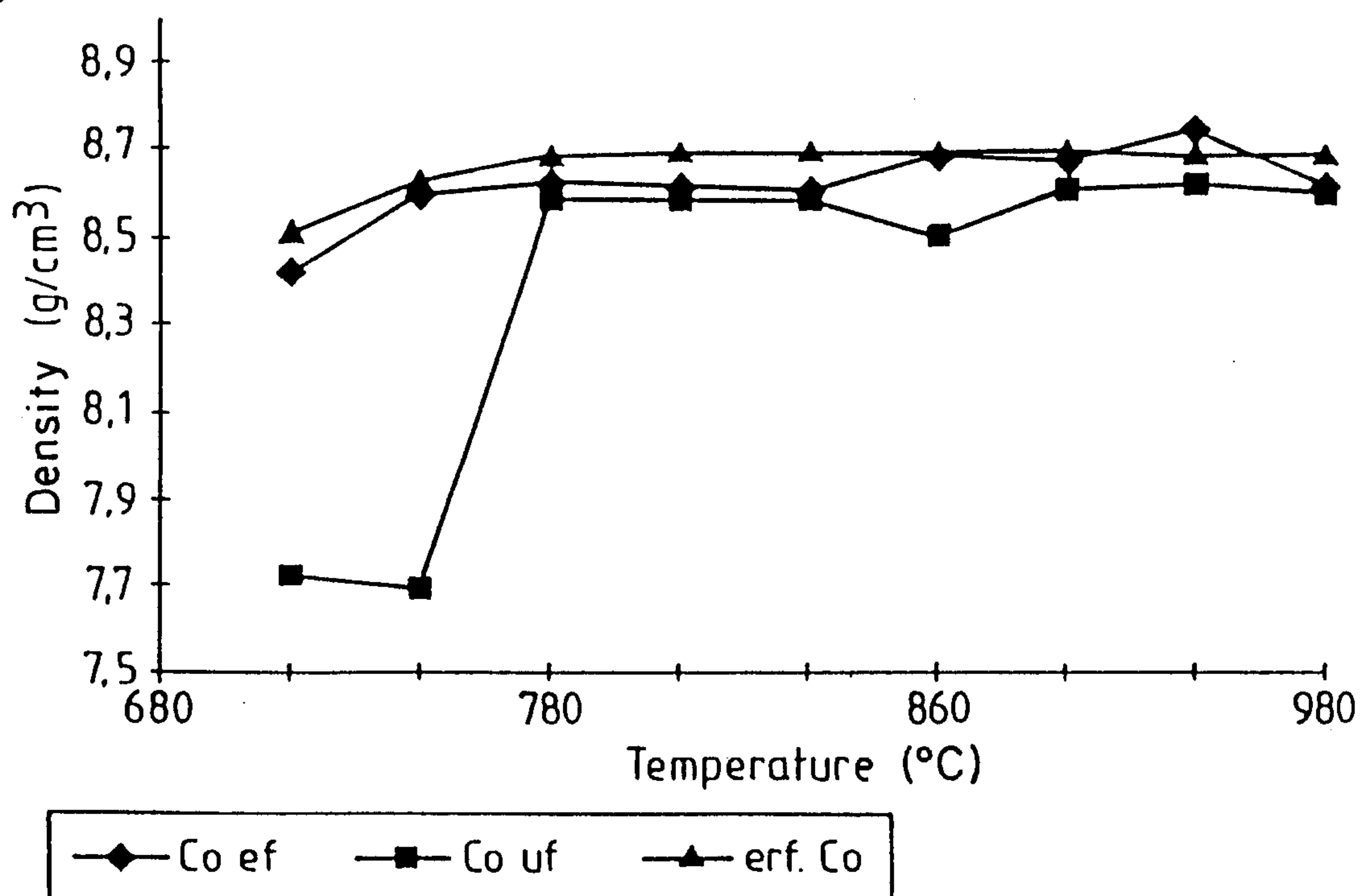
