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DISPERSION OF SILVER, YTTERBIUM AND SOME OF REFRACTORY TRANSITION METALS BY IMPULSE PLASMA IN LIQUID

In this article, we present a new synthesis method of metallic nanoparticles, oxides, sulfides, and 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: impulse plasma in liquid, synthesis of nanomaterials.

ДИСПЕРСИЯ СЕРЕБРА, ИТТЕРБИЯ И НЕКОТОРЫХ ТУГОПЛАВКИХ ПЕРЕХОДНЫХ МЕТАЛЛОВ ИМПУЛЬСНОЙ ПЛАЗМОЙ В ЖИДКОСТИ

В этой статье мы представляем новый метод синтеза металлических наночастиц, оксидов, сульфидов и с помощью 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: импульсная плазма в жидкости, синтез наноматериалов.

ABSTRACT

A new method to fabricate nanomaterials by using Impulse Plasma in Liquid is presented. Impulse plasma appears from inter-electrode space break-down in high potential difference between two electrodes submerged into a dielectric liquid. And the power supply is relatively small that is insufficient to excite an arc discharge. By changing the dielectric liquid, we can obtain either metallic particles, oxide, sulfide or carbide of metal. Nanocrystalline powder of TiO_2 (anatase, rutile) was prepared using purified water as a dielectric liquid. Pure metallic nanoparticles of silver ytterbium were also prepared using styrene as an agent to prevent forming metallic particles from oxidization. It was conducted dispersion of titanium, tungsten, tantalum in carbon containing medium. This method does not require vacuum chamber and high energy, thus, can provide economical preparation of various types of nanomaterials.

INTRODUCTION

Synthesis of nanoparticles has been of a great activeness because of their interesting properties different from the bulk substances[1]. There are many methods for nanoparticles synthesis. For example, arc discharge in liquid nitrogen[2], liquid ammonia[3] for production of metal nitrides or carbides and so on. These methods are high cost due to rapid consuming the liquid nitrogen/ammonia and high energy consumption. Recently, a synthesis method of copper nanoparticles/oxides by arc discharge in ascorbic acid/water solution was reported[4]. This method requires high energy consuming systems and produces colloids, which contain metallic/oxide particles of copper rather than copper powder. On the other hand, the above mentioned methods are based on the arc discharge. 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.

METHOD

A schematics of our apparatus is 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.

We have chosen a single impulse energy and liquid for discharge depending on the being dispersed material's properties. Similarly, for silver and ytterbium, styrene was chosen to prevent the forming powder from oxidization. For titanium, water was used to obtain titanium dioxide. In this way, chemical composition of forming powders can be controlled.

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.

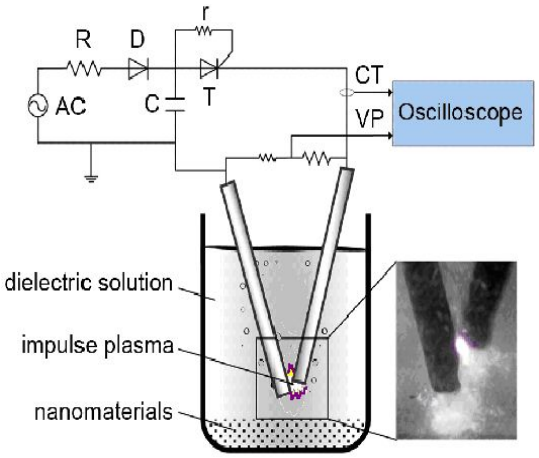

Fig. 1. Schematics of the apparatus used for Impulse Plasma in Liquid method

EXPERIMENTAL

For silver dispersion by Impulse Plasma, two electrodes made from 6 mm pure silver 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, silver particles formed about 4 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. For titanium, two rods of 6mm 99.7% purity titanium electrodes were submerged into 100ml distilled water. After discharge for several hours, a black powder formed at the bottom, which was then filtrated and dried at the room temperature in an open air.

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. Chromatogram and UV-vis spectrum for the extracted fullerene soot were taken by HPLC with the following conditions: MD-2010 Plus, Sil-ODA-14 column, 254nm, hexane mobile phase, flow rate of 1ml/min, column temperature of 30°C.

