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Metallic particle formation by MeV proton irradiation in liquid

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ABSTRACT

Ion irradiation in liquid was performed using a tandem accelerator and beam injection with a glass capillary. Nanoparticles of transition metals (Ni, Cu, Ag, Pt, and Au) were grown in the solution by reduction of the metallic ions in a process induced by proton irradiation. We could deposit the particles directly on the substrate at the irradiated position. The size of the particles was controllable by continuing the irradiation. Bimetallic Pt–Cu particles could be formed at any elemental ratio. Incorporation of oxygen into the particles was suppressed by selecting a scavenger at an appropriate concentration.

1. Introduction

Radiation reduction of metallic ions in liquid is one of the promising methods for nanoparticle fabrication [1]. Gamma-rays and electrons radiation are commonly used for this process because of their penetrating power and uniformity [2]. In contrast, a feature of ion beams is the high-density excitation resulting from its large linear energy transfer (LET). In this study, we used radiation with MeV protons and observed nanoparticle formation of transition metals. A simple ion irradiation system in a liquid using a glass capillary has been developed to perform the experiment swiftly and efficiently [3–6]. Nanoparticle formation with an ion beam is in a disadvantaged position against gamma-ray and electron regarding production rate and cost. However, it can be available for particle deposition at the micro-region by using its straight-running ability in liquid and microbeam technique with a tapered capillary.

The mechanism of particle formation is as follows [7]. Aqueous electron (e^-_{aq}), a hydrogen radical ($H^\cdot$) and a hydroxyl radical ($OH^\cdot$) are formed by radiolytic decomposition of water.

$$H_2O \rightarrow e^-_{aq}, H^+, H^\cdot, OH^\cdot, H_2O_2, H_2 \quad (1)$$

$H^\cdot$ and $OH^\cdot$ react with alcohol to form the reductive alcoholic radical. Alcohol scavenges the strong oxidant $OH^\cdot$.

$$(CH_3)_2CHOH + OH^\cdot \rightarrow (CH_3)_2\dot{C}OH + H_2O \quad (2)$$

$$(CH_3)_2CHOH + H^\cdot \rightarrow (CH_3)_2\dot{C}OH + H_2 \quad (3)$$

e^-_{aq}, $H^\cdot$ and alcoholic radicals reduce metal ions and form metallic particles.

$$M^+ + e^-_{aq} \rightarrow M^o \quad (4)$$

$$M^+ + H^\cdot \rightarrow M^o + H^+ \quad (5)$$

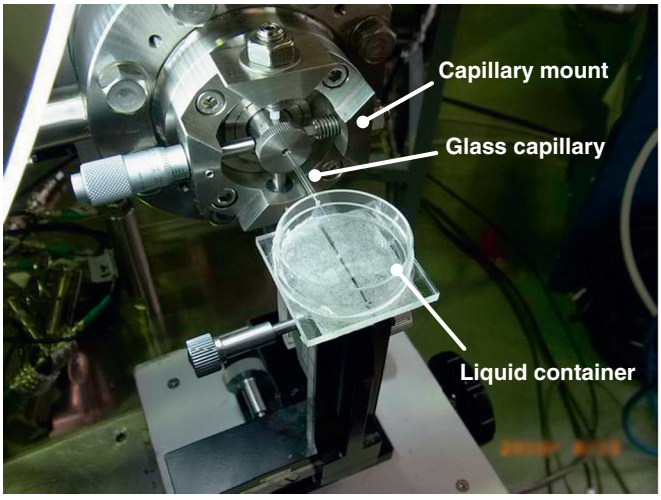

Fig. 1. The liquid irradiation system for a MeV ion beam. A capillary set at the end of the beamline is inserted in a liquid container.

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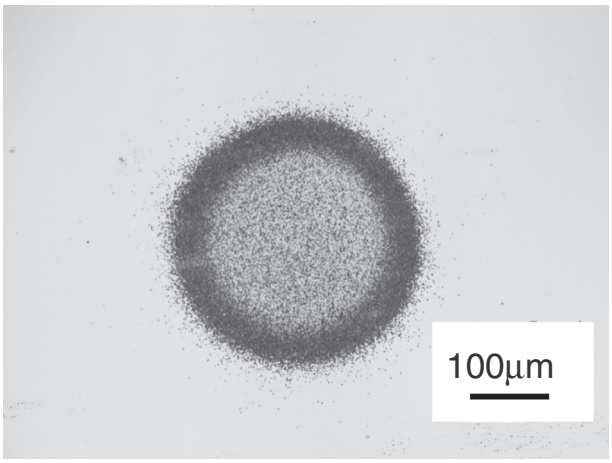

Fig. 2. Micrograph of the surface of the CR-39 polymer track recorder etched in KOH after being irradiated with 3 MeV protons. The irradiation was performed in air, in contiguity with the capillary tip.

$$M^{+} + (CH_3)_2\dot{C}OH \rightarrow M^{o} + (CH_3)_2CO + H^{+} \quad (6)$$

Particle growth is affected by the ion/radical concentration and their diffusion rate, agitation intensity and presence or absence of supporting materials.

