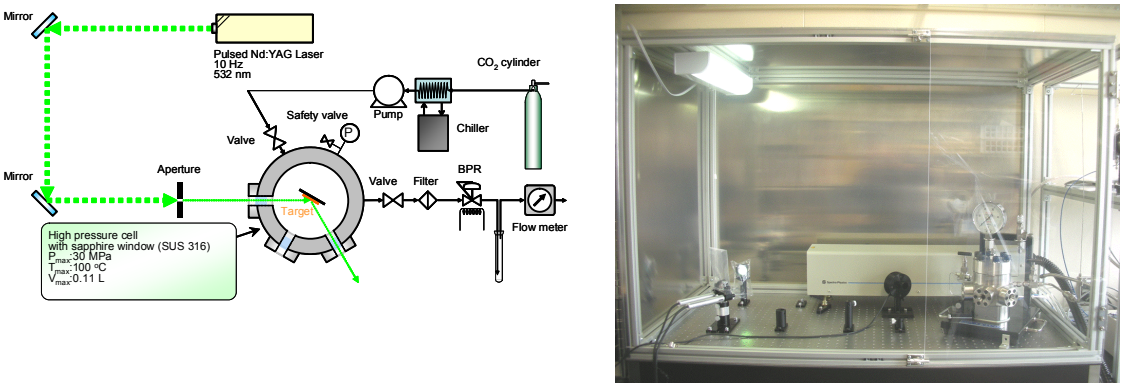
Research Activity on Supercritical Fluids Technology at Kumamoto University

Material Synthesis using Pulsed Laser Ablation in Supercritical CO_2

Pulsed laser ablation has been widely employed in industrial and biological applications and in other fields. The environmental conditions in which pulsed laser ablation is conducted are important parameters that affect both the solid particle cloud (plume) and the deposition (debris) produced by the plume. In most studies, particles are generated either in a vacuum or in ambient conditions. Some studies, however, use a different ambient medium such as a gas, a surfactant solution [43, 44], organic solvent [45], liquid N_2 [46], and supercritical CO_2 [47, 48]. Saitow et al. have reported that silicon nanoclusters and gold nanonecklaces could be generated by performing pulsed laser ablation in supercritical CO_2 [47, 48]. However, they did not discuss the synthesis behavior in much detail. Moreover, only those two investigations of pulsed laser ablation in supercritical CO_2 have been reported.

Recently, our laboratory has investigated pulsed laser ablation of copper in supercritical CO_2 [49]. We also conducted ablation at atmospheric condition with air and liquid hexane. We obtained that laser ablation of a metal in high pressure was affected by pressure and surrounding environment. The ablation of copper plate resulted deeper crater in supercritical CO_2 compared with in atmospheric condition. Furthermore, we develop pulsed laser ablation of gold substrate in supercritical CO_2 to generate synthesized gold nanoparticles.



(a) (b)

Figure 8. Experimental apparatus of pulsed laser ablation in supercritical CO_2 for material synthesis. (a) Schematic diagram; (b) Photograph.

