Journal of Photochemistry and Photobiology A: Chemistry 145 (2001) 201–207

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Preparation of metal colloids by a laser ablation technique in solution: influence of laser wavelength on the ablation efficiency (II)

Takeshi Tsuji [a,*], Kenzo Iryo [b], Yukio Nishimura [a,b], Masaharu Tsuji [a,b]

[a] Institute of Advanced Material Study, Graduate School of Engineering Science, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan

[b] Applied Science of Electronics and Materials, Graduate School of Engineering Science, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan

Received 1 March 2001; received in revised form 1 June 2001; accepted 6 June 2001

Abstract

Laser ablations of silver and copper targets in water were performed to prepare nanosize metal colloids. The influence of the laser wavelength, focusing conditions, and laser fluence on the ablation efficiency was studied. The relation between the ablation efficiency and wavelength varied with laser fluence. The ablation efficiency at shorter wavelengths was higher at low fluence, while the ablation efficiency at longer wavelengths was higher at high fluence. These findings were discussed in terms of the “intra-pulse” and “inter-pulse” self-absorptions of the incident laser light by colloidal particles.

Keywords: Laser ablation; Metal colloids; Silver; Copper; Solution; Ablation efficiency; Wavelength; Fluence

1. Introduction

In recent years, requirements for new functional materials are considerably increasing. Laser ablation is one of the useful techniques to produce new materials. Recently, it has been reported that ablation of metal targets in solvents prepared colloidal solutions of nanoparticles [1–3]. Due to the unique photochemical and photophysical properties of nanoparticles differing from those of bulk, nanoparticles of metals are expected to be used as functional materials. In addition, because of the simplicity of the procedure, laser ablation in the solution system was applied on other materials such as C_{60} [1].

Although the control of the size and size distributions of particles is important, the mechanisms of colloid formation by laser ablation have not been sufficiently investigated. Thus far, some researchers have investigated on the influence of the ablation conditions on the ablation efficiency and the size of particles. Procházka et al. [4,5] studied on the influence of the focusing conditions and the energy of laser pulse. They also mentioned about the absorption of incident laser lights by colloidal particles (self-absorption) and its effect on the particle size. Very recently, Mafuné et al. [6] reported on the colloid formation mechanism in an aqueous solution of sodium dodecylsulfate (SDS). They examined the influence of the laser fluence, spot size, and the number of laser shots on the ablation efficiencies and particle size, in addition to the effect of SDS on the growing process of particles.

In this study, we have investigated on the influence of the laser wavelength on the ablation efficiency. The wavelength of the irradiated laser light will significantly affect the ablation efficiency because it is associated with the absorption efficiency of the laser light by the surface of the metal targets and with the energy of the incident photons. However, most of the previous studies have performed using laser light with single wavelength. Recently, Jeon and Yeh [7] have reported the wavelength dependence of the ablation efficiencies at 1064 and 532 nm, though the influence of the focusing the laser light was examined only for 1064 nm. In this work, we have examined various fluence and focusing conditions using laser light at 1064, 532, and 355 nm. In the previous paper [8], we have reported that the efficiencies of the Ag colloid formation depended on the laser wavelength. A remarkable finding was that the ablation efficiencies increased with an increase in laser wavelength when the laser light was focused on the targets.

Recently, Semerok et al. [9] reported the wavelength dependence of ablation efficiencies of various metals (Al, Cu, Mo, Fe, Pb, and Ni) in the atmospheric circumstances using laser light at 1064, 532, and 266 nm. The ablation efficiencies were higher at shorter wavelengths for all metal species. These results were contrary to our work in solution. In this report, we have studied the dependence

* Corresponding author. Tel./fax: +81-92-583-7816.
E-mail address: ta-tsuji@cm.kyushu-u.ac.jp (T. Tsuji).

1010-6030/01/$ – see front matter
PII: S1010-6030(01)00583-4

of the ablation efficiency on the laser wavelength more precisely using Ag and Cu targets to elucidate this feature.

