Laser Production of Ultra-Fine Particles†

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Extremely small particles of less than 1 μm in size are generally termed "ultra-fine particles"[1),2)]. Since they possess excellent properties different from those of bulk materials, ultra-fine metallic and ceramic particles attract a good deal of public attention as new promising high-performance materials for magnetic materials, chemical catalyst, sintering promoting materials, sensor, etc.[2)–7)] There are many methods for the production of ultra-fine particles.[5)–8)] The most available means are considered to be evaporation techniques in gas atmosphere using the heating sources such as resistance heater, high frequency induction heater, plasma jet, electron beam, laser beam, arc plasma, etc.[5)] The laser heating-evaporation process has several advantages[8)–12)]: that is to say, (1) this process is clean, (2) it can heat a material up to vaporization temperature within an extremely short time by irradiating a laser with high energy (power) density and afterwards consume the laser energy efficiently in evaporating a material, (3) it can freely choose evaporated parts, (4) the laser energy density or power density on the evaporated parts can be selected in a wide range, (5) the atmosphere and pressure are easily controllable, (6) the collection of ultra-fine powders is easy and efficient because of the formation of directional high-speed vapors from the target, etc. However, there are few papers dealing with the laser process.[11),12)]

Therefore, the authors have attempted to produce ultra-fine particles of metals, oxides and nitrides directly or chemically from various metallic materials by pulsed Nd : YAG laser heating-evaporation process in argon (Ar), helium (He), oxygen (O_2) or nitrogen (N_2) atmosphere, and to reveal the characteristics of their morphology, crystal structure, size distribution, etc.

Materials used were commercially available pure metals of Fe, Ni, Al, Ti, Zr, Cr, Mo, Ta, W, Si, etc., and a pulsed Nd : YAG laser apparatus (Control laser: Model 428, delivering an average power of 200 W at 1.06 μm wave length and 3.6 ms pulse width) and an atmosphere- and pressure-controllable chamber were utilized. The laser with pulse energy (E_1) of 10 to 33 J/p through the quartz glass was irradiated by 130 mm focal-length lens at the defocused distance (f_d) of 0 to 40 mm on each metal sheet of 3 mm thickness (1 mm thickness for Cu and W), whose surface was polished with No. 400 emery paper and cleansed by acetone.

Ultra-fine particles produced were observed and identified by TEM (transmission electron microscopy) using conventional carbon-extraction replicas from the collection glass, which was placed about 10 to 50 mm above the target plate, their shapes were examined, and the particle size and distribution were determined. Moreover, identification of the powders collected by spray method was carried out by using X-ray diffractometer.

First, the production of ultra-fine metal particles was performed in Ar or He atmosphere at 0.1 MPa (1 atm). **Figure 1** (a) and (b) exhibit the TEM photos (at lower and higher magnification, respectively) of particles produced by the laser irradiation under the plume formation condition (E_1 = 33 J/p & f_d = 15 mm) in Ar atmosphere and collected on a glass plate placed about 30 mm above the Fe sheet surface, and Fig. 1 (c) and (d) show the electron diffraction rings of particles and particle size distribution, respectively. Fig. 1 (e) indicates the X-ray diffractometer result of ultra-fine powders collected by spray method.[10)] Based upon the analytical results in Fig. 1 (c) and (e), particles were identified as bcc type α-Fe (a_0 = 2.867Å). These Fe particles are in the projection shape of mainly polygon or globule, as seen in Fig. 1 (a) and partly ox-