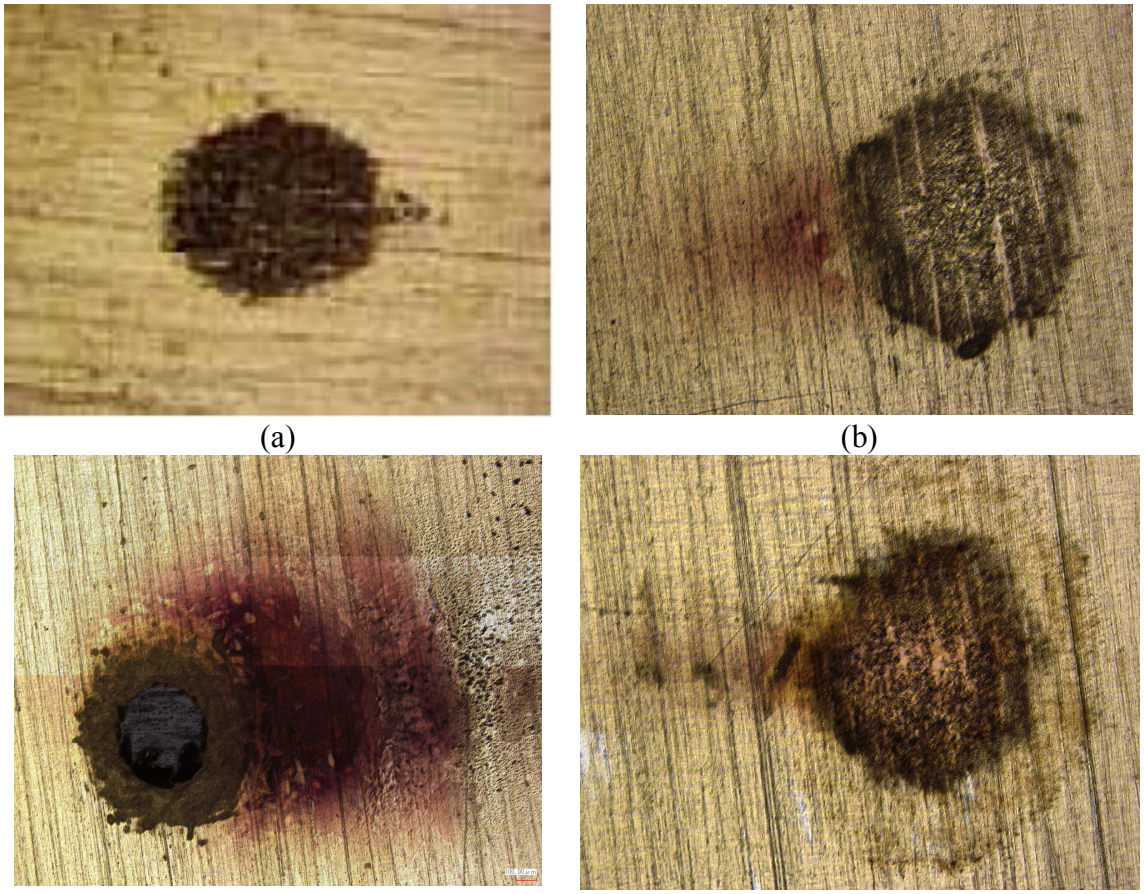


Figure 9. Laser scanning microscopy image of Au plate after ablation at 40°C for 3000s by Nd:YAG laser. (a) in air at ambient pressure; (b) in liquid CO_2 at 6.5 MPa; (c) in supercritical CO_2 at 10 MPa; (d) in supercritical CO_2 at 20 MPa.

Experiment of laser ablation in supercritical field for material synthesis was carried out in a high-pressure cell with three sapphire windows as shown in Figure 8. The second harmonic of a Q-switched pulsed Nd:YAG laser (Spectra-Physics Quanta-Ray INDI-40-10, wavelength: 532 nm, pulse energy: maximum 200 mJ/(cm^2.pulse), pulse duration: 8 ns, repetition frequency: 10 Hz) was used. Target was fixed in a high-pressure cell (AKICO). Incident angle of the laser beam was 30° and the laser was located 1 m from the target. A gold plate (Nilaco, purity: 99.99%, thickness: 0.03 mm) was used as the target. Liquid CO_2 was pressurized and pumped into the cell using a high-performance liquid chromatography (HPLC) pump (Jasco PU-1586).

Surface morphology of gold plate after ablation at 40°C and various pressures for 3000 s is shown in Figure 9. A circle crater was clearly observed in the irradiated gold plate at all conditions. The crater was more clearly generated as increasing pressure. In addition, the surface around irradiation region was slightly rough due to the solid particle cloud (plume) deposited.

Figure 10 shows the crater depth generated by PLA at various pressures. As expected, the increasing pressure causes increasing the crater depth due to CO_2 properties change in the system. However, the deepest crater was observed at critical pressure of CO_2 and it has similar trend line with constant volume heat capacity of CO_2.

The craters depth at critical pressure and 10 MPa were thicker than initial gold plate thickness because the plume deposited around the hole was generated.

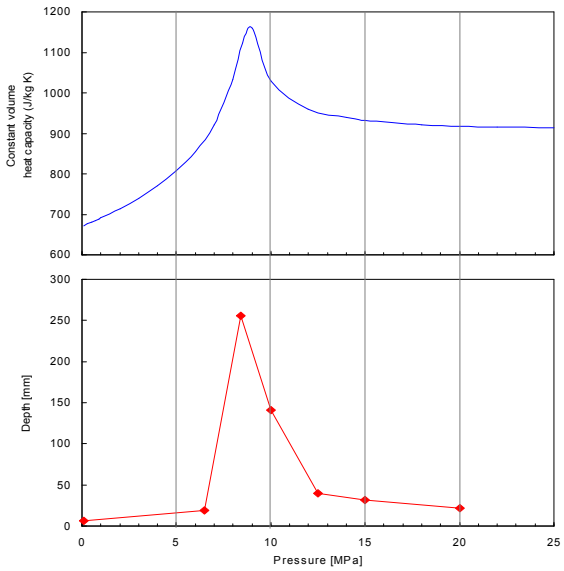


Figure 10. Depth of crater generated by pulsed laser ablation at various pressures and 40°C for 3000 s.

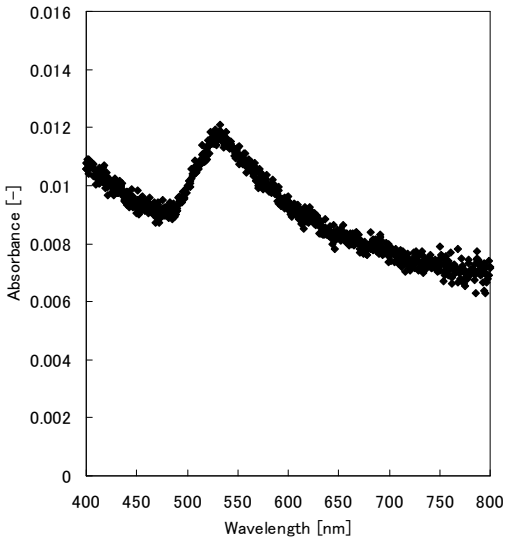


Figure 11. Extinction spectra of gold nanoparticles deposited in glass slide at 40°C and 20 MPa for 3000 s

Extinction spectra of gold nanoparticles deposited in glass slide was also measured for confirmation of generated gold nanoparticles. Figure 11 shows the spectra of generated gold nanoparticles in glass slide, measured after CO_2 depressurizing. The spectra contain bands near 530 and 650. The peak near 530 nm has been known to correspond to the plasmon band of gold nanospheres with diameters <50 nm [48].

References

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