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Study on the Carbon Dispersion in (UO_3+C) Microsphere Prepared by Internal Gelation Process

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An internal gelation process has been adopted for the preparation of carbon-dispersed UO_3 microspheres which will be used for preparing uranium nitride microsphere fuels by the carbothermic reduction. The proper conditions for homogeneous carbon dispersion in UO_3 microspheres were investigated. Firstly a range of feed solution compositions for preparing good UO_3 gel spheres was defined by observing the gelation behavior. Within the defined solution compositions carbon-dispersed microspheres were prepared. The distribution of carbon in microspheres were analyzed. The production of good carbon-dispersed microspheres was possible, and the EPMA analysis showed that most of the carbon was evenly distributed in the microspheres, although large carbon-rich aggregates were sparsely existent.

Keywords: Gelation, Carbon Dispersion, Microsphere, UO_3

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* Korea Atomic Energy Research Institute

内部ゲル化法により調製する（UO_3＋C）微小球中の炭素分散の研究

日本原子力研究所東海研究所燃料研究部
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（1993年8月9日受理）

窒化ウラン微小球燃料を炭素熱還元法で調製するために使用する炭素分散UO_3微小球の調製に内部ゲル化法を適用した。UO_3微小球中への均一な炭素分散に適切な条件について研究した。最初に良質UO_3ゲル球調製に適した原液の組成範囲をゲル化挙動の観察により明らかにした。その組成範囲内で数種の炭素分散微小球を調製した。微小球中の炭素の分布を解析した。良質の炭素分散微小球調製が可能であった。EPMA分析の結果は，大きな炭素リッチの塊がまれに存在するが微小球中に炭素は平均して分散していることを示した。

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1. Introduction

The MX-type (M=U,Pu; X=C,N) ceramic fuels are being studied as advanced nuclear fuels for liquid metal reactors [1-3] and for space reactors [4]. High melting point, thermal conductivity and heavy metal atom density of the MX-type fuels could meet the present requirements of fast reactors towards higher linear power rating and breeding. Particularly the nitride fuel is more attractive because of its compatibility with the existing reprocessing techniques; besides, the nitride fuel fabrication could take place in existing oxide facilities. Presently nitride fuel pellets are prepared by the carbothermic reduction of the oxide powder in nitrogen, and then by pelletization [5,6]. However this involves handling of radioactive and chemically active powder. As an alternative method, the sol-gel process has been studied [7,8]. By this method the process flow-sheet can be simplified and the radioactive dust problem can be avoided. It also readily gives a homogeneous mixed nitride and allows remotely controlled operations.

The sol-gel approach for preparing nitride microspheres consists of dispersing large surface-area carbon black in a uranyl-nitrate-based feed solution, forming gel microspheres, and then converting the microspheres to nitride by appropriate heat treatments. Mixing of carbon in aqueous solution could give homogeneous mixture of carbon and UO_3 particles, which facilitates the later carbothermic conversion. The internal gelation process is one of the sol-gel processes for the preparation of microspheres [9-11]. In this process homogeneous gelation can be achieved by the internal supply of ammonia by the thermal decomposition of premixed hexamethylenetetramine. This homogeneity may be an important advantage for the gelation of carbon-dispersed microspheres.

The purpose of this study is to investigate the proper conditions in the internal gelation process for preparing homogeneously carbon-dispersed UO_3 microspheres which is necessary for the fabrication of good-quality nitride microspheres. A proper range of feed solution compositions for the UO_3 microspheres was sought at the first step. Then, carbon-dispersed microspheres were prepared and the distribution of the carbon was examined.

2. Experimental

2.1 Survey of feed solution compositions preferable to gelation

A range of the preferable compositions was examined by using carbon-free feed solutions in the following way. An acid deficient uranyl nitrate solution (ADUN; uranium concentration 3.0 mol/l, and nitrate/uranium mole ratio 1.55) was prepared by dissolving U_3O_8 powders in nitric acid. A gelation agent which was a solution of 3 mol/l hexamethylenetetramine (HMTA) and 3 mol/l urea was prepared by dissolving solid HMTA in a urea solution. Both of the ADUN and (HMTA+urea) solutions were cooled to 0°C and then mixed to various uranium concentrations and (HMTA,urea)/uranium mole ratios. For adjusting uranium concentration, the mixed solution was diluted with water. The final concentration is calculated, neglecting a volume change after decomposition of premixed hexamethylenetetramine. This homogeneity may be an important advantage for the gelation of carbon-dispersed microspheres.

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2.2 Preparation of carbon dispersed microspheres

2.2.1 Preparation of carbon-dispersed feed solutions.

A general flow-sheet of this part of experiments is shown in Fig.1. The carbon-dispersed feed solution having a carbon/uranium mole ratio of 2.5 was prepared by dispersing carbon black powders in the ADUN solution. Carbon black of ASTM grade "N326" was dispersed in the ADUN solution for 1 h by applying ultrasonic vibration. The "N326" carbon black has the average particle size around 28 nm and the specific surface area around 84 m^2/g [12]. As described in the previous section, the carbon-dispersed solution was cooled and then mixed with the gelation agent (3 mol/l HMTA + 3 mol/l urea). Volumetric concentration of the components in the feed solutions was calculated by assuming carbon black density to be 1.8 g/ml.

2.2.2 Gelation

Gelation was carried out in a column of 1.1 m in height. It consisted of a double-walled glass tube where a silicone oil was heated to 90°C by hot water circulating in the outer tube. About 1 ml of the feed solution was dropped into the hot silicone oil with a syringe having a nozzle size of 0.3 mm ID × 0.7 mm OD. The droplets gelled within the period of their contacting the hot oil and were kept in the cold bottom of the column for 30 min for completing gelation.

2.2.3 Washing, drying and calcination

Gel microspheres were washed with carbon tetrachloride (CCl_4) to remove the silicone oil and aged in a 3 mol/l NH_4OH solution for 20 h. Thereafter they were washed by flowing 0.05 mol/l NH_4OH solution at a rate around 35 ml/h for 7 h to remove ammonium nitrate and residual gelation agent. The washed gel microspheres were dried on filter paper exposed to laboratory room atmosphere for 1 d. The dried microspheres were calcined at 500°C for 1 h in Ar atmosphere.

