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NANOCRYSTALLINE PARTICLES OF COPPER, SILVER AND YTTERBIEM BY IMPULSE PLASMA IN LIQUID

Introduction

Synthesis of metal nanoparticles has been of a great activeness because of their interesting properties different from the bulk substances[1]. Arc discharge in liquid is one of methods for metal nanoparticles synthesis[2]. Recently, a synthesis method of copper nanoparticles/oxides by arc discharge in ascorbic acid/water solution was reported[3]. This method requires high energy consuming systems and produces colloids, which contain metallic/oxide particles of copper rather than copper powder. Arc discharge produces continuous plasma between the electrodes that cause energy loss to the surrounding media, which lead to high temperature widening throughout the electrodes and surrounding media. Impulse plasma is a pulsed discharge, where the energy loss to the surrounding area is low. Impulse plasma energy is mainly consumed for dispersion of the electrodes.

In this article, we present a new synthesis method of metallic nanoparticles by using the Impulse Plasma in Liquid. Although the impulse plasma in gas was effectively used in metal surface processing, so far, it had not been utilized in nanocrystalline materials synthesis. Impulse Plasma in Liquid method does not require vacuum system, high-energy and complex purification procedures and is based on the low voltage impulse plasma in liquid dielectrics.

Keywords: nanoparticles, synthesis, oxides, ascorbic acid, water solution, Impulse plasma.

НАНОКРИСТАЛЛИЧЕСКИЕ ЧАСТИЦЫ МЕДИ, СЕРЕБРА И ИТТЕРБИЯ ПО ИМПУЛЬСНОЙ ПЛАЗМЕ В ЖИДКОСТИ

Синтез металлических наночастиц имеет большую активность из-за их интересных свойств, отличных от объемных веществ1. Дуговой разряд в жидкости является одним из методов синтеза металлических наночастиц2. Недавно был описан метод синтеза наночастиц меди / оксидов дуговым разрядом в растворе аскорбиновой кислоты / воды3. Этот метод требует систем с высокой потребляемой энергией и производит коллоиды, которые содержат металлические / оксидные частицы меди, а не медного порошка. Дуговой разряд создает непрерывную плазму между электродами, которые вызывают потерю энергии окружающим средам, что приводит к высокотемпературному расширению по всему электроду и окружающим средам. Импульсная плазма представляет собой импульсный разряд, при котором потеря энергии в окружающую область является низкой. Импульсная энергия плазмы в основном расходуется на дисперсию электродов.

В этой статье мы представляем новый метод синтеза металлических наночастиц с использованием импульсной плазмы в жидкости. Хотя импульсная плазма в газе эффективно использовалась в обработке поверхности металла, до сих пор она не использовалась в синтезе нанокристаллических материалов. Импульсная плазма в жидком методе не требует вакуумной системы, высокоэнергетических и сложных процедур очистки и основана на низковольтной импульсной плазме в жидких диэлектриках.

Ключевые слова: наночастиц, синтез, оксиды, аскорбиновая кислота, водный раствор, импульсная плазма.

Method

Schematics of our apparatus are shown in Fig.1. Impulse Plasma in Liquid is pulsed plasma between two electrodes submerged into a dielectrics liquid. Unit is very simple and does not require vacuum system, high-energy, cooling system, but can evaporate even refractory metals. Energy of a single impulse is controlled by changing the capacity of the condensers.

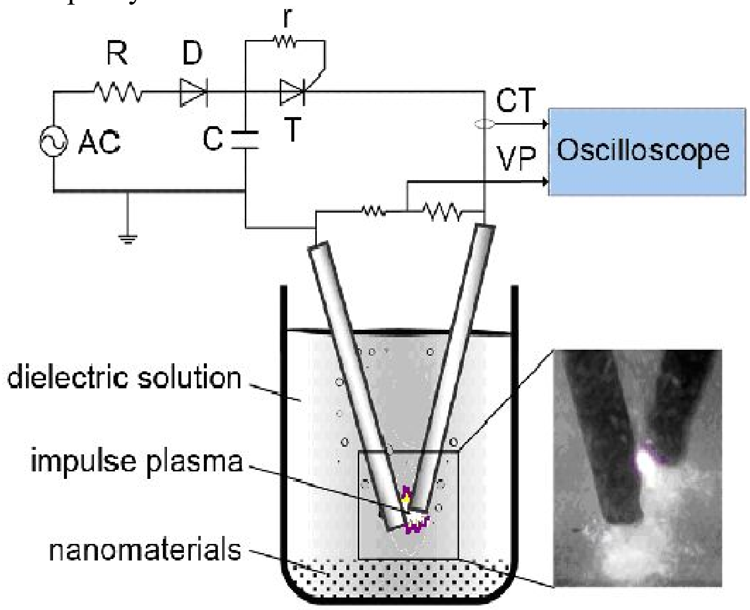

Fig. 1. Schematics of the apparatus used for Impulse Plasma in Liquid method

We have chosen a single impulse energy and liquid for discharge depending on the being dispersed material's properties. For copper, silver and ytterbium, styrene was chosen to prevent the forming powder from oxidization.

