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Highly efficient formation of metal and metal alloy particles from methyl metal compounds by a single pulse laser irradiation

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Highly efficient processes for fine particle formation of metal alloys and metal oxides were developed using a high-power laser. In these processes, laser light was used only for the ignition of a thermal chain reaction. This reaction was suppressed by adding inert gases, and the suppression effect was in the order $C_3H_8 > C_2H_6 > CH_4 >$ He > Ar > Xe. Oxygen accelerated the reaction because of the large exothermicity of the reaction of oxygen with methyl metal compounds.

Keywords: Excimer laser, organometallic compounds, fine particles, metal particles, metal alloy particles, metal oxide particles, ignition, explosive reaction

1 INTRODUCTION

Formation of fine particles by the chemical vapor deposition (CVD) method has been studied extensively. In this process, laser light (as well as plasma, thermal energy and so on) is used for the decomposition of reactant materials. Laser-assisted CVD[1] has also been applied to the production of ceramic particles such as SiC,[2-4] Si_3N_4,[2,5,6] TiO_2,[7,8] and other particles such as silicon,[2,9] iron,[10] and boron.[11] In these processes, one laser photon is usually consumed for the decomposition of one reactant molecule, so that energy efficiency is below unity. We have found a highly efficient process for the formation of fine metal particles, in which laser light is used only for the ignition of an exothermic chain reaction. This unique process is called a 'Laser Ignited Mild Explosive Reaction' (LIMER).[12-14]

The outline of the LIMER process is briefly summarized as follows. Active species such as excited metal atoms and hot methyl radicals are produced in high density by high-power laser irradiation from an organometallic compound, which has a large molar extinction coefficient at the laser irradiation wavelength and a small bond dissociation energy. If the decomposition reaction is exothermic, an explosive thermal chain reaction is initiated by these active species, and finally, fine metal particles are produced in the gas phase and on the wall of the reaction apparatus. Accordingly, quantum efficiency, defined as the number of decomposed molecules to the input laser photons, is very high, for example above 10^5 in the case of 25 Torr of reactant in a volume of 10 liter irradiated with 100 mJ of an ArF excimer laser. Table 1 shows thermochemical data for some alkyl metal compounds and methyl iodide. In this table, D_n is an average bond dissociation energy to form a metal atom and methyl radicals, and ΔH is the enthalpy change with the reaction shown in Eqn [1].

$$M(CH_3)_n \rightarrow M + (n/2)C_2H_6 \qquad [1]$$

Among these compounds, TMB and TML, whose decomposition is exothermic, were found to cause the LIMER. In the decomposition of TML, *ca* 90% of TML was converted into metal particles and gaseous products (84% was ethane and the other part was composed of methane, ethylene and propane), so that the reaction was confirmed to proceed primarily according to Eqn [1].

Table 1 Thermochemical data for some alkylmetal compounds and methyl iodide

Compound	Abbreviation	D_n kJ mol^{-1}	ΔH kJ mol^{-1}
$Bi(CH_3)_3$	TMB	428	−124
$Pb(CH_3)_4$	TML	632	−104
$Sn(CH_3)_4$	TMT	896	160
$Ge(CH_3)_4$	TMG	1040	304
$Si(CH_3)_4$	TMS	1276	540
CH_3I	MI	236	52

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Though there are only a few organometallic compounds which cause an explosive reaction, their energy release can be utilized for the decomposition of other molecules contained in the same reaction cell. In this paper, we would like to describe the uniform metal alloy formation processes in which mixtures of more than two kinds of organometallic compounds and/or other organic compounds are irradiated with a laser to cause the LIMER. We shall also describe two types of effect of added gas on the LIMER; one is a suppression effect by inert gases such as rare gases or saturated alkanes, and the other is an acceleration effect by reactive gases such as oxygen. In the latter case, metal oxide particles are efficiently produced.

2 EXPERIMENTAL

Tetramethyl-lead (TML, stated metal purity 99.99%) and trimethylbismuth (TMB, stated metal purity 99.99%) were purchased from TRI Chemical Laboratory Inc., tetramethyltin (TMT, >99.9 %) and methyl iodide (MI, 99.5 %) were from Aldrich, and tetramethylgermanium (TMG, >98 %) was purchased from Tokyo Kasei Kogyo Co. The organometallic compounds were purified by trap-to-trap distillation under vacuum and were degassed by at least two freeze–pump–thaw cycles just before they were transferred to the reaction cell. Rare gases (helium, argon and xenon) were purchased from Nippon Sanso and methane, ethane and propane were from Takachiho Chemical Co. Ltd. These compounds were used without further purification.