2. Experimental details

2.1. Irradiation system

An ion irradiation system in liquid was constructed using a tapered glass capillary placed at the end of the vacuum beamline. The capillary was made by tearing a 3 mm diameter glass tube by pulling both ends in a heater. The tip of the capillary was covered by a thin glass or polymer film that separated between the vacuum and the liquid. The capillary was inserted in a liquid container through a hole in the sidewall (Fig. 1). To avoid a liquid spill, an O-ring was placed around the hole. The roles of the capillary were to serve as the beam slit, beam condenser, and pressure bulkhead. In case of an accidental vacuum break, the conductance of the capillary was so small that we had enough time to protect the accelerator and the pumps by using a conventional automatic vacuum valve. The diameter of the ion beam was controlled by the inner diameter of the capillary tip from several μm to several mm. The advantage of this system was that we could visually recognize the ion ejection point and the beam spot size. As a result, we could irradiate the target position with absolute certainty. The samples were set perpendicular to the beam, hanged with a three-axis manipulator and dipped in the solution from above. The distance between the capillary tip and the sample surface was controlled with the manipulator and checked by using a lateral camera set. We set the capillary diameter of the thin (beam ejection) side at 300 μm. Fig. 2 shows the surface of the CR-39 polymer track recorder etched with a potassium hydride (KOH) solution after irradiation with 3 MeV protons ejected from the capillary. The density of the etch pit increased at the outer edge presumably due to proton scattering at the glass wall. This image suggests that the capillary has some beam focusing ability as a result of scattering at the inner wall. The focusing efficiency will depend heavily on the shape of the capillary.

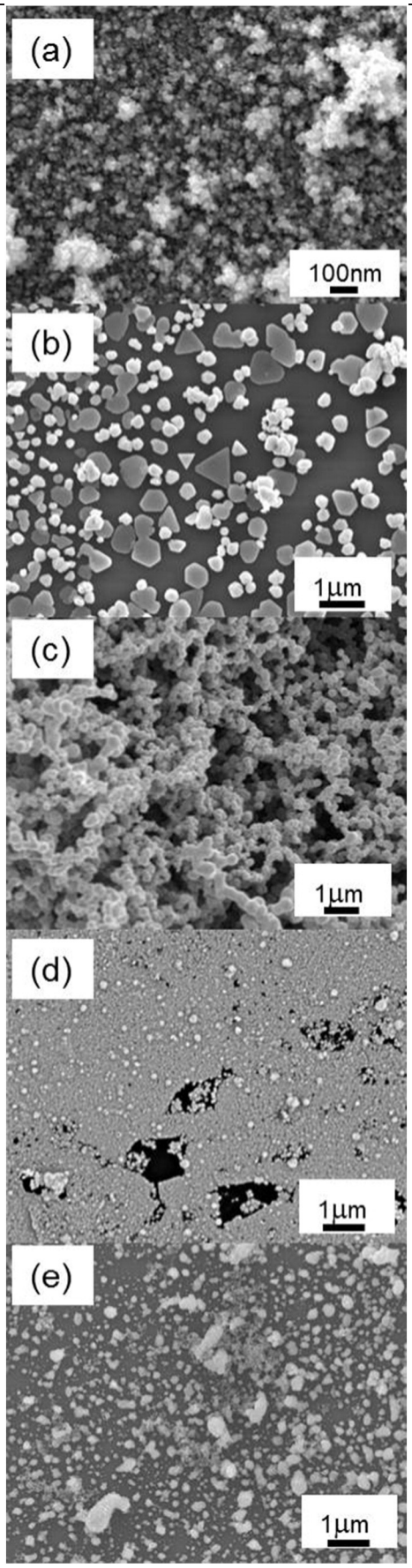

Fig. 3. SEM micrographs of (a) Pt, (b) Ag, (c) Au, (d) Ni, and (e) Cu particles collected on substrates.

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