2. Experimental

Fig. 1 depicts a configuration of experimental apparatuses. The fundamental (1064 nm) and frequency-multiplied outputs (355 and 532 nm) of a Nd:YAG laser (Spectra Physics GCR-200) were used as an irradiation source. The laser was operated at 10 Hz and the pulse duration was 5–9 ns. The central part of the laser beam was selected with an aperture to control the spot size of nonfocused laser light. The laser light was conducted onto the target through the opening of the cell. The energy of the irradiation beam was corrected for absorption by the solvent at each wavelength. Focused or non-focused laser light was used to ablate targets. A lens ($f = 100$ mm) was placed above the cell when laser light was focused on the surface of the targets. To change the focusing conditions of laser light, the relative position of the lens to the targets was varied. Ag and Cu targets (Nilaco, >99.99%) were washed with distilled water and placed in a quarts cell containing 5 ml high-pressure liquid chromatography grade water. The solutions were not stirred during the ablation except for the case of examining the influence of stirring the solutions. A magnetic stirrer was used when the solutions were stirred. On stirring, no ripple was observed on the surface of the solutions. Absorption spectra of the colloid solutions were measured with a UV–visible spectrometer (JASCO V-570). Transmission electron micrographs of the colloidal particles were measured with a transmission electron microscope (JEOL JEM-200CX) operating at 200 kV. To prepare samples for electron microscopy, a small amount of SDS solution was added (final concentration 10 mM) into the colloid solution before a drop of the solution was placed on a microgrid (Oken type A) and dried in air. Without SDS, the solution was repelled by the microgrid.

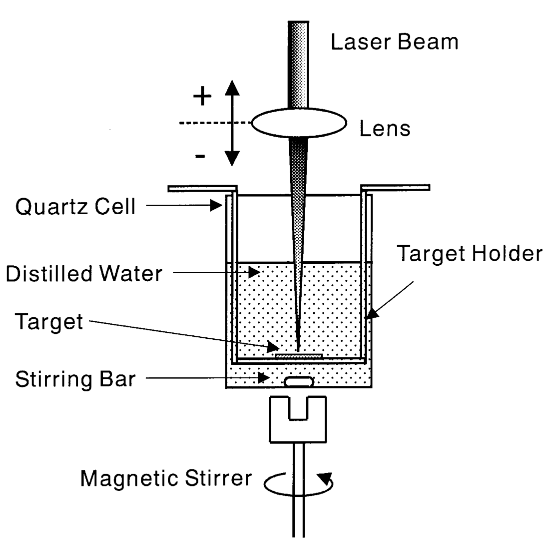

Fig. 1. Experimental setup for laser ablation of metals in water.

3. Results and discussion

3.1. Ablation of silver

Fig. 2a shows typical absorption spectra of colloidal solutions prepared by ablating an Ag target in water with nonfocused laser light. The spot size and fluence of laser light were 3 mm and 0.9 J/cm^2, respectively, and the ablation was carried out for 10 min. The solutions were not stirred. The spectrum showed characteristic features of Ag colloidal solutions [10,11]. The prominent band observed at 405 nm was assigned to the plasmon transitions of Ag particles. The observation of the plasmon band indicates that nanoparticles of silver were prepared in water. The band in the UV region was assigned to the interband transitions of Ag particles. The ablation efficiency was evaluated from the absorbance of the interband absorption at 250 nm because the plasmon band was greatly affected by the size and shape of the Ag

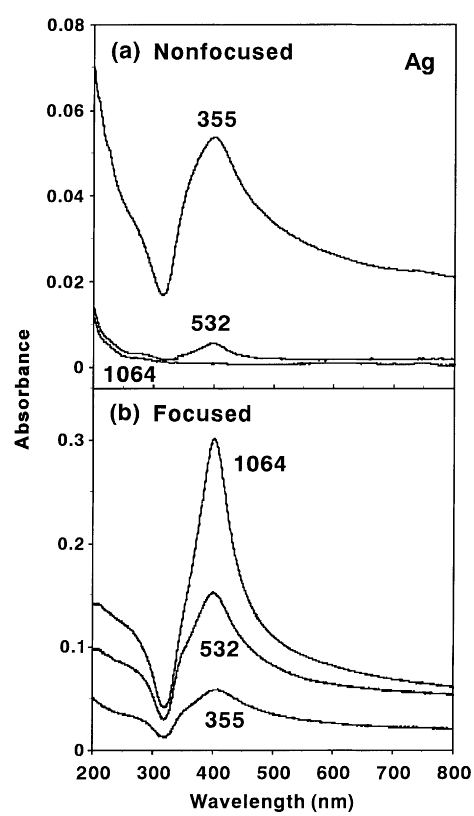

Fig. 2. Absorption spectra of Ag colloidal solution prepared with various wavelength laser lights. Exposure time: 10 min. (a) Laser beam was not focused. Laser fluence: 900 mJ/cm^2. (b) Laser beam was focused. Laser fluence: >12 J/cm^2.

particles [6]. It is clear from Fig. 2a that the ablation efficiency significantly depended on the laser wavelength. The ablation efficiency was decreased as the laser wavelength increased. Irradiation at 1064 nm caused no effective colloid formation at this fluence. The dependence of the ablation efficiency on the laser wavelength was identical with that observed in the gas system [9].