RESULTS AND DISCUSSIONS

Nanoparticles of silver and ytterbium

Nanoparticles of silver formatted in impulse plasma 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 2.

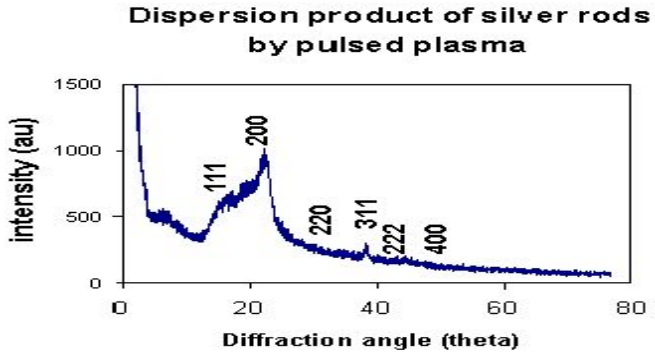

Fig. 2. XRD pattern dispersion of silver in styrene by Impulse Plasma in Liquid

Figure3 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.

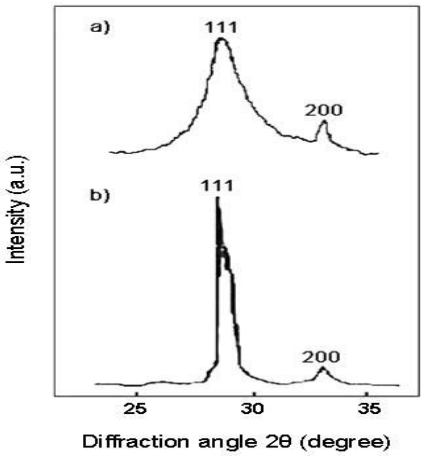

Fig.3. XRD pattern for the sample formed by the impulse plasma between ytterbium electrodes in styrene (a) and XRD pattern of the initial bulk ytterbium (b)

In Fig. 3a, 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. 3b. 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.

Stabilization of the nanoparticles and forming of polymer shell

The reasons for increasing of the reactivity of the solids during their dispersion is the decreasing of the particle sizes by increasing the surface area, which lead to the increasing of the free surface energy and formation of the thermodynamically non-stable state. Freshly-formed surface of the substances are easily oxidized in air right up till the spontaneous combustion, if the formation of the particles take place without formation of the protective shell. The stabilization problem rises in the synthesis of nanoparticles, which are naturally concerned as the substances of active (energy-saturated) state.

Let us consider the formation mechanism of the polymer shell on the surface of the particles, produced

by the impulse plasma in styrene. During the direct formation of the particles in a monomer, the physical-chemical characteristics of the solids have a big significance. Polymer formation activity of metals (in some particular media) directly depends on the electron emission value: larger the electron emission, larger the yield of polymer.

Kinetics of the polymer shell growth was studied in relation with various factors. It was shown that the shell growth speed is proportional to the intensity of the radiation and does not depend on the substrate material. The growth speed slows down by time and the formation of the shell depends on three factors:

1. vapors that can form polymer (in our case styrene);
2. surface, where the shell is being created (particle surfaces);
3. electron beam (surface of the clusters are full of electrons, defects, dislocations).

Polymer shell growth speed does not depend on the radiation time, but strongly depends on the substrate temperature. Since the surface temperature of the particle formed by the impulse plasma in liquid changes from up to down, the ionic mechanism of polymerization of the being used monomer can be considered. Radical polymerization of the excited metal atoms can flow as follows:

$$CH_2 = CH_2 + M^* \longrightarrow CH = CH_2 + MH$$

or

$$CH_2 = CH_2 + M^* \longrightarrow CH = CH_2 + M + H$$

Most probably the styrene polymerization according to the radical mechanism will look similar, because, there is a large number of excited metallic atoms on the particle surface, especially, the surface atoms are connected each other weaker than the inner atoms.

The formation of the polymer protective shell in the conditions of the impulse plasma in liquid is natural, since the energy of the impulse plasma is enough high to destroy any metal with forming energy-saturated media. Also this energy is sufficient for the maintaining the nanoparticles in the excited state during a certain period of time, which is required for the polymerization process of any monomer. In addition, non-equilibrium state of the impulse plasma process promotes the formation of polymerization centers on the fresh particle surfaces.