Due to small energy-intensiveness that is conditioned by locality of the single plasma impulse due to its small duration (0.01-1ms) and placement of electrodes into a liquid, the system has no need for cooling system. This is conditioned by small duration of a single impulse that does not cause high temperature widening or significantly moving on the electrode surface. Another significant advantage of this method is that the plasma discharges are produced in a simple beaker filled with a liquid and placed in an open air. These conditions provide more opportunity for in-situ investigations of nanomaterials forming mechanism by the pulsed plasma in liquid. Accordingly, all these advantages make the method effective and provide versatile capability.

experimental

For copper and silver dispersion by Impulse Plasma, two electrodes made from 6 mm pure copper rods placed inside a beaker, which contains 200ml pure styrene. The discharge voltage and current were 220 V and 6A respectively. Two electrodes were vibrated within the 0.5-1 mm gap. After the Impulse Plasma applied to the electrodes for about 3 hours, copper particles formed about 3 gram powder at the bottom. Formed powder was filtrated and dried in an inert atmosphere. Ytterbium dispersion has also the same procedures and has same production rate of about 1g/h. The X-Ray Diffraction (XRD) patterns were obtained using the powder method by Rigaku Geigerflex X-Ray Diffractometer. The electron diffraction patterns of the products were taken by Transmission Electron Microscopy (TEM) JEOL-200FX: powders were solved in methanol and stirred by ultrasonic treatment to disperse the nanoparticles at the room temperature prior to the TEM analyses. Then the particles dropped onto copper grids covered with carbon film and dried in the air for TEM observations.

Results and discussions

Nanoparticles of copper, silver and ytterbium

Figure 2 shows the XRD patterns of the product of copper dispersion by Impulse Plasma (a) and initial bulk copper (b). XRD analysis showed that dispersion of bulk copper by Impulse Plasma in styrene resulted in formation of metallic nanoparticles of copper. As prepared nanostructures are particles of copper with fcc structure (spatial group O_h^5-Fm3m, Z-4). Crystal lattice of copper after the discharge (a=3.6215Å) slightly widened comparing to a bulk one (a_{mass}=3.6147 Å). Particle size of the copper nanoparticles was estimated by the Scherrer's formula to be 23-25 Å . From top of the Fig. 2, TEM image of the copper particles formed by the impulse plasma between two copper electrodes in styrene is shown. Very small particles of about 3 nm were observed.

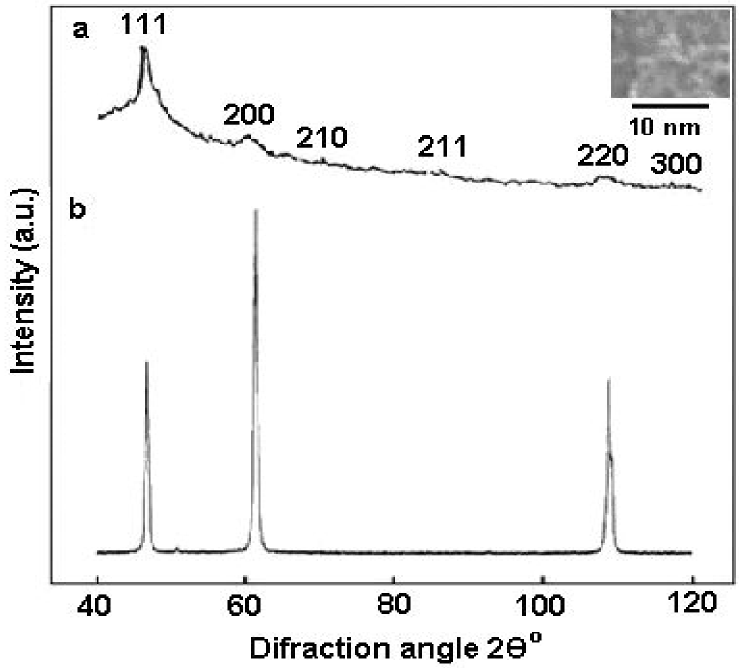

Fig. 2. XRD patterns of dispersion product of copper in styrene (a) by Impulse Plasma in Liquid method and bulk copper (b)

Nanoparticles of silver formatted in impulse plasma also with fcc structure (spatial group Oh5-Fm3m, Z-4). Crystal lattice of silver after the discharge - a=4,0823 Å, of bulk silver – a_{mass} = 4.0812 Å. Particle size of nanoparticles was estimated by the Scherrer's formula to be 22-28 Å. XRD patterns of the product of silver is shown on the Figure 3.