Fig. 2b shows the absorption spectra of colloidal solutions prepared with focused laser light. Focusing was optimized by maximize the ablation efficiency (see the following section). The spot size and the laser power without a focusing lens were 5 mm and 4 mJ/pulse, respectively. Since the spot size at the focal point was estimated to be less than 0.2 mm by SEM observations, the fluence on the target was estimated to be more than 12 J/cm^2. It should be noted that the dependence of the ablation efficiency on the laser wavelength was opposite between Figs. 2a and b. The fact that the ablation efficiency increased as the laser wavelength increased under focused conditions will be discussed in the following sections.

Fig. 2b also showed that the shape of the plasmon band depended on the laser wavelength. Compared with the spectrum obtained with 1064 nm laser light, the plasmon bands obtained with 355 and 532 nm laser light are more broadened in the red spectral region, and the relative intensities of the plasmon bands to the interband bands are reduced. The difference in the shape of the plasmon bands suggested the change in particle size under different laser wavelengths.

3.2. Ablation of copper

Figs. 3a and b show the absorption spectra of colloidal solutions obtained by ablating Cu targets under nonfocused and focused conditions at 355, 532 and 1064 nm. The ablation conditions were the same as those for Ag. The band due to the plasmon transition of Cu particles was observed at 600 nm in the spectrum obtained by ablation at 1064 nm in Fig. 3b. However, the plasmon band was less prominent in the other spectra in Fig. 3b, and disappeared in Fig. 3a. The spectral features of these colloidal solutions are similar to those of solutions containing CuO particles [3,12,13]. Cotton and coworkers [3] suggested that surface of Cu particles produced by laser ablation was rapidly oxidized or hydroxidized by water because of high reactivity of copper. Thus, the band at 220 nm observed here was assigned to the interband transitions of Cu and CuO.

The ablation efficiency of Cu also depended on the laser wavelength. In the case of the nonfocused laser light, ablation efficiency increased in the order of 532 nm > 355 nm > 1064 nm, although the order of 355 and 532 nm was opposite to that observed in the ablation of Ag. In the case of the focused laser light, the ablation efficiency at longer wavelengths was higher than that at shorter wavelengths, being agreement with the results of Ag.

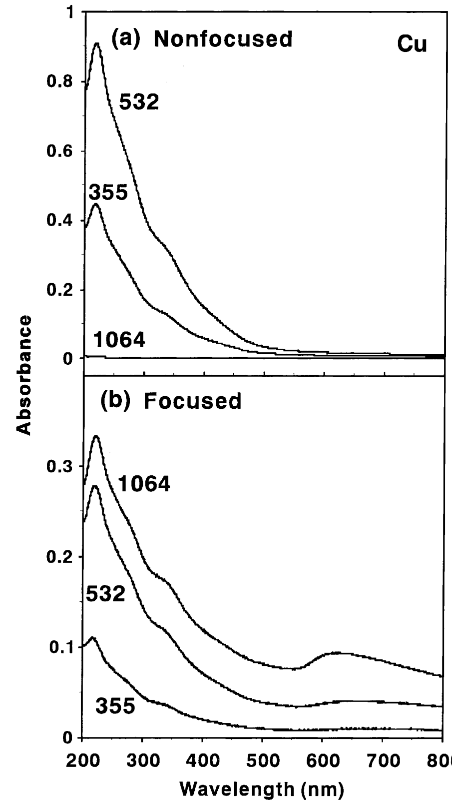

Fig. 3. Absorption spectra of Cu colloidal solution prepared with various wavelength laser lights: (a) laser beam was not focused; (b) laser beam was focused. Ablation conditions were identical with those shown in Fig. 2.