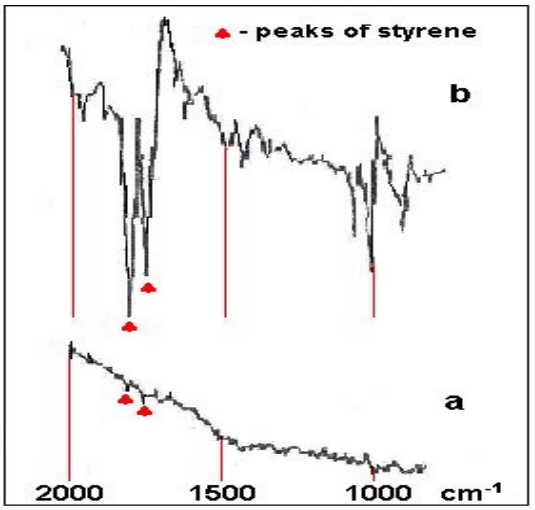

Fig.4. a) the washed copper particles and b) IR spectra of the separated polymer shell from the copper particles prepared by the impulse plasma between copper electrodes submerged into styrene

Protective polymer shell was formed on the surfaces of copper nanoparticles produced by the impulse plasma between two copper electrodes in styrene (single energy 0.05 J). The copper sample was solved repeatedly in order to solve the polymer shell from the particle surfaces. The filtrated sample was studied by IR spectroscopy (400-4000 cm^{-1}).

Figure 4 shows the IR spectra of the sample by the impulse plasma between copper electrodes submerged into styrene and the separated from the copper particles polymer shell. The IR spectrum of the

polymer shell, which was solved out from the copper nanoparticles showed similar pattern with the polystyrene. This suggests that the polymer shell on the surface of the copper particles was formed.

Dispersion of holmium by Impulse Plasma

The XRD pattern of Ag and Yb remain same after 2-6 months. But, the case of holmium is different (Figure 5). Apparently, we obtained a media, where the structural relaxation occurs by formation of stable crystal phases for the first time.

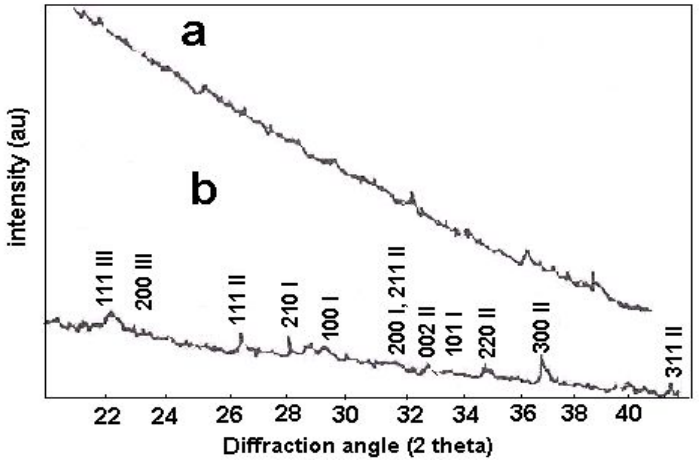

Fig.5. XRD pattern of holmium dispersion by IPL, a) initial, b) after 2 weeks (I-metallic holmium, II – fcc holmium carbide, III – cubic holmium carbide)

Analysis of XRD pattern showed that at least 3 phases exist: metallic holmium with hcp structure, phase with fcc structure, phase with primitive cubic structure

Taken just after the preparation XRD pattern looks like amorphous system. Later after keeping the sample in inert atmosphere for 2 weeks, the XRD pattern started to show reflexes. These peaks keep increasing for next 2 weeks.

Dispersion of refractory transition metals by IPL in carbon containing medium

It is very difficult to prepare nanoparticles of refractory metals and their compound by the existing methods due to their high melting temperature and extreme hardness.

We conducted dispersion of titanium, tungsten, tantalum in carbon containing medium. Particles size were estimated by XRD (Figure 6) analysis to be about 45-60 Å for tantalum and tungsten, 25-30 Å for titanium.