2.2.4 Analysis

The emphasis in this analysis was placed on the determination of the homogeneity of carbon dispersion in UO_3 matrix. Observation and analyses with a scanning electron microscope (SEM, JEOL JSM-5300) and an electron probe microanalyzer (EPMA, Shimadzu EPM-810) were performed on the fractured surfaces of the calcined microspheres. For the quantitative analysis of carbon contents, a calibration curve (Fig.2) was made with standard $C+UO_3$ pellets, which were prepared from the intimate powder mixture of the components. Since the standard was essentially inhomogeneous, the electron beam of 60 μm diameter scanned its surface for 500 ~ 1000 s with moving the sample at a speed of 1 mm/min. This rapid movement decreased the deposition of carbon during electron bombardment on the sample surface and enabled us to neglect the errors due to the carbon contamination. Similar technique was applied to the analysis of the microspheres, as described later.

3. Results and discussion

3.1 Gelation behavior

Proper compositions for gelation were surveyed by using carbon-free feed solutions, as described in Sect.2.1. Three types of gel formation behavior were identified (Fig.3). At high uranium concentrations and low (HMTA,urea)/uranium mole ratios, the dried gel was cracked and fractured as shown in Photo.1(a); these compositions were marked as "Failed" in the figure. The feed compositions with low uranium concentrations and high (HMTA,urea)/uranium mole ratios gave a crack-free gel having a smooth surface (Photo.1(c)), and were marked as "Good" in Fig.3. The compositions marked as "Intermediate" in the figure occasionally yielded cracks on the gel surface (Photo.1(b)). The volume decrease of this "Intermediate" type of gel was less than that seen in Photo.1(a). Therefore, if the gel had been removed from the minivial and washed before drying, such cracks could have been avoided. In the present experiment good quality gel was obtained within the compositions ranging from 0.7 to 1.1 mol-U/l. It is considered, however, that the range will be extended when washing and drying are properly applied; as described later, good gel microspheres can be obtained from a 1.3 mol-U/l feed solution during electron bombardment on the sample surface and enabled us to neglect the errors due to the carbon contamination. Similar technique was applied to the analysis of the microspheres, as described later.

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Similar gelation behavior of uranyl nitrate solutions was observed by Vaidya et al [13] although the evaluation method was different from ours. They recommended the feed compositions ranging within the shaded area in Fig.3 for an actual microsphere-gelation using a hot silicone oil column. This area overlaps our "Good" region except the range of uranium concentration higher than 1.1 mol-U/l. The disagreement would be caused by the differences in gelation method and evaluation method.

3.2 Gelation of carbon-dispersed microspheres

On the findings in the preceding section, a series of experiments for preparing carbon-dispersed microspheres were conducted by using three feed solutions listed in table.1; although the feed composition of 1.3 mol-U/l is of "Intermediate" grade in Sect.3.1 (Fig.3), it is selected to examine the applicability of such a high uranium concentration. Smooth gel microspheres could be obtained, though clogging of the nozzle occurred at the highest uranium concentration of 1.3 mol/l. The effect of feed compositions on the properties of carbon-dispersed microspheres was examined. The appearance of gel microspheres with different feed compositions was not significantly different (Photo.2). Photo.3 shows the microspheres dried in ambient atmosphere for 1 d. At the compositions of 1.05 and 0.7 mol-U/l, crack-free dried microspheres with a good sphericity could be obtained in spite of large shrinkage of about 50 %. Microspheres from the feed solution of the highest uranium concentration 1.3

Table 1 The solution compositions used for preparing carbon-dispersed microspheres

uranium concentration (mol/l)	(HMTA,urea)/uranium mole ratio	carbon/uranium mole ratio
1.3	1.2	2.5
1.05	1.8	2.5
0.7	2.2	2.5

mol/l cracked after drying. Photo.4 shows carbon-dispersed microspheres calcined at 500°C in Ar atmosphere for 1 h. The feed solutions of 1.05 and 0.7 mol-U/l yielded microspheres with a good sphericity and smooth surface, but fine cracks were occasionally observed. Microspheres prepared from the 1.3 mol-U/l solution cracked. Such cracking is not considered to change the state of carbon dispersion in the microspheres. In the present study, therefore, the simplest treatment was selected for the drying and no attempt was made to avoid the cracking of the microsphere. To prepare crack-free microspheres, more systematic investigation is needed for each processing step.

3.3 Distribution of carbon in microspheres

Photo.5 shows fractured surfaces of carbon-dispersed microspheres calcined in Ar. There was no difference in appearance among the different feed compositions. Black coarse (max. 30μm) inclusions as shown in Photo.6 were distributed in all the cases. These were confirmed to be carbon-rich aggregates with a C/U mole ratio of 20 or more by EPMA analysis. Photo.7 indicates a significant difference in uranium and carbon contents between the aggregates and matrix. In the apparently homogeneous area without the large carbon-rich aggregates, however, finer carbon-rich aggregates were evenly distributed (Photo.8). Carbon contents on the fractured surface of Photo.5(b) were quantitatively analyzed in two ways. For obtaining the macroscopic average of the carbon contents, the specimen surface was scanned with the electron beam of 80 μm diameter at the speed of 500 μm/min for 10 min. The result was 9.4±0.9 wt% carbon, which agreed with the nominal value of 9.5 wt% assuming that the calcined products were UO_3+C. For obtaining the carbon contents in the area free from carbon-rich aggregates, the electron beam of 1 μm diameter was used; ten randomly-selected points were analyzed. The average carbon content in those areas was 4.6±0.5 wt%. Thus, it may be roughly estimated that about one half of carbon is distributed uniformly in the UO_3 matrix as particles of 1 μm or smaller and that the rest was contained in carbon-rich aggregates of a few μm or more. Moreover, most of the aggregates are a few μm in size while the aggregates far larger than 10 μm are very limited in number as shown in Photo.5.

It is desirable that the size of dispersed carbon aggregates is as small as possible. However, it may be considered that homogeneous distribution of carbon particles of a few μm or smaller will be sufficient for the carbothermic reduction of (UO_3+C) into UN. Therefore, if the larger aggregates were eliminated, the present distribution of carbon would be accepted. The

elimination is expected to be attained by stronger vibration with dipping an ultrasonic vibrating chip into the feed solution.

4. Conclusion

For investigating the proper conditions for homogeneous carbon dispersion in UO_3 microspheres, a range of feed solution compositions for obtaining good UO_3 gel was defined. Within and near the defined range, carbon-dispersed microspheres were prepared and analyzed for the appearance and the distribution of carbon in microspheres.