An excimer laser (Lumonics, HE-460, 10 ns pulse duration, and 10–400 mJ pulse^{-1}) was used for the irradiation of organometallic compounds at both 193 nm and 248 nm. After measuring the samples into the reaction cell, laser light was introduced through a Suprasil quartz window. Just after laser irradiation, fine metal and/or metal alloy particles were formed on the wall of the reaction cell and in the gas phase. The particles were collected and analyzed with a scanning electron microscope (SEM, Hitachi S-800), an electron probe microanalyzer (EPMA, Shimazu EPM-810) and an X-ray diffractometer (XRD, Rigaku RAD-2B). Emission spectra were measured with a multichannel analyzer. Details of the detection systems were reported elsewhere.[14]

3 RESULTS AND DISCUSSION

3.1 Metal alloy formation by the LIMER process

When a mixture of TML and TMB was irradiated with an ArF excimer laser, the LIMER was observed, accompanied by an orange light emission. From EPMA analyses of the product particles, the shape images of lead and bismuth were the same and the composition of the particles reflected the relative concentration of TML and TMB in the gas phase. Therefore, uniform lead and bismuth alloy particles of desired composition could be produced.

On the other hand, decomposition of TMT and TMG is endothermic, so these compounds do not cause the LIMER by themselves. However, even for such molecules an explosive decomposition is possible by using the energy release of added organometallic compounds, the decomposition of which is exothermic. Accordingly, formation of uniform metal alloy particles could be expected, provided that the reaction as shown in Eqn [2] is exothermic as a total. The reaction shown in Eqn [2] was confirmed to proceed as a main process.

$$M^1(CH_3)_n + M^2(CH_3)_m \rightarrow M^1\text{—}M^2 + (n+m)/2C_2H_6 \quad [2]$$

When a mixture of 5 Torr of TMT and 20 Torr of TML was irradiated with laser light, the LIMER could be actually observed because the total enthalpy change was negative at this ratio. The LIMER could take place within the concentration range of TMT up to *ca* 40 %, where the enthalpy change turns positive. TMG and TMS could also be decomposed by mixing with TML. The threshold concentrations of these compounds when mixed with TML for the LIMER to occur were different for each compound because of the difference in the ΔH values of these compounds, and because of the occurrence of other types of decomposition process, e.g. SiC formation, which is more exothermic than formation of silicon. Product analysis of particles by XRD showed that a trace of a silicon peak was observed when mixtures of TML and TMS were irradiated.

Figure 1 shows the emission spectra obtained by the KrF laser irradiation of a mixture of TML and TMT. It is clear from this spectrum that excited atoms of both lead and tin are produced.

In the XRD pattern of metal particles produced shown in Fig. 2, both lead and tin patterns were observed. EPMA analyses indicated that these particles were of uniform composition. It was also confirmed that the melting point measured on these particles was the eutectic point of lead and tin alloy, i.e. 183 °C.

In the CVD processes amorphous particles are generally obtained, whilst all of the particles obtained by the LIMER were in the crystalline form because of the exothermicity corresponding to *ca* 4000 °C.[14] The shapes and the sizes of the alloy particles were different for different metal ratios, probably because of the different melting points of the alloy.

3.2 Suppression effect on the LIMER of various foreign gases

When inert gases were added to TML, the LIMER was inhibited because of removal of the excess energy by collisions. On increasing the amount of foreign gas added, the active species were effectively quenched, and finally the LIMER could not take place at some threshold pressure of foreign gas. As shown in Fig. 3, this threshold pressure increased drastically with an increase in the laser flux i.e. with an increase in active species which were effectively produced, and it reached to a limiting pressure, e.g. 80 Torr for helium gas. Two types of foreign gases were tested. In the case of rare gases, the order of quenching eficiency was He > Ar > Xe, whilst the order $C_3H_8 > C_2H_6 > CH_4$ was observed for saturated hydrocarbons. Since rare gases are monoatomic, this ordering could be interpreted by elastic collision. The energetically active species collide elastically with rare gas atoms with the conservation of the translational energy. Therefore smaller rare gas atoms such as helium can effectively remove the excess energies which active species have. Hydrocarbon molecules have several vibrational degrees of freedom, so that the excess energy of active species colliding with these molecules can be transferred into the internal energy. As a result, the quenching efficiency

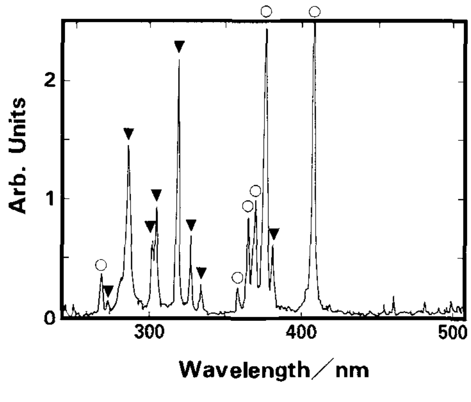

Figure 1 Emission spectra obtained by KrF excimer laser irradiation of the mixture of 25 Torr of TML and 4.5 Torr of TMT. Emission was detected at 2 mm from the irradiation surface. The bands with open circles (○) are assigned to the emission from excited lead atoms and those with solid triangles (▼) are assigned to emission from tin atoms.