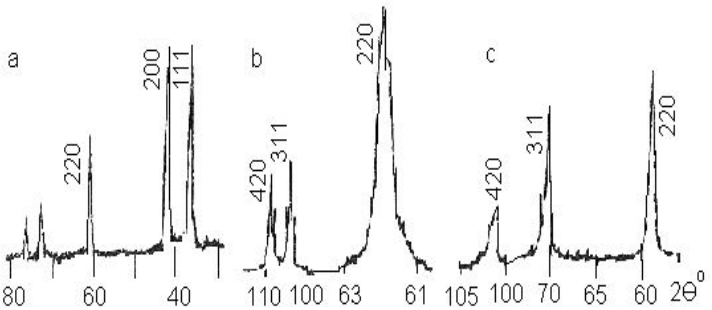

Fig.6. XRD pattern of dispersion product of Ti (a), W (b), Ta (c)

Analysis of XRD pattern showed that under dispersion Ti, W, Ta in carbon containing medium are formated nanoparticles of monocarbides of these metals. Crystal lattice(fcc, type of structure – NaCI) of

TiC, β-TaC and β-WC 4,332 Å, 4,445 Å , 4,421 Å respectively.

Nanocrystalline powder of TiO_2

Figure 7 shows XRD pattern of titanium powder prepared by Impulse Plasma in water. By XRD analysis, we determined that powder contains of titanium dioxide rutile and anatase phases. Although the rutile and anatase phases have different melting points at the temperature range of 300-1000 ºC, dispersion by Impulse Plasma formed both phases.

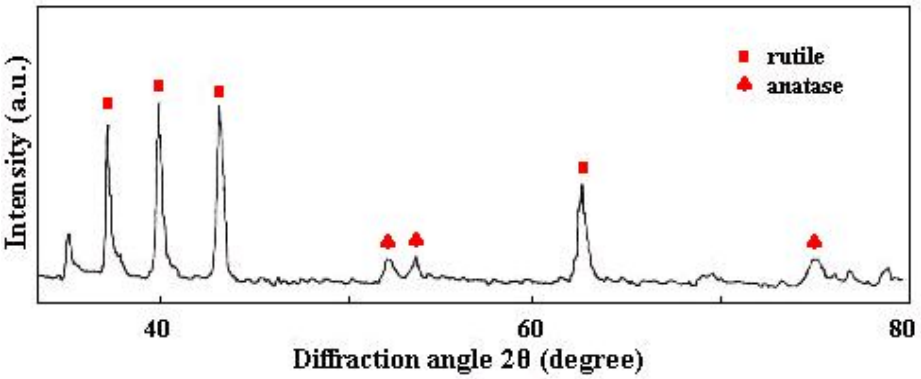

Fig.7. XRD pattern for the titanium dioxide nanoparticles

There are other peaks in the XRD pattern, which do not belong to any of titanium phases. These peaks probably correspond to the phases that might form in the conditions of Impulse Plasma in Liquid, where the interactions of dynamic pressures and temperatures occur. Conditions of the Impulse Plasma are more intensive comparing to the static temperature and pressure. More surprises are expected, since the Impulse Plasma in Liquid is not studied totally. Ultra fast cooling of the forming titanium clusters by the surrounding water medium provided the nascent Ti nanoclusters reaction with water and formation of titanium oxides.

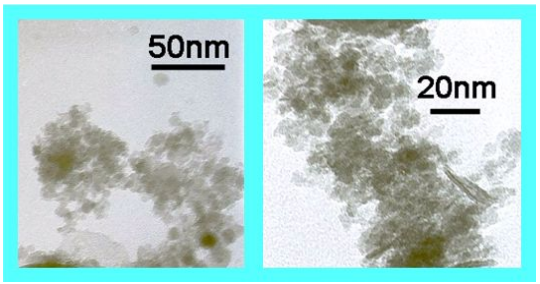

Fig.8.TEM images of the TiO_2 powder prepared by Impulse Plasma in Liquid

TEM images of the self-assembled in the water TiO_2 particles are shown in Fig. 8. As we can see, as prepared nanoparticles are spherically formed and have grain size of about 15 nm, which was also estimated from XRD pattern to be 20 nm.

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 Ag, Yb, monocarbides of Ti, Ta, W and TiO_2. 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 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. The protective polymer shell was formed on the surface of the particles by the impulse plasma in liquid.

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