(1) The proper compositions for carbon-free UO_3 gel formation were confirmed to range from 0.7 to 1.1 mol/l of uranium.

(2) Carbon-dispersed microspheres with C/U ratio of 2.5 were successfully prepared by the internal gelation process.

(3) Although large carbon-rich aggregates distributed sparsely on the fractured surface, the carbon distribution in the microspheres was generally uniform.

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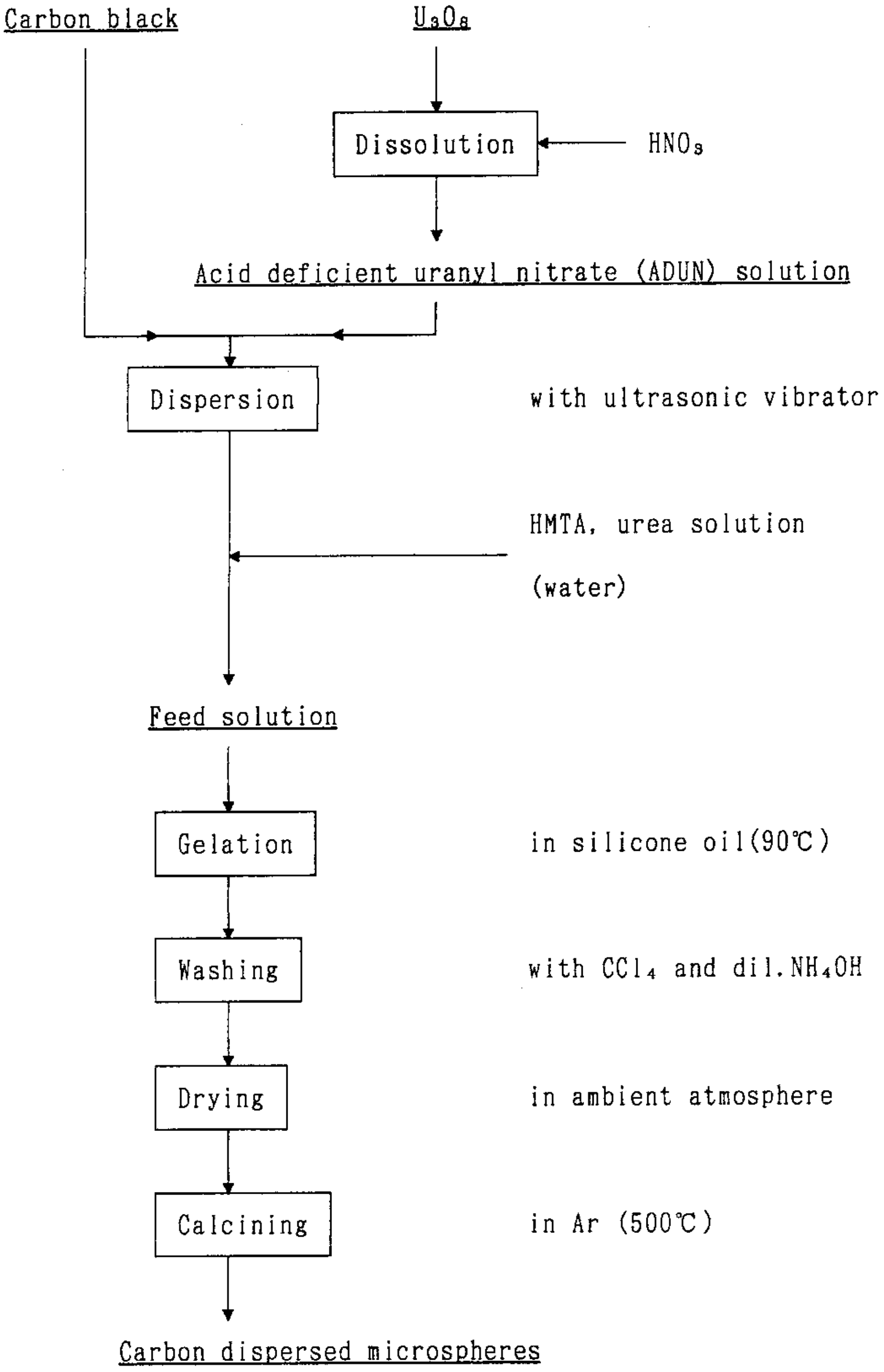

Fig. 1 Flowsheet of the present process

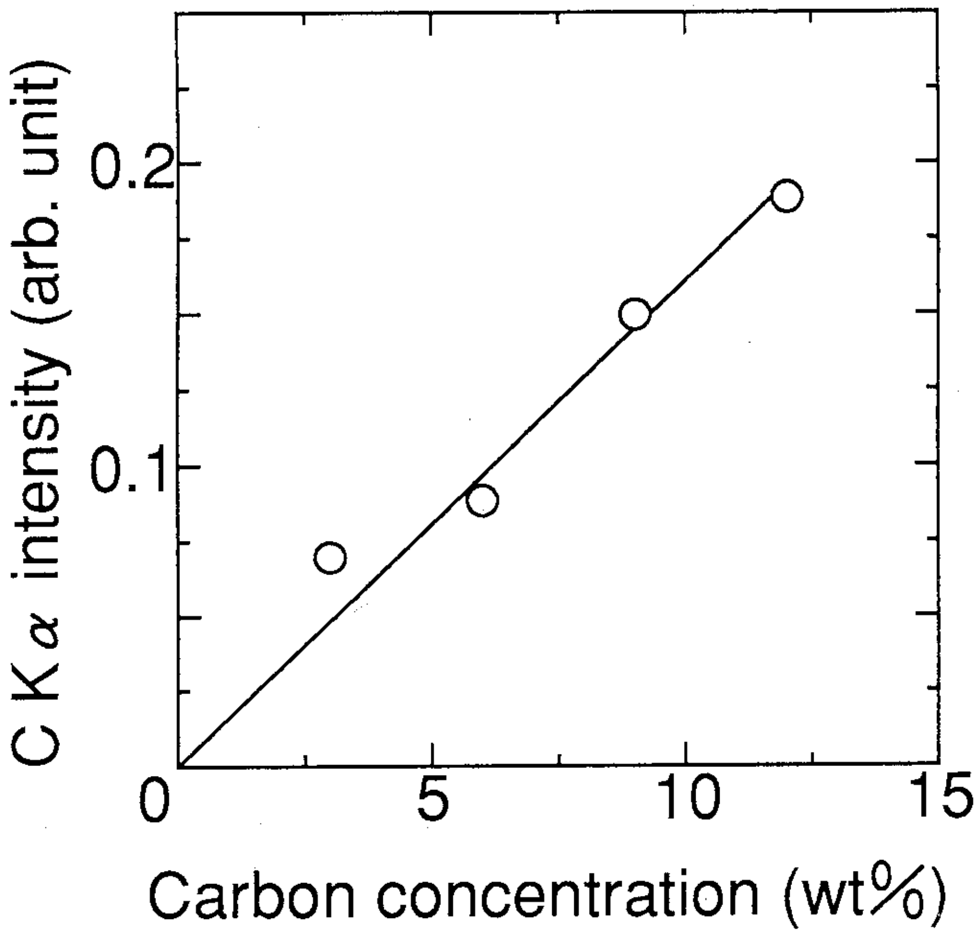

Fig. 2 The calibration curve for carbon analysis with EPMA.