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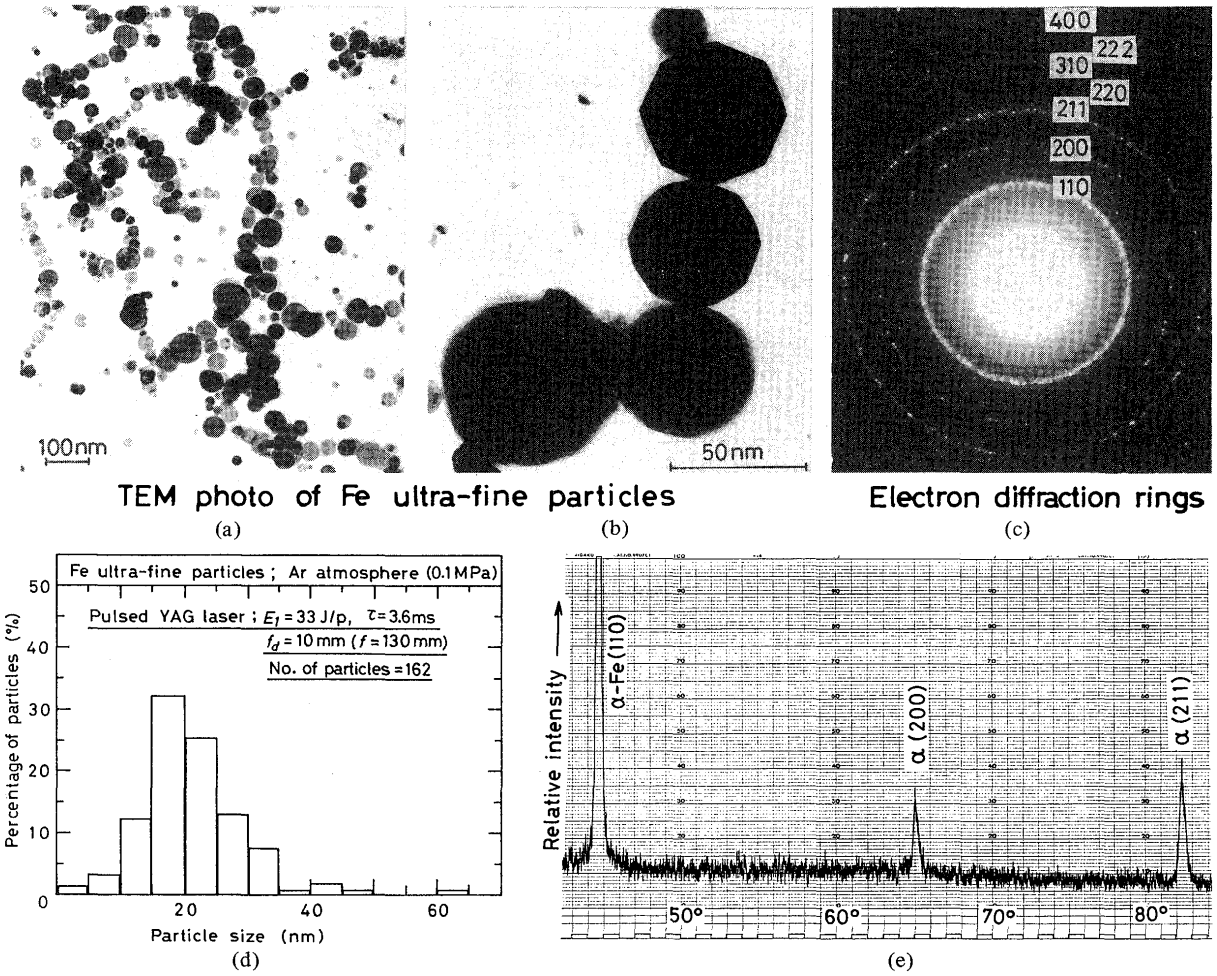

Fig. 1 TEM photos of ultra-fine Fe particles at lower (a) and higher (b) magnifications, electron diffraction rings from particles (c), particle size distribution (d) and X-ray diffractometer result (e).

tagon as shown in Fig. 1(b). Moreover, they had a tendency to be linked together like chains. About 95% of particles were less than 40 nm in size and the average diameter was approximately 20 nm. Such powders were found to be pretty uniform in size. Fe particles made in He atmosphere showed the same physical characteristics as those in Ar; however, the particles in He had a smaller average size of 15 nm and narrower particle size distribution than those in Ar.

The ultra-fine particles made from the other metals were investigated, and consequently it was revealed that respective metallic ultra-fine particles having a median size of 10 to 30 nm and a maximum size of less than 100 nm could be produced by the laser process in Ar or He at 0.1 MPa (1 atm). (See the results summarized in **Table 1**.)