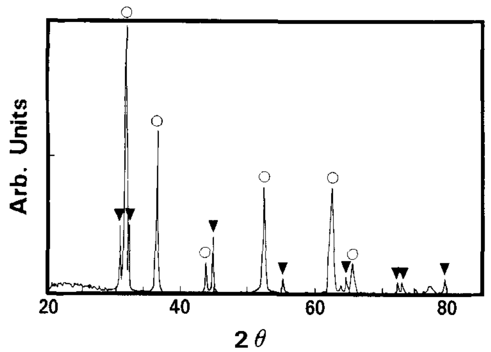

Figure 2 X-ray diffraction (XRD) pattern of lead–tin alloy particles obtained from the mixture of 20 Torr of TML and 5 Torr of TMT by the LIMER. Peaks with open circles are assigned to lead and those with solid triangles to tin.

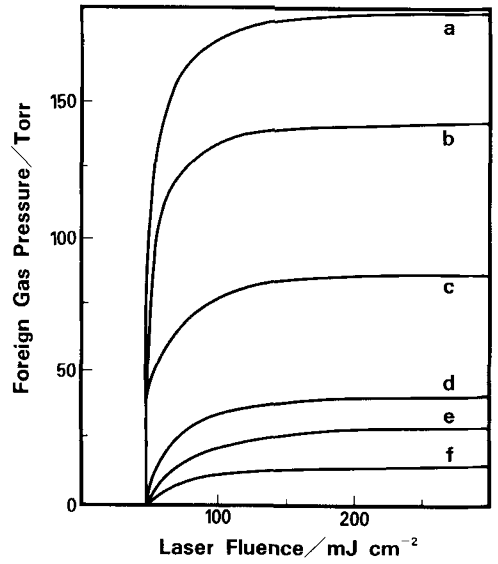

Figure 3 Suppression effect of foreign gases on the LIMER: (a) Xenon; (b) argon; (c) helium; (d) methane; (e) ethane; (f) propane. Each foreign gas was added to 25 Torr of TML and the samples were irradiated by a KrF excimer laser.

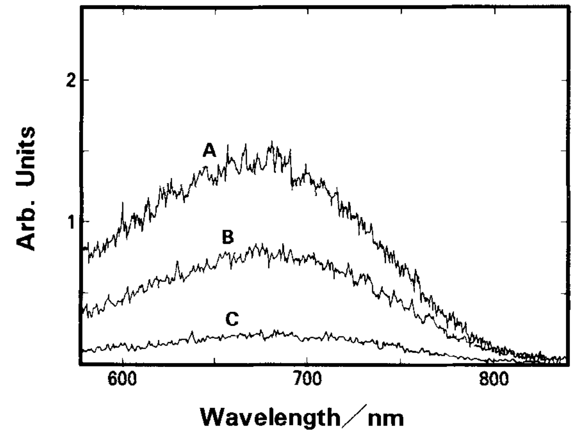

Figure 4 Suppression effect of foreign gases on the emission of black body radiation: (A) TML, 25 Torr; (B) TML, 25 Torr, and methane, 10.5 Torr; (C) TML, 25 Torr, and propane, 11 Torr.

of hydrocarbon molecules increases as the number of vibrational modes of the molecule increases.

The quenching effect was also confirmed in the emission spectra of black body radiation observed during the LIMER.[14] The emission intensity and the peak position correspond to the amount and the temperature of energetic materials. It is clearly shown in Fig. 4 that the emission intensity decreases and the peak of the spectrum shifts slightly to a longer wavelength on addition of the more effectively quenching molecules.

3.3 Acceleration effect on the LIMER with reactive foreign gases

When reactive molecules such as oxygen are added to TML, the LIMER is accelerated. This effect may be due to two energetically favorable processes. One is the reaction of oxygen with metal atoms to form metal oxides, because the standard enthalpy of formation of a metal oxide is generally negative. Figure 5 shows the XRD pattern of products from the mixture of TML and air. Bands of lead oxide were observed as well as peaks of lead. The intensity of lead oxide relative to lead increased with the increase in oxygen content.

The other process is the reaction of oxygen with a hydrocarbon. For example, the heats of combustion of ethane and TMT are 372.8 kcal mol^{-1} (1560 kJ mol^{-1}) and 934 kcal mol^{-1} (3908 kJ mol^{-1}), respectively.[15] Therefore, in the case of complete oxidation, large exothermic energies can be expected to be obtained according to Eqns [3], [4] and [5].