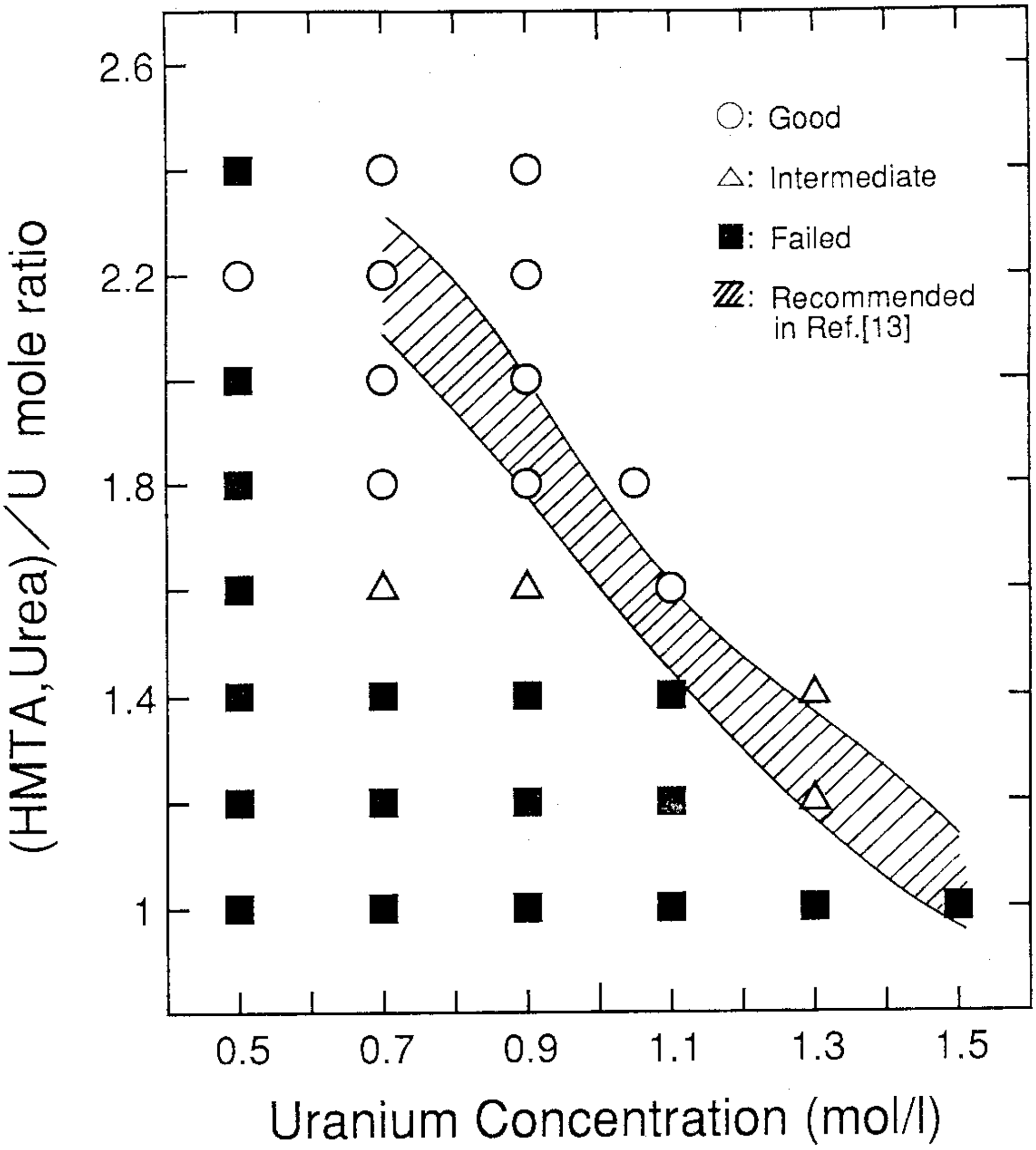

Fig. 3 Gelation field diagram; the shaded area is a range of optimum compositions observed by ref. (13).