3.3. Effects of the focusing conditions on the ablation efficiency

The most remarkable feature among the results of the laser ablation of Ag and Cu in water is the relation between the ablation efficiency and the wavelength of the focused laser light. The ablation efficiency was higher at longer wavelengths than that at shorter wavelengths. In order to elucidate these phenomena, we have investigated the relation between the ablation efficiency and the focusing conditions at each ablation wavelength. Figs. 4a and b show the intensities of the interband transitions of colloidal solutions of Ag and Cu as a function of the relative position of the target to the focal point. The position of the focal point was defined as the position where the maximum ablation efficiency was observed for each laser wavelength. At the focal point, the highest and the lowest ablation efficiencies were obtained with 1064 and 355 nm, respectively, being consistent with the results shown in Figs. 2b and 3b. The ablation efficiencies at all laser wavelengths decreased with increase in the distance between target and focal point. The ablation efficiencies at longer wavelengths decreased more rapidly than those at shorter wavelengths. Thus, the ablation efficiency at longer wavelengths became lower than that at shorter wavelengths as the focusing of laser light was weakened.

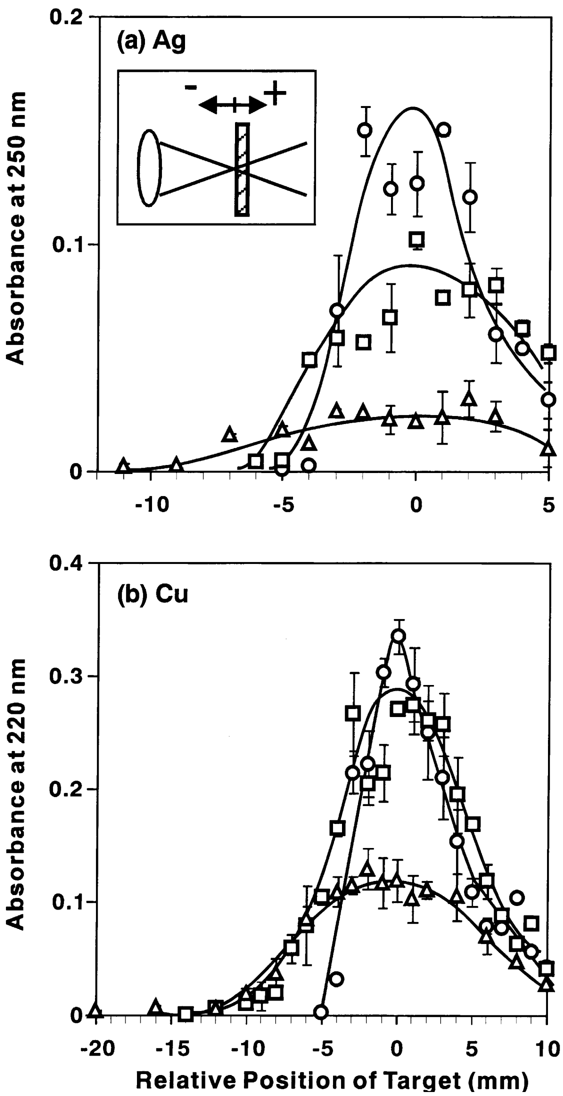

Fig. 4. Absorbance at the interband transitions of colloidal solution of (a) Ag and (b) Cu, as a function of the relative position of the targets to the focus. The relative position was changed by moving the focal lens. Laser wavelengths were: (○) 1064 nm; (□) 532 nm; (△) 355 nm. The sign of the relative position was defined in the insertion.