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O \qquad [3]$$

$$Sn(CH_3)_4 + 7O_2 \rightarrow Sn + 4CO_2 + 6H_2O \qquad [4]$$

$$Sn(CH_3)_4 + 8O_2 \rightarrow SnO_2 + 4CO_2 + 6H_2O \qquad [5]$$

Since the energy release for the complete oxidation of an organometallic compound is larger than that for the decomposition of the compound, not only the exothermic organometallics such as TML but also the endothermic ones such as TMT and TMG could cause the LIMER on addition of oxygen. Table 2 summarizes the results of the LIMER on changing the ratio of oxygen to TMT where the TMT pressure was kept constant at 25 Torr. When the ratio was less than 0.3, the LIMER did not take place, presumably because of the quenching effect of oxygen. The LIMER occurred at a ratio above 0.33. The products were different depending on the ratio of oxygen to TMT. The color of the products was black at ratios of 0.33–1.96, brown at 3.09, pale yellow between 3.97 and 8.36, and white at 8.82. Figure 6 shows the XRD pattern of the product particles obtained by experiments 5 and 6 in Table 2. As shown in Fig. 6(b), small peaks of SnO were detected at a ratio of 3.09, whilst no SnO band was observed at 1.96 as shown in Fig. 6(a). It is noteworthy that not metal oxide but metal particles are obtained even if the mixture of oxygen and organometallic compounds is used, which may mean that the oxidation process follows Eqn [4]. Details of the reaction mechanism are presently under investigation by means of analyses of gaseous products and emission spectra.

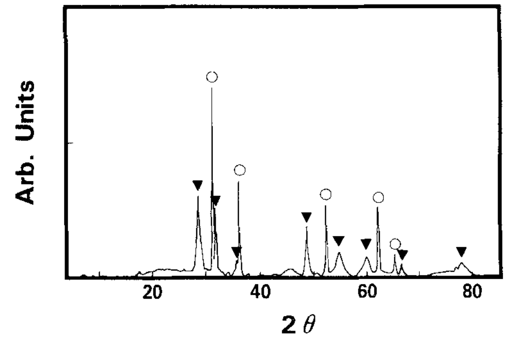

Figure 5 X-ray diffraction (XRD) pattern of lead and lead oxide particles obtained from the mixture of 25 Torr of TML and 204 Torr of air. Peaks with open circles are assigned to lead and those with solid triangles to lead oxide.

Table 2 Products from TMT and oxygen through LIMER

Expt	Oxygen (Torr)	Oxygen/TMT[a]	LIMER[b]	Color of products	XRD
1	4.5	0.18	×	—	—
2	7.3	0.29	×	—	—
3	8.2	0.33	○	Black	—
4	31.6	1.26	○	Black	—
5	48.9	1.96	○	Black	Fig. 6(a)
6	77.3	3.09	○	Brown	Fig. 6(b)
7	99.2	3.97	○	Pale yellow	—
8	164.2	6.57	○	Pale yellow	—
9	209.0	8.36	○	Pale yellow	—
10	220.5	8.82	○	White	—

[a] Pressure of TMT was 25.0 Torr.
[b] ×, failure; ○, success.

4 CONCLUSIONS

We have investigated the fine-particle formation processes of metal alloys and metal oxides. Since this exothermic reaction was initiated by a single pulse laser irradiation, a highly efficient production process was established. By using energy release from exothermic reactions, it is possible to synthesize various kinds of materials. For instance, yellowish lead iodide (PbI_2) particles were obtained from the mixture of TML and methyl iodide. Inert gas molecules inhibited the reaction. On the other hand, when reactive gases such as oxygen were added, more energetically favorable oxidation processes can be expected to take place. Metal and/or metal oxide particle formation processes can be controlled by changing the ratio of oxygen to organometallic compounds.

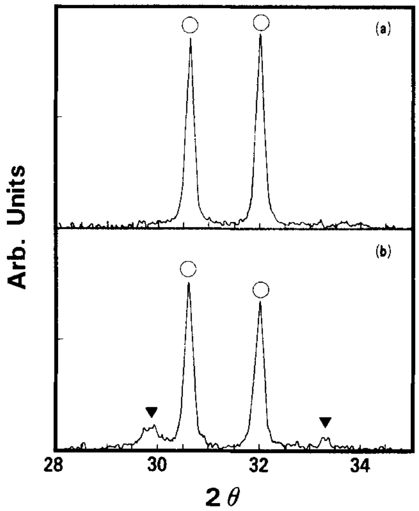

Figure 6 X-ray diffraction (XRD) pattern of tin and tin oxide particles obtained from mixtures of TML and oxygen: (a) TMT, 25 Torr, and oxygen, 48.9 Torr; (b) TMT, 25 Torr, and oxygen, 77.3 Torr. Peaks with open circles are assigned to tin and those with solid triangles to tin oxide.

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