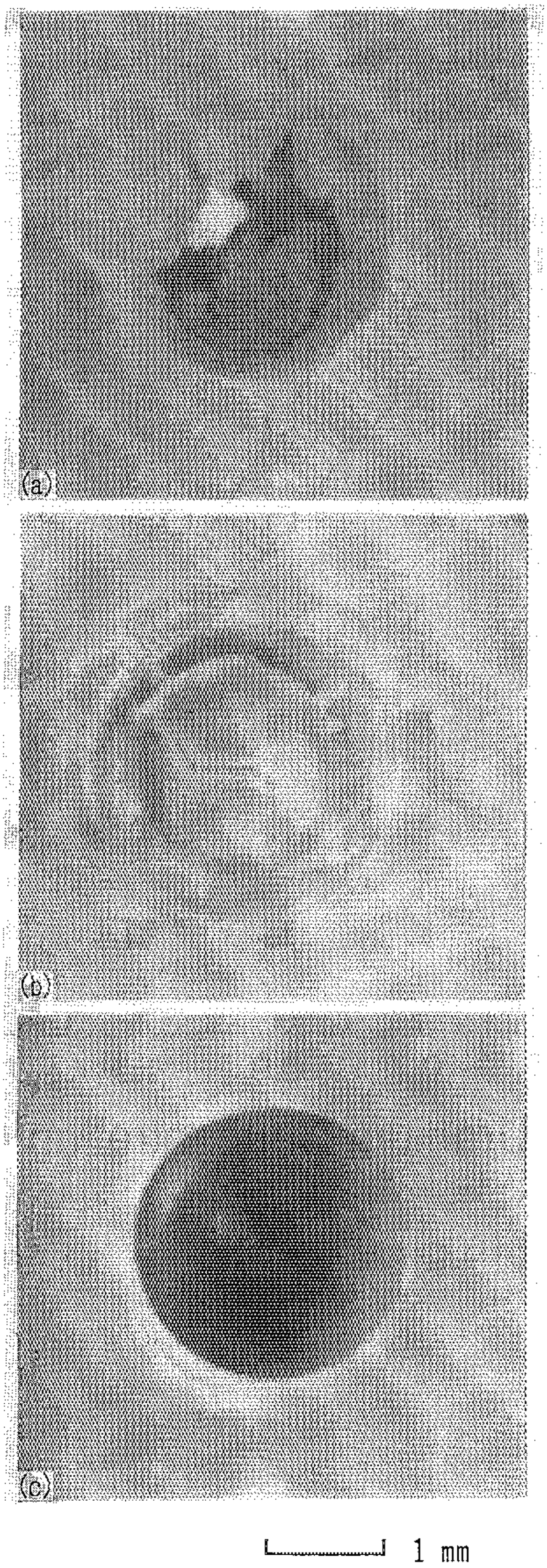

Photo. 1 Appearance of UO_3 gel; (a) Cracked (b) Intermediate (c) Good.

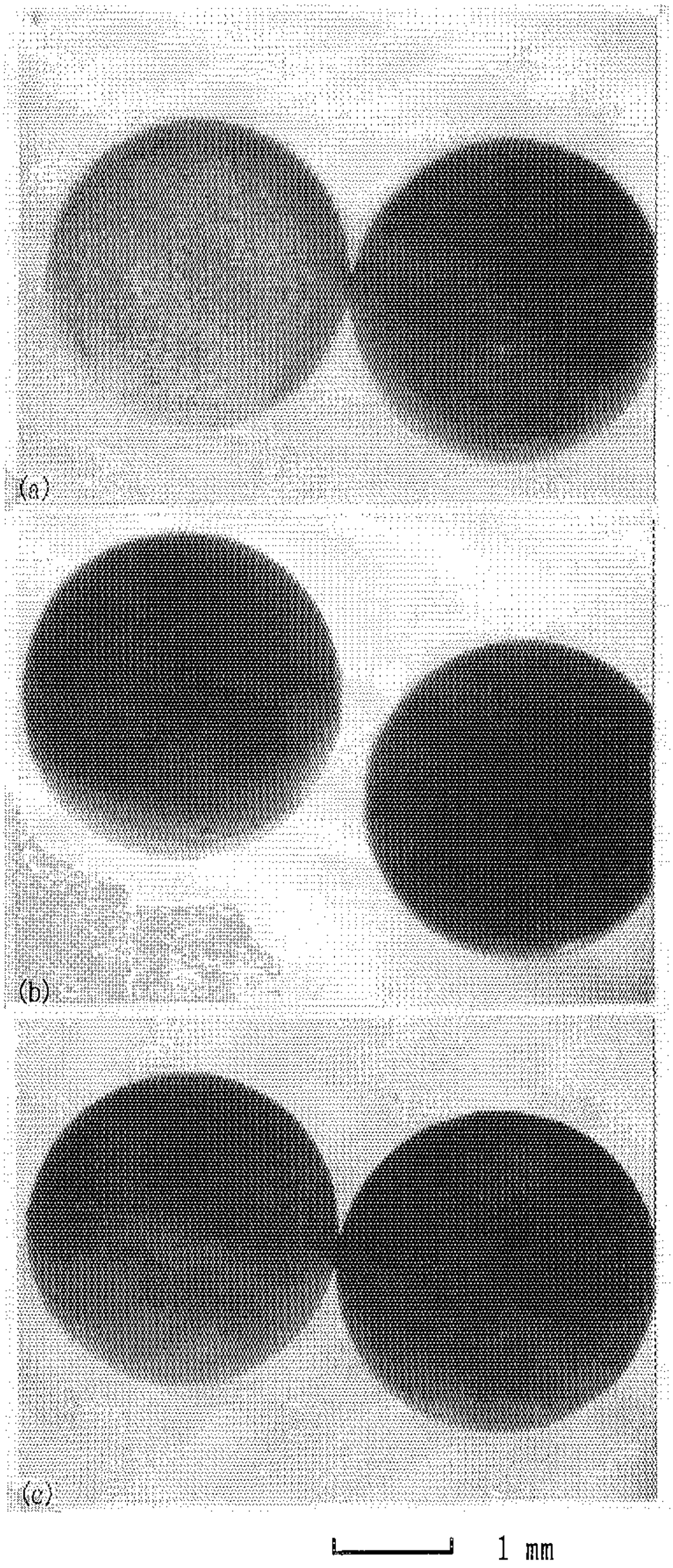

Photo. 2 Gel microspheres derived from the carbon-dispersed feed solutions of (a) 1.3 mol-U/l, (b) 1.05 mol-U/l and (c) 0.7 mol-U/l listed in Table 1.