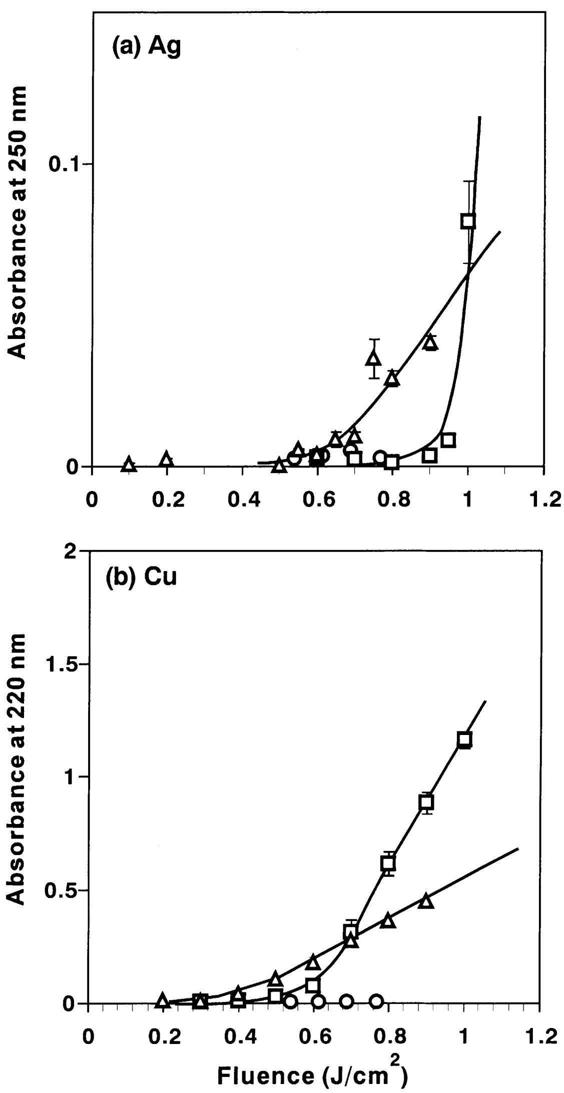

Fig. 5. Absorbance of the interband bands of colloidal solution of (a) Ag and (b) Cu, as a function of the fluence of laser beams. Laser wavelengths were: (○) 1064 nm; (□) 532 nm; (△) 355 nm.

The change in the ablation efficiency depends on the laser fluence. Because both the spot size and the fluence of the laser light varied with focusing in the above experiments, experiments with constant spot size must be performed to estimate the relation between the fluence and ablation efficiency. Thus, we have investigated the influence of the laser fluence on the ablation efficiencies at each wavelength with nonfocused laser light because the fluence of the focused laser light could not be accurately determined. As shown by Mafuné et al. [6], increase in the spot area only caused a linear increase in the ablation efficiency. Figs. 5a and b show the absorbance of the interband transitions of Ag and Cu colloidal solutions as a function of the laser fluence. The maximum fluence was limited to 1 J/cm^2 under the present experiments. For both Ag and Cu, the threshold of the colloid formation at 355 nm is lower than that at 532 nm. No effective colloid formation was obtained with 1064 nm laser light. The ablation efficiency increased with laser fluence at both 355 and 532 nm. However, the increase rates were quite different between the two cases. The ablation efficiency at 532 nm increased much rapidly than that with 355 nm. Then, the ablation efficiency at 532 nm became higher than that at 355 nm at the fluence above 1 J/cm^2 for Ag and above 0.7 J/cm^2 for Cu. These findings led us to conclude that the relation between the ablation efficiency and laser wavelength is changed from that observed in the gas system at high fluence. In addition, the data in Fig. 5b can explain the ablation efficiency of Cu with the nonfocused laser light (Fig. 3a). It is clear that the laser fluence at which the experiments were performed was above the “cross-point” between the ablation efficiency at 355 nm and that at 532 nm.

3.4. Effects of the self-absorption of the irradiations by colloidal particles

Figs. 4 and 5 indicate that the ablation efficiency at shorter wavelengths is higher at low laser fluence, while the ablation efficiency at longer wavelengths is higher at high laser fluence. It is very important to note that the relation between the ablation efficiencies and laser wavelengths shown by Semerok et al. [9] in the gas system were examined at very high fluence above 100 J/cm^2. Thus, the dependence of the ablation efficiency on the laser wavelength observed in this work still reflects characteristic features in ablations of metals in solutions.