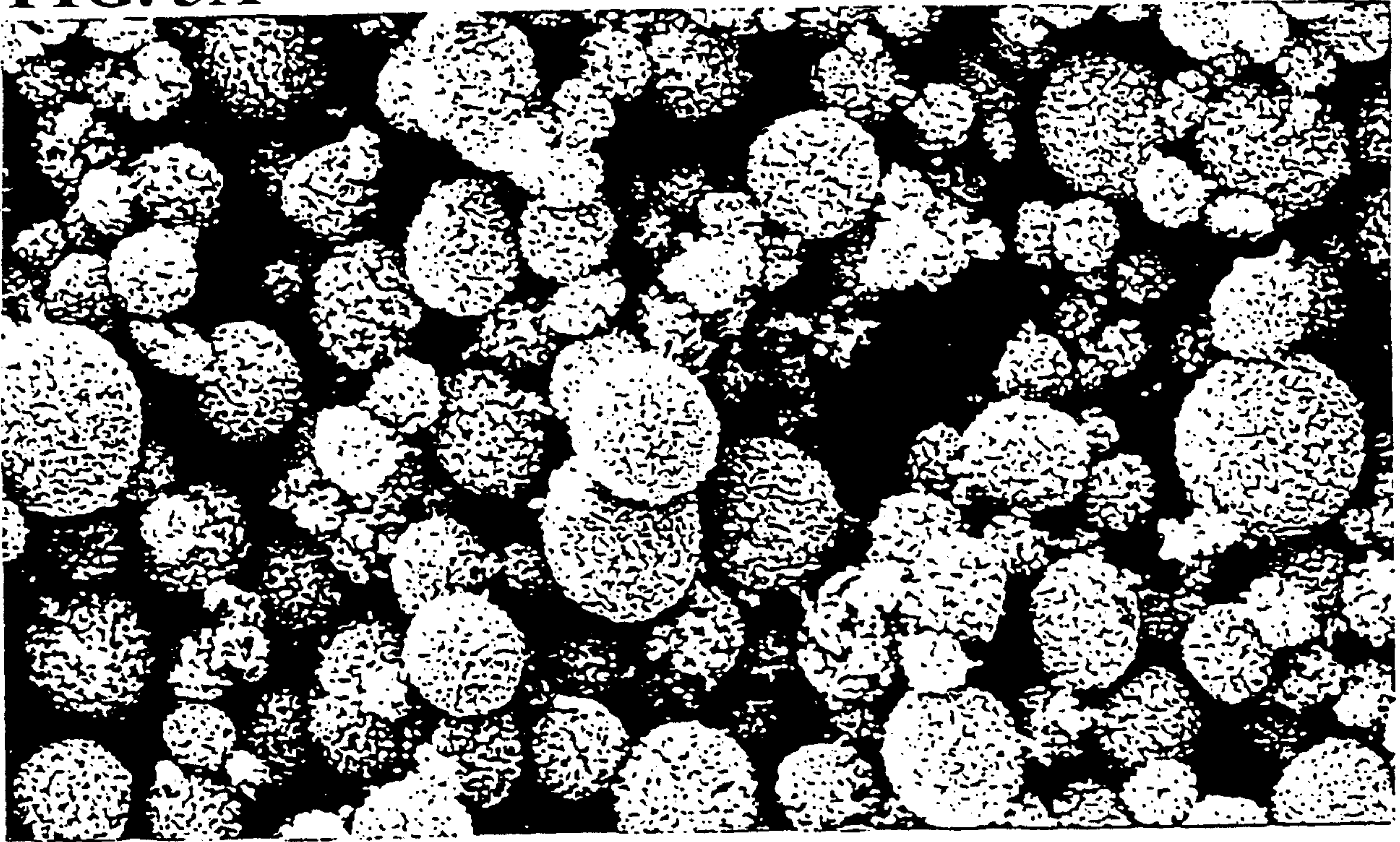