The evaporated weight loss of each metal was measured as an index of production yield of ultra-fine particles. The evaporation and yield of Fe, Ni and Ti particles were larger than those of Cu, Al and Mo as compared at the same conditions of laser power density and metal surface. It was found that the evaporated weight losses per unit time (vaporization rate) of metals by the laser process were extremely large (fast) in comparison with other evaporation techniques in gas.

The procedure for controlling the particle sizes and size distribution was further investigated by changing laser irradiation conditions or chamber atmospheric pressures. The sizes of Fe, Ni and Ti particles decreased slightly as the laser energy or intensity increased at the same pulse width of 3.6 ms. On the other hand, it was confirmed by the TEM observation and the broadening degree of diffraction peak in X-ray diffractometer patterns that the particle sizes of Fe, Ni and Ti powders decreased gradually with a decrease in the pressure. For example, the median and maximum sizes of Fe particles were 17 and 35 nm for 13.3 kPa (100 Torr), 10 and 20 nm for 1.3 kPa (10 Torr), and 5 and 15 nm for 0.1 kPa (1 Torr), respectively. From these results it was found that the decrease in pressure was most beneficial in obtaining much smaller particle size and extremely narrower size distribution.

Since physical and chemical properties of ultra-fine oxide particles are notable, the production of ultra-fine oxide powders was tried by the laser irradiation on metal target sheets in O_2 atmosphere. **Figure 2** (a) to (d) show

Table 1 Summary of physical and crystalline characteristics of ultra-fine particles of metals, oxides and nitrides produced from pure metals by pulsed YAG laser process in Ar, He, O_2 or N_2 atmosphere.

Atmos-* sphere / Material	Ar or He		O_2		N_2	
Fe	α-Fe (bcc) hex.,oxt.,poly. 21(65), 12(55)	Black	γ-Fe_2O_3(T)+ε-Fe_2O_3(M) polygon 32(135)	Brown	α-Fe (bcc) hex.,oxt.,poly. 14(60)	Black
Ni	Ni (fcc) poly.,globule 19(45), 7(35)	Black	NiO (H) hex., cubic 12(40)	Gray	Ni (fcc) hex.,oxt.,poly. 12(45)	Black
Al	Al (fcc) globule 20(50), 30(60)	Gray	γ-Al_2O_3(C)+δ-Al_2O_3(T) globule 25(150)	White	Al(fcc)+AlN(H) glo.,squ.,poly. 40(155)	Gray
Ti	α-Ti (hcp) globule 22(40), 13(35)	Black	A-TiO_2(T)+R-TiO_2(T) globule 21(125)	White	TiN (C) rhombus 18(70)	Black
Zr	α-Zr (hcp) hex., poly. 14(50), 16(45)	Black	ZrO_2(C) + ZrO_2(M) hex., poly. 25(100)	White	ZrN (C) hex., poly 14(40)	Black
Cr	α-Cr (bcc) oct., poly. 8(50), 12(45)	Black	Cr_2O_3 (H) square, hexagon 7(65)	Green	β-Cr_2N (H) squ.,hexa., 7(50)	Black
Mo	Mo (bcc) glo.,poly 12(40), 22(45)	Black	η-MoO_3(-) globule 17(45)	Creamy white (+green)	Mo (bcc) glo.,poly.	Black
Ta	Ta (bcc) hex.,poly.,glo. 13(40)	Black	δ-Ta_2O_5(Pseudo H) globule 15(50)	White	Ta_2N (H) glo., poly. 10(30)	Black
W	β-W(W_3O)(C)	Black	WO_3 (OR)	White (+light brown)	β-W(W_3O)(C)	Black
Si	Si (C)	Ocher	Amorphous(SiO_2) globule	White	Si (C)	Ocher

* Atmospheric pressure = 0.1 MPa (1 atm)
** (T): tetragonal
(M): monoclinic
(H): hexagonal
(C): cubic (NaCl type