The most characteristic factors in the solution system differing from the gas system are the presence of solvent and colloidal particles. Possible factors that affect the ablation efficiency must be the absorption of laser light by solvent and/or metal particles. Since we have corrected the laser fluence for the absorption of water at each wavelength, the effect of the absorption by solvents can be neglected. Thus, the absorption of the laser light by the metal particles will be an important factor. Unlike in the vacuum and gas systems, the ablation of metals in the solution system results in the formation of metal particles on the path of the incident laser light. These particles can absorb the incident laser light. It is important to note that the efficiency of the self-absorption of laser light depends on absorption spectra of the colloidal solutions. At high fluence, the influence of the self-absorption must be significant because many metal particles are generated. Based on the absorption spectra of the colloidal solutions of Ag and Cu and CuO, the efficiencies of the self-absorption by Ag particles at 355 and 532 nm must be higher than that at 1064 nm due to the plasmon bands around 400 nm (Fig. 2). Thus, the effective fluence of the 355 and 532 nm laser lights on the surface of the targets became lower than that of the 1064 nm laser light. Similarly, the efficiency of the self-absorption by Cu and CuO particles at 355 nm must be higher than those at 532 and 1064 nm (Fig. 3) due to the interband absorption rising from 400 nm. Thus, the laser fluence of the 355 nm laser lights on the surface of the targets became lower than that of the 532 and 1064 nm laser light.

It has been reported that the absorption of laser light by colloidal metal particles caused change in the size of particles [14]. Procházka et al. [4] also showed that particle size was reduced by the self-absorption due to fragmentation. The changes in particle size will affect the spectral features of the colloidal solutions. As shown in Fig. 2b, plasmon band of the Ag colloidal solutions obtained with 355 and 532 nm laser lights was broadened, compared with that obtained with 1064 nm laser light. These results suggested that the self-absorption at 355 and 532 nm have a greater influence on the particle size than that at 1064 nm. We have also observed TEM images of Ag colloids. Unfortunately, colloidal solutions with enough amount of particles to prepare TEM samples could not be obtained at the laser power of

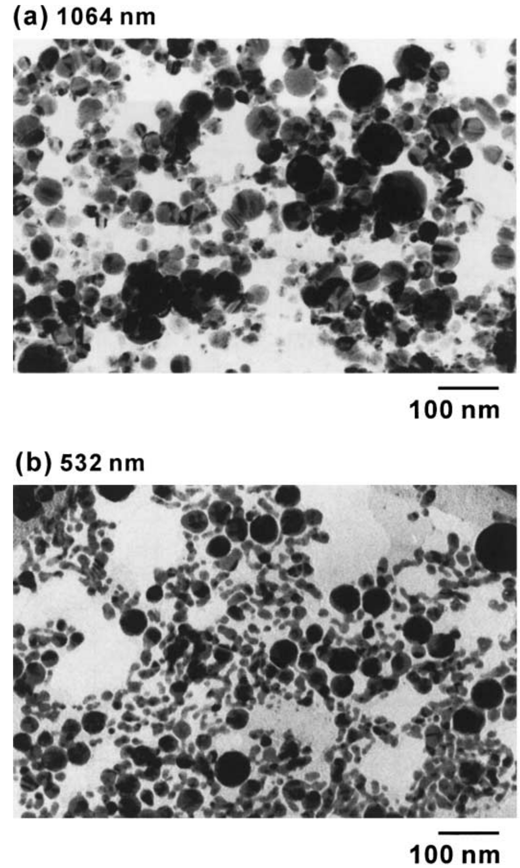

Fig. 6. TEM images of silver colloid particles prepared with (a) 1064 and (b) 532 nm irradiations under the focused conditions. The laser power was 40 mJ/pulse. The average diameters (D_{av}) and the standard deviations (σ) of the particles are: (a) $D_{av} = 31\,nm, \sigma = 11\,nm$ and (b) $D_{av} = 12\,nm, \sigma = 5\,nm$.

4 mJ/pulse (the experimental conditions for Figs. 2b and 3b). Therefore, we had to increase the laser power up to 40 mJ/pulse (>120 J/cm^2). Fig. 6 shows the TEM images of Ag colloids prepared with focused laser light at 532 and 1064 nm. Even at this fluence, it was difficult to prepare enough colloids with the 355 nm irradiation. The size distributions were analyzed by counting 200 particles. The TEM images clearly showed that the size and size distribution of particles depended on the laser wavelength. The average diameter of the particles prepared with 532 nm laser light (12 nm) is smaller than that prepared with 1064 nm laser light (31 nm). The decrease in the particle size must be due to fragmentations of particles caused by the self-absorption of irradiations.

3.5. The relation between the colloid concentration and the self-absorption

The above discussion indicated that the self-absorption of laser light by colloidal particles had a great influence on the ablation efficiency in the solution system. There are two possible processes for the self-absorption. One process is "inter-pulse" self-absorption, in which particles produced by the earlier pulses stay in the laser light path and absorb the latterly coming pulses. The other is "intra-pulse" self-absorption, in which particles produced by the earlier part of one pulse immediately absorb the photons of the later part of the same pulse. The latter process must be taken into account when the nanosecond laser pulses are used for the ablation of metals because the ejection of the ablated matter begins in picoseconds scale [9].