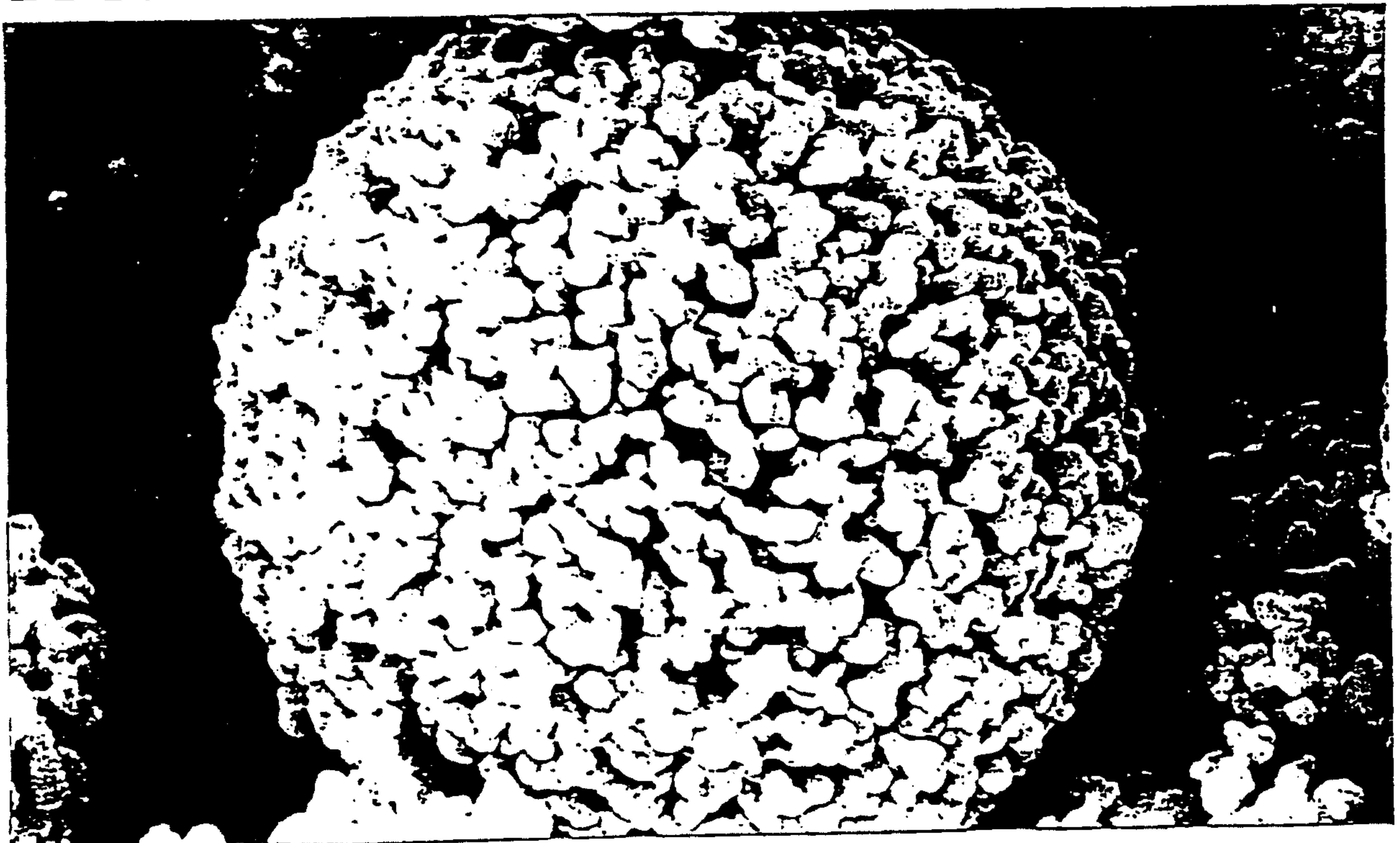
Fig. 2



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FIG. 3A