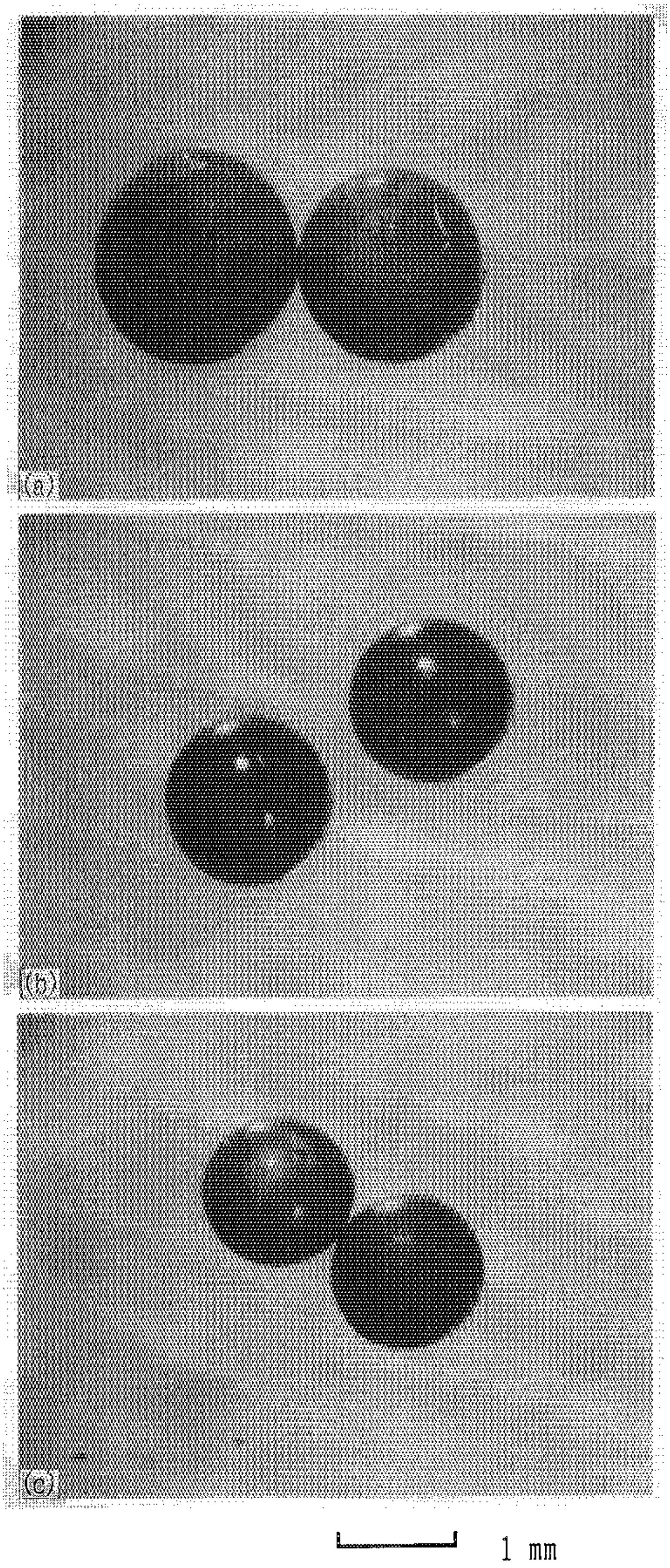

Photo. 3 Dried microspheres derived from the carbon-dispersed feed solutions of (a) 1.3 mol-U/l, (b) 1.05 mol-U/l and (c) 0.7 mol-U/l.

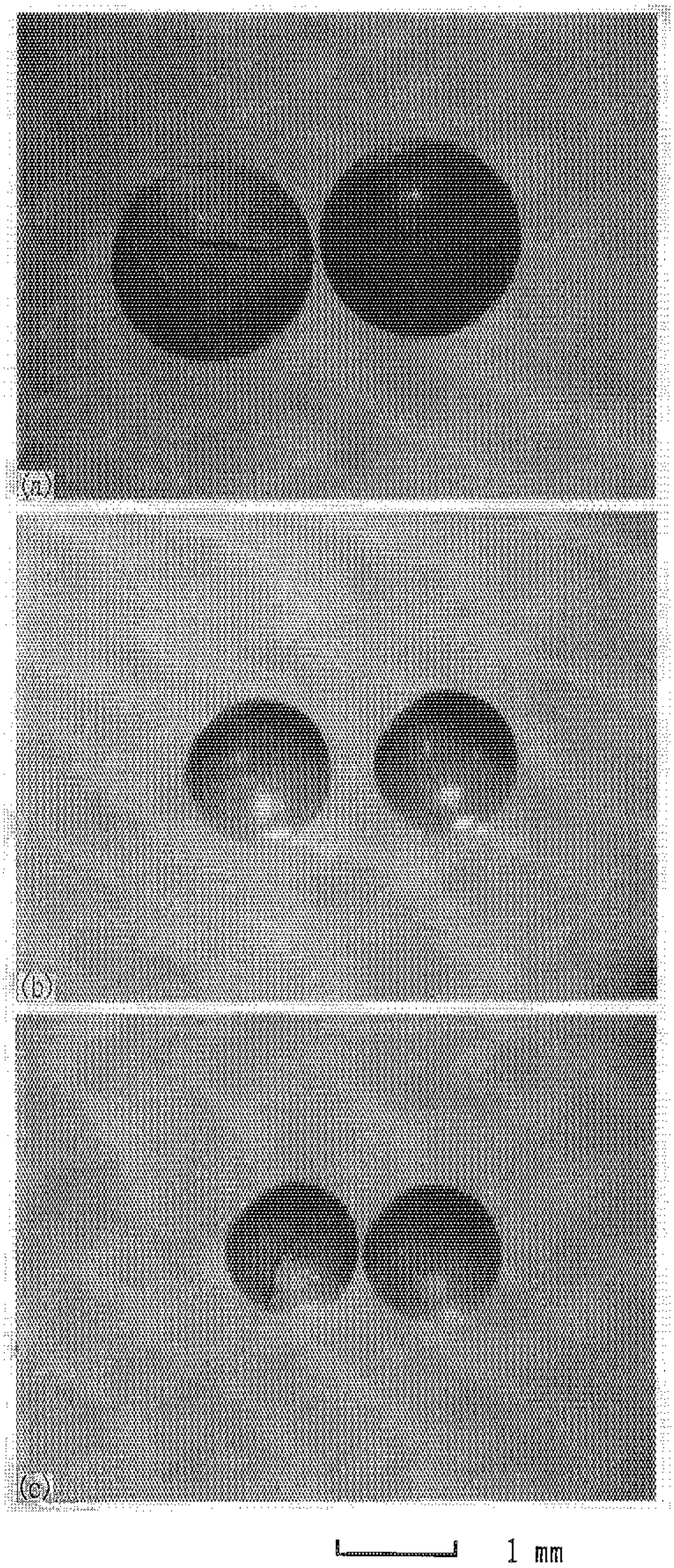

Photo. 4 Calcined microspheres derived from the carbon-dispersed feed solutions of (a) 1.3 mol-U/l, (b) 1.05 mol-U/l and (c) 0.7 mol-U/l.