The relative contribution of the inter-pulse and intra-pulse self-absorptions to the ablation efficiency has been determined from the fact that the efficiency of the inter-pulse self-absorption will increase with the accumulation of the particles, while that of the intra-pulse self-absorption will be constant. Fig. 7a shows absorbance of the Ag colloidal solution at 250 nm as a function of the number of laser shots. It is clear from the slope of the evolution curves that the increasing rate of the particle abundance gradually decreased with the number of laser shots at all wavelengths. The decrease in the ablation rate must be due to an increase in the inter-pulse self-absorption. It should be noted that the particle abundance obtained by shorter wavelength laser light was lower than that obtained by longer wavelength laser light in the entire laser shots. This finding indicated that the effect of the self-absorption on the shorter wavelength laser light was brought by a very low concentration of colloidal particles. A possible explanation for such efficient absorption is due to the localized particles in the vicinity of the surface of the target. It may be possible that the concentration of the particles at the ablation spot may be higher than that estimated by absorbance of the colloidal solution. To reduce such a "micro-concentration" effect, solutions were stirred during ablation. Fig. 7b shows that the ablation efficiencies decreased by stirring the solutions. The decrease in the ablation efficiency by stirring solutions was also reported by Procházka et al. [4] and explained in terms of the increased effect of the inter-pulse self-absorption by stirring solutions because the particles spread over the entire laser light path. Furthermore, the ablation efficiency at shorter wavelengths is still lower than that at longer wavelengths even in the very low particle concentration. In the case of the stirred solution, the efficiency of the inter-pulse self-absorption can be estimated from the absorbance of colloidal solutions at wavelengths of the laser light, if we assume that particles are almost completely diffused by stirring. Fig. 7c shows the absorbance at the wavelengths of the laser light for Ag colloidal solutions as a function of the laser shots. The absorbance of the solution at 355 nm obtained with 355 nm laser light was lower than that at 532 nm obtained with 532 nm laser light in the entire shots. This finding indicated that the efficiency of the inter-pulse self-absorption should be lower for 355 nm laser light than that for 532 nm laser light, which is inconsistent with ablation efficiencies observed. Thus, the influence of the intra-pulse self-absorption should be taken into account to explain the efficient absorption of the shorter wavelength laser light. Because the intra-pulse self-absorption will occur in definite area and will not be concerned with the entire concentration of the solutions, the absorption of shorter wavelength laser light can occur even at a very low entire concentration. To confirm these assumptions, we are planning to do further