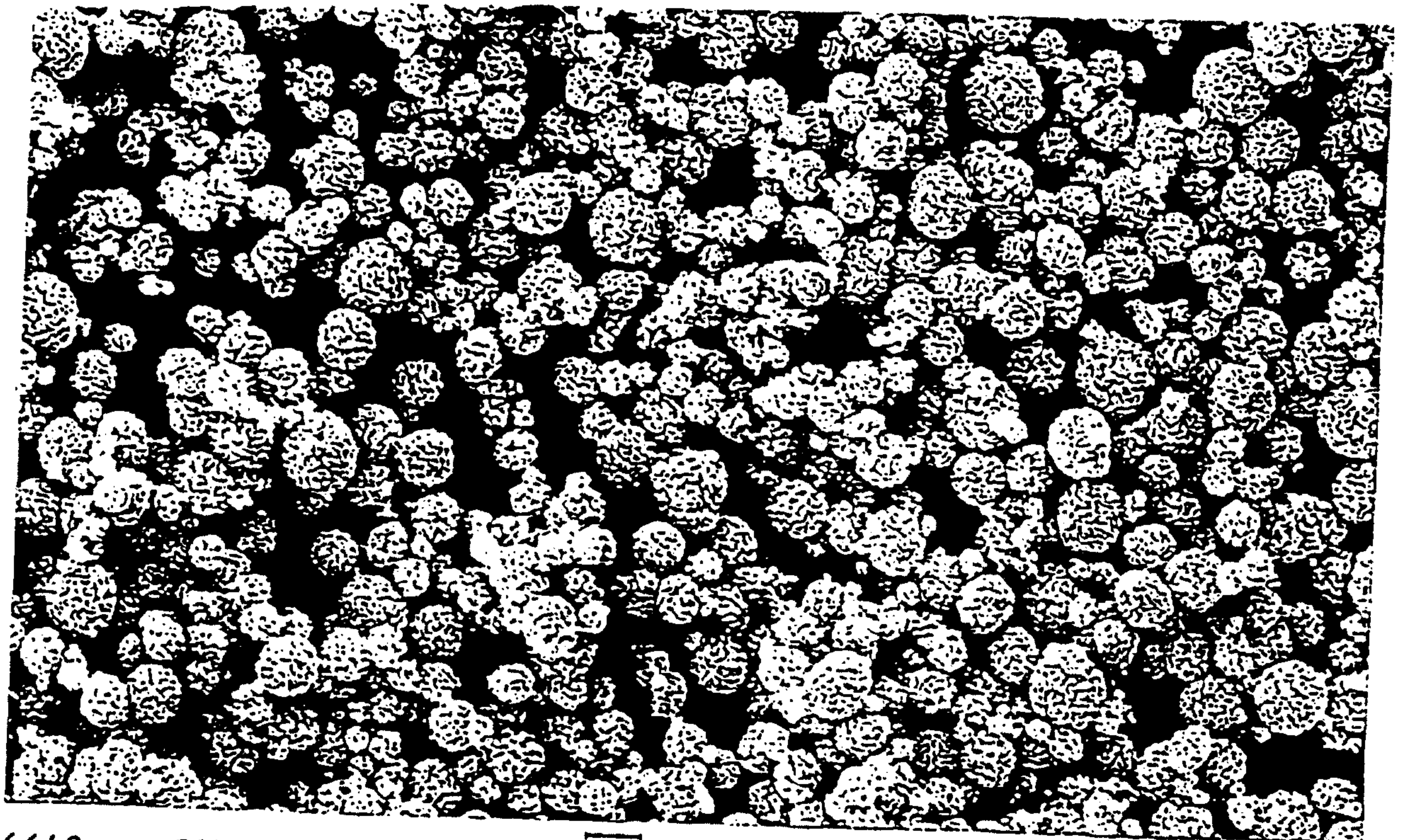
6624 20KV X1,000 10µm WD15

FIG. 3B

6624 20KV X5,000 1µm WD15

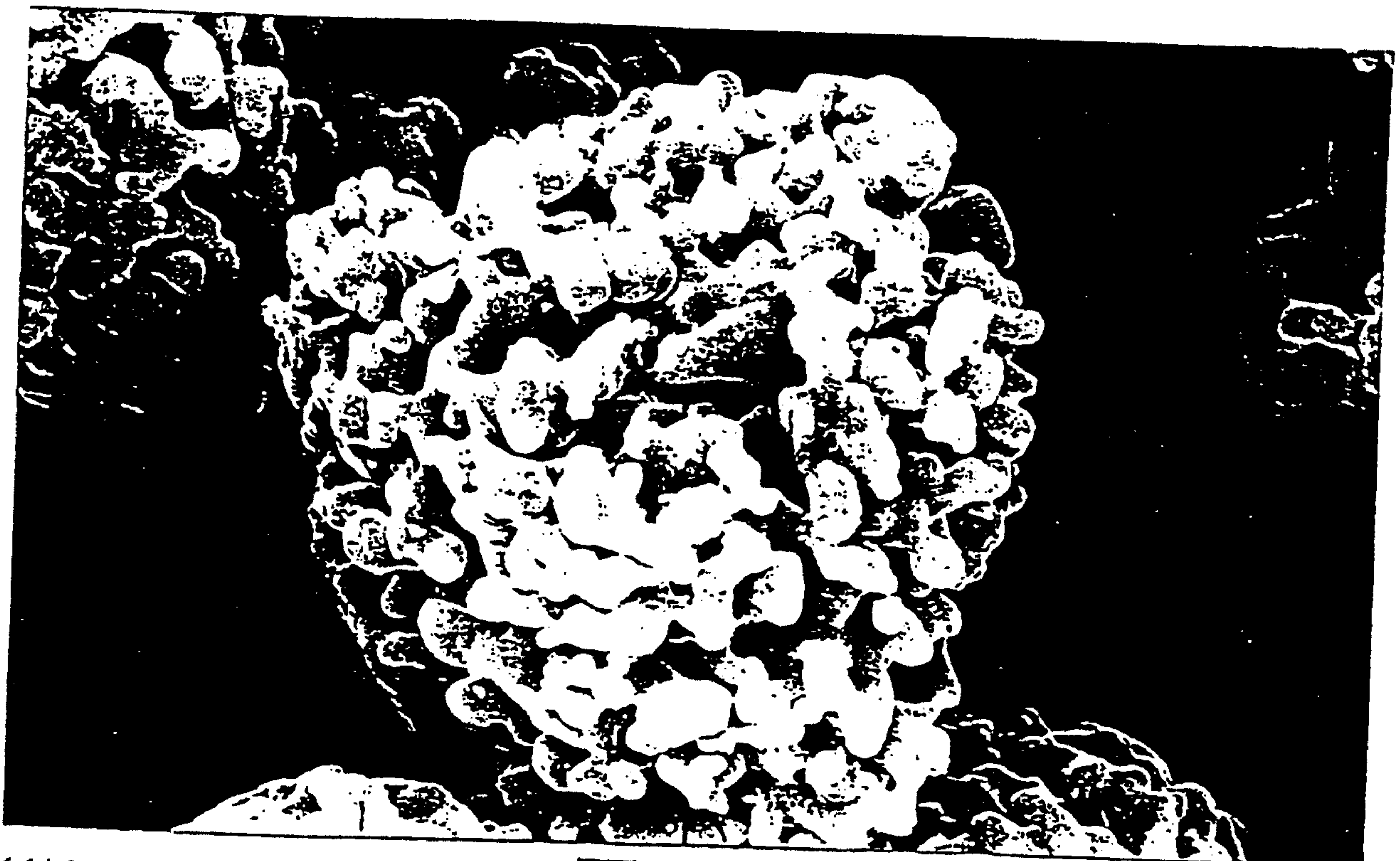
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FIG. 4A



6648 20KV X500 10 μ m WD16

FIG. 4B



6648 20KV X5,000 1 μ m WD16