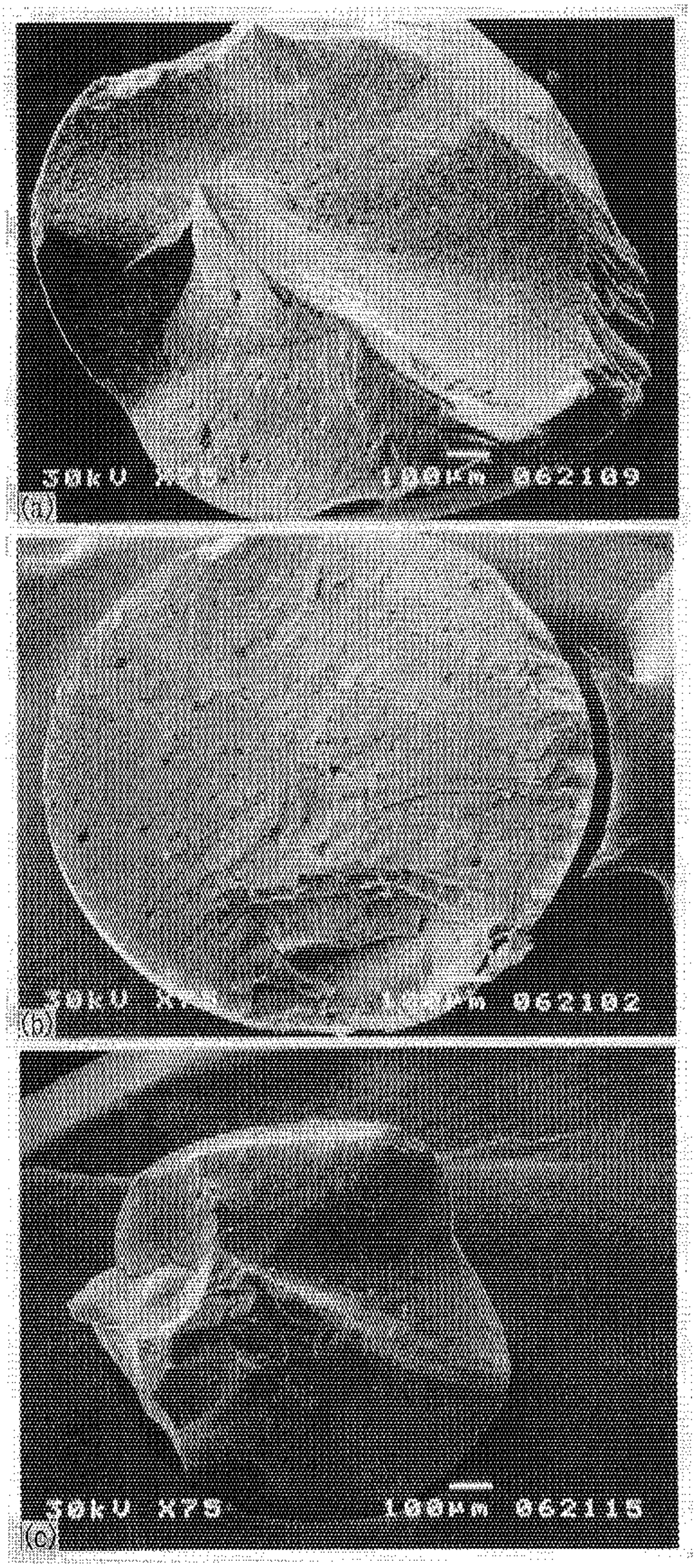

Photo. 5 SEM micrographs of calcined microspheres derived from the carbon-dispersed feed solutions of (a) 1.3 mol-U/l, (b) 1.05 mol-U/l and (c) 0.7 mol-U/l.

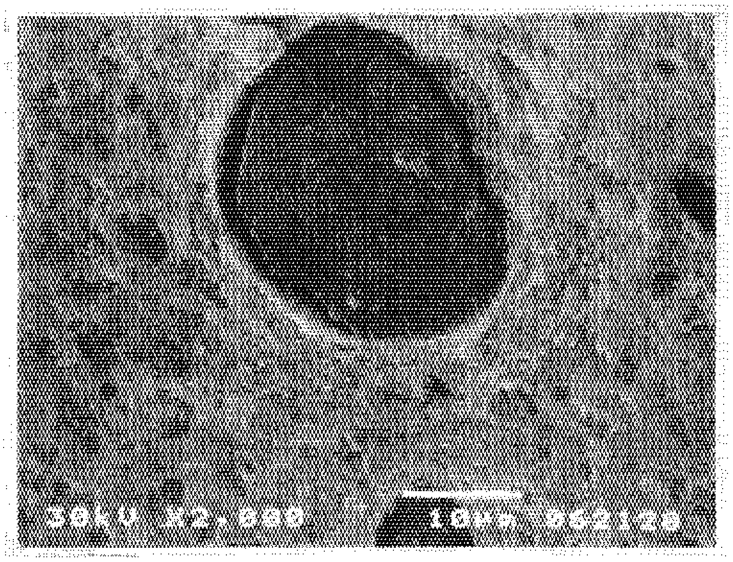

Photo. 6 SEM micrographs of a carbon-rich inclusion in the fractured surface.

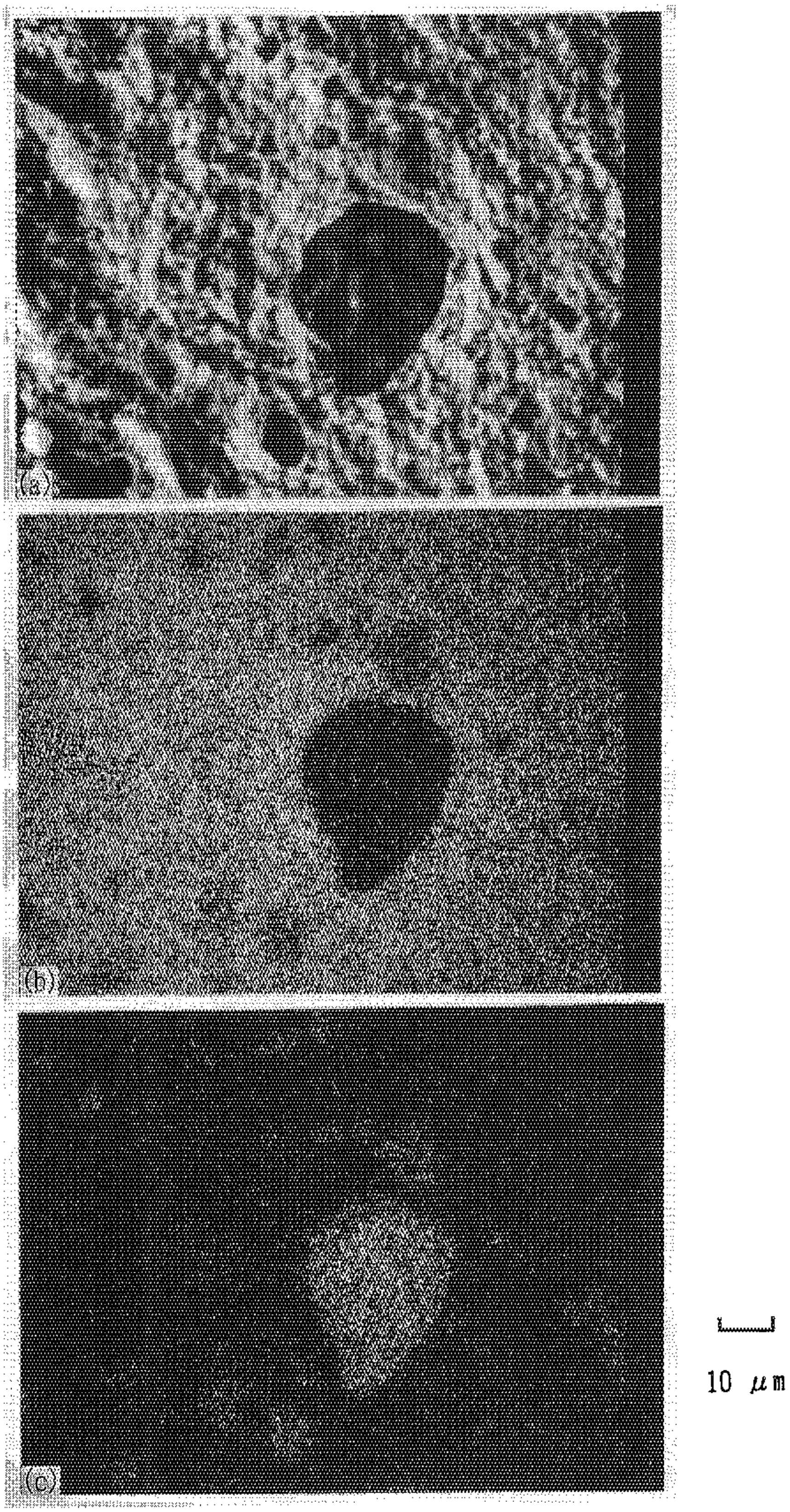

Photo. 7 EPMA micrographs of a carbon-rich inclusion of calcined microspheres;
(a) back-scattered electron image (b) U-Mα X-ray map
(c) C-Kα X-ray map.

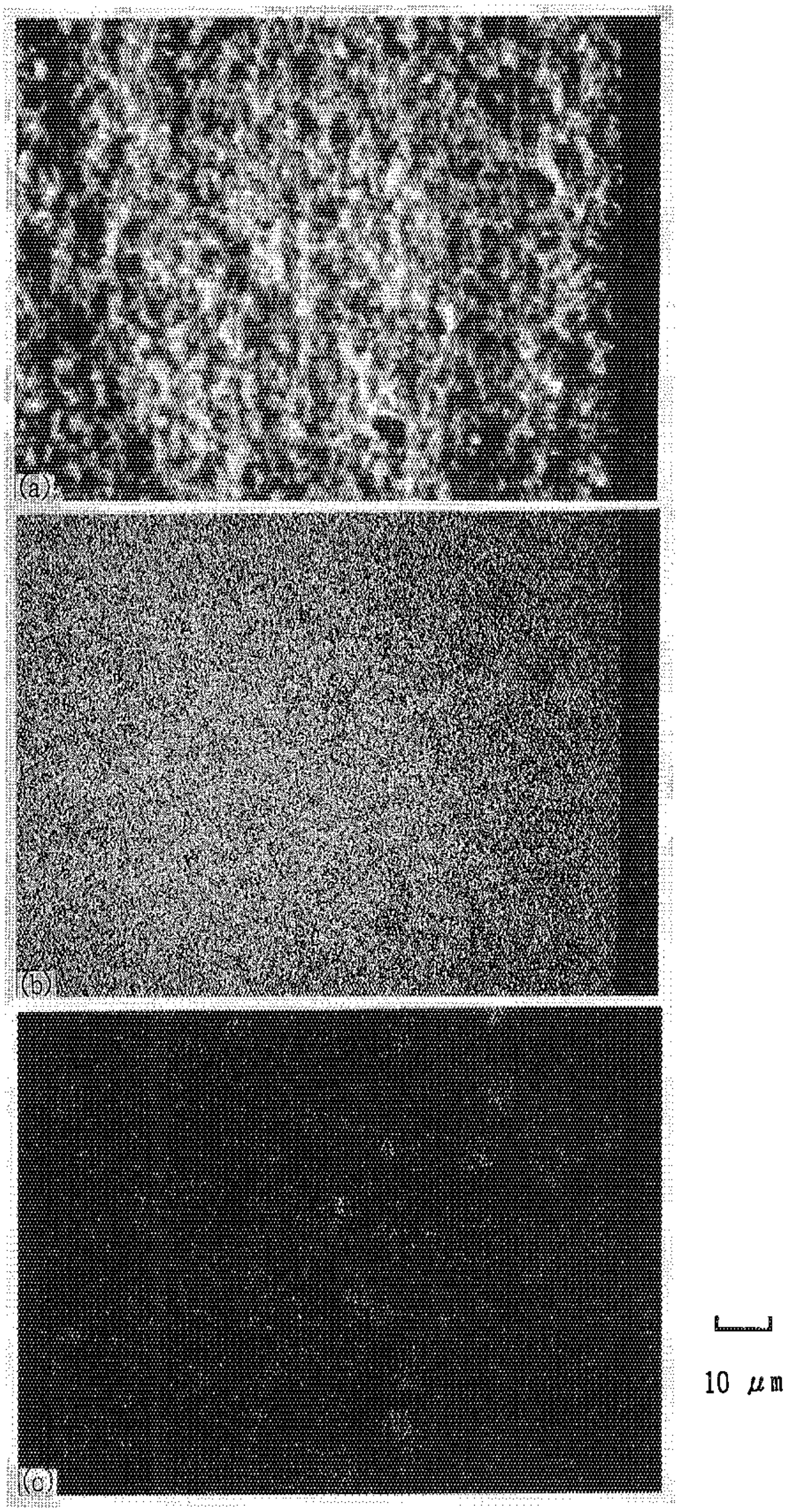

Photo. 8 EPMA micrographs of homogeneous area of calcined microspheres;
(a) back-scattered electron image (b) U-Mα X-ray map
(c) C-Kα X-ray map.