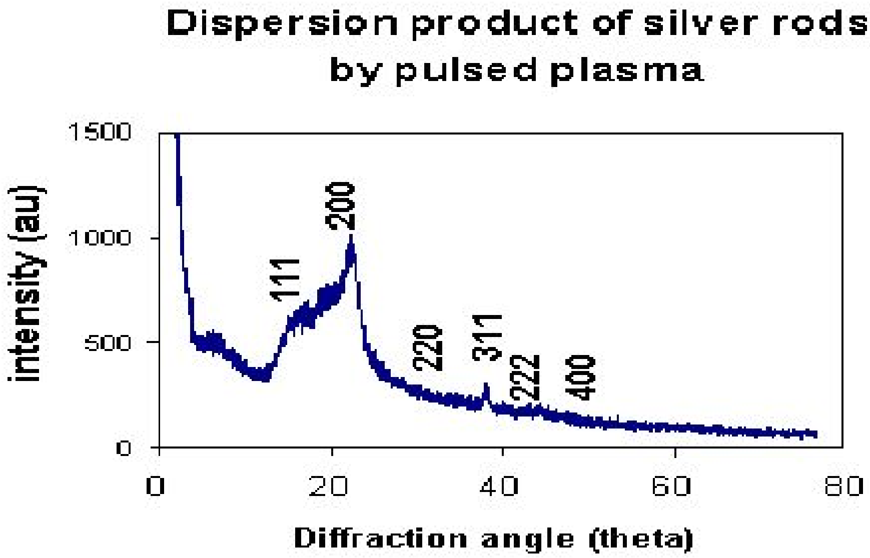

Fig. 3. XRD pattern dispersion of silver in styrene by Impulse Plasma in Liquid

Figure 4 shows the XRD pattern of the dispersion product of ytterbium by Impulse Plasma in styrene (a) and XRD pattern of the initial bulk ytterbium (b). Dispersion of electrodes made from ytterbium by Impulse Plasma in styrene also resulted in forming metallic nanostructures of ytterbium.

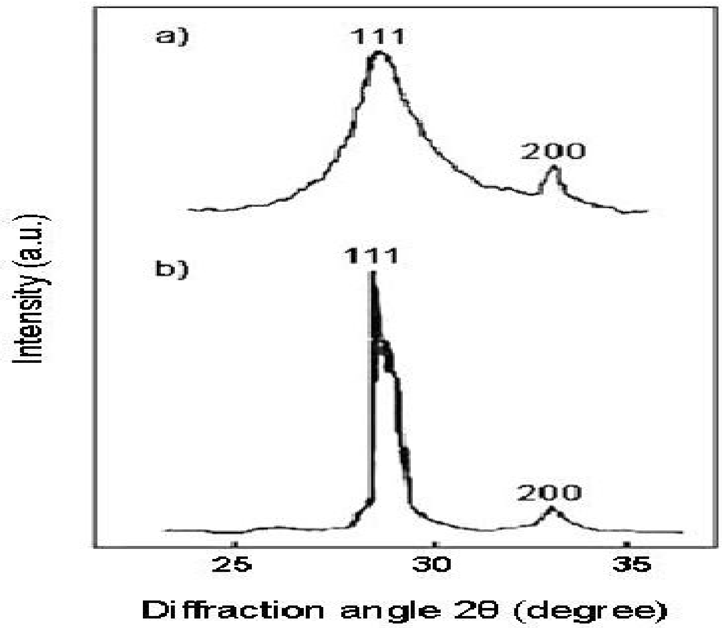

Fig.4. XRD pattern for the sample formed by the impulse plasma between ytterbium electrodes in styrene (a) and XRD pattern of the initial bulk ytterbium (b)

In Fig. 4a, we can see that XRD analysis of this sample revealed the reflexes of (111) and (200) planes, which correspond to the metallic ytterbium with fcc lattice like copper's. For comparison, the XRD pattern of bulk ytterbium is given in Fig. 4b. Analysis shows that the formed powder consists of metallic nanoparticles of ytterbium with the average particle sizes of 25-30 nm. Accordingly, the dispersed from the tips of electrodes copper, silver and ytterbium clusters immediately react with the surrounding styrene that lead to forming of metallic particles and prevent from oxidation.

Conclusion

In this article, we presented a new method, Impulse Plasma in Liquid, for synthesis of nanocrystalline materials by using the low voltage pulsed plasma in liquid. We have successfully produced metallic nanoparticles of Cu, Ag, Yb. The apparatus is easily adoptable for additional in-situ analysis equipment. Advantages of this method such as small energy-intensiveness, no necessity for vacuum system and low cost of the final product make it original and versatile in the synthesis of nanocrystalline materials. The impulse plasma in liquid enables us to quench from plasma state, by which we can synthesize nanomaterials, metastable materials, etc. Copper and silver nanoparticles prepared by this method were smaller than those by arc method by a factor of >5. The present method can be used for the synthesis of various kinds of metal and compound nanomaterials.

References

1.D.L. Feldheim, C.A. Foss Jr., Metal Nanoparticles; Synthesis, Characterization, and Applications, Marcel Dekker, New York, 2002.

2.T. Satsuta, M. Hasegawa, N. Harada, S.J. Asai, Jpn. Inst. Metal.57 (1993) 296.

3.S.Y. Xie, Z.J. Ma, C.F. Wang, S.C. Lin, Z.Y. Jiang, R.B. Huang, L.S. Zheng, J.Solid State Chem. 177 (2004) 3743.