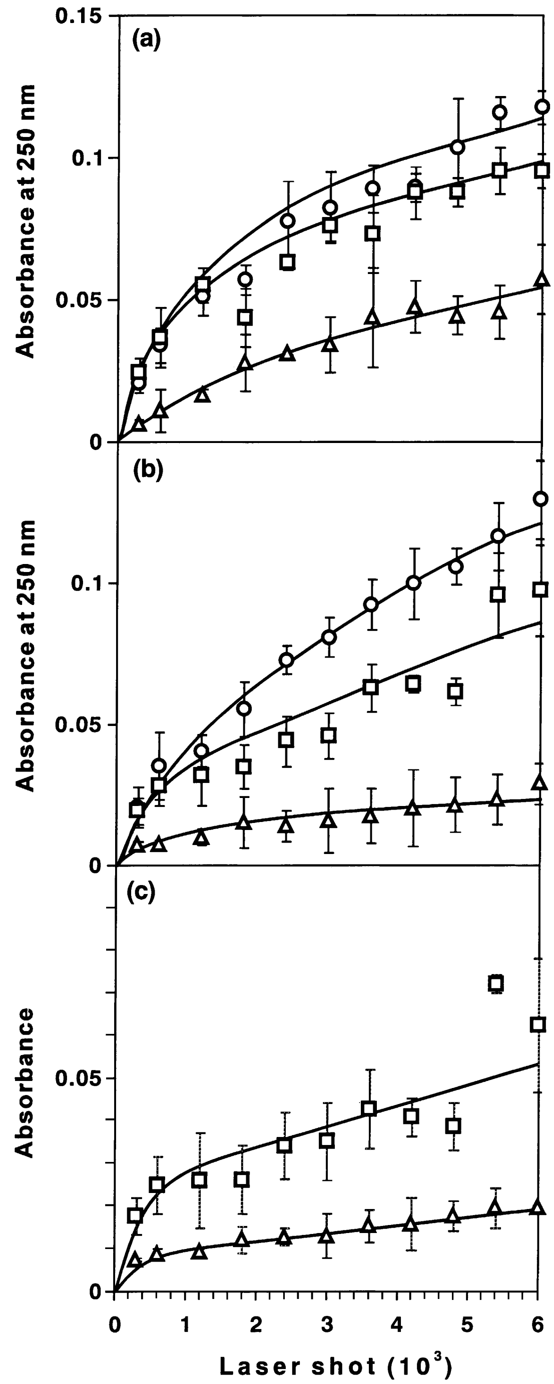

Fig. 7. Absorbance of Ag colloidal solution as a function of the laser shot. The laser lights were focused. (a) Absorbance at 250 nm of solutions prepared with 1064 nm (○), 532 nm (□), and 355 nm (△) laser light. (b) Same as (a), except solutions were stirred during ablation. (c) Absorbance at 532 nm of colloidal solutions prepared with 532 nm laser light (□), and absorbance at 355 nm colloidal solutions prepared with 355 nm laser light (△).

detailed experiments using femtosecond laser pulse in a flow-cell system.

4. Conclusions

Colloid preparation by the laser ablation was investigated on Ag and Cu targets using different wavelength laser light. The ablation efficiency depended on the laser wavelength. The relation between the ablation efficiencies and the laser wavelength varied with the fluence of the laser light. It was suggested that the self-absorption of the shorter wavelength laser light by colloidal particles efficiently occur at high laser fluence. It was proposed that the self-absorption occurred by intra-pulse process as well as inter-pulse process.

Acknowledgements

The authors gratefully acknowledge Dr. K. Sugioka, Riken, and Dr. Y. Tsuboi, Kyoto Institute of Technology, for useful discussions. This work was supported by a Grant-in-Aid for Science Research (No. 12740382) from Ministry of Education, Science, Sports, and Culture, Japan.

References

[1] A. Fojtik, A. Henglein, Ber. Busenges Phys. Chem. 97 (1993) 252.
[2] A. Henglein, J. Phys. Chem. 97 (1993) 5457.
[3] J. Heddersen, G. Chumanov, T.M. Cotton, Appl. Spectrosc. 47 (1993) 1959.
[4] M. Procházka, P. Mojzeš, J. Štepánek, B. Clcková, P.-Y. Turpin, Anal. Chem. 69 (1997) 5103.
[5] I. Srnová, M. Procházka, B. Clcková, J. Štepánek, P. Malý, Langmuir 14 (1998) 4666.
[6] F. Mafuné, J. Kohno, Y. Takeda, T. Kondow, H. Sawabe, J. Phys. Chem. B 104 (2000) 9111.
[7] J.S. Jeon, C. Yeh, J. Chin. Chem. Soc. 45 (1998) 721.
[8] T. Tsuji, K. Iryo, H. Ohta, Y. Nishimura, Jpn. J. Appl. Phys. Part 2 39 (2000) 981.
[9] A. Semerok, C. Chaleard, V. Detalle, J.-L. Lacour, P. Mauchien, P. Meynadier, C. Nouvellon, B. Salle, P. Palianov, M. Perdirix, G. Petite, Appl. Surf. Sci. 138 (1999) 311.
[10] M. Kerker, J. Colloid Interf. Sci. 105 (1985) 297.
[11] J.A. Creighton, D.G. Eadon, J. Chem. Soc., Faraday Trans. 87 (1991) 3881.
[12] Y.H. Yeh, M.S. Yeh, Y.P. Lee, C.S. Yeh, Chem. Lett. 1998 (1998) 1183.
[13] M.S. Yeh, Y.S. Yang, Y.P. Lee, H.F. Lee, Y.H. Yeh, C.S. Yeh, J. Phys. Chem. 103 (1999) 6851.
[14] S. Link, M.B. Mohamed, B. Nikoobakht, M.A. El-Sayed, J. Phys. Chem. 103 (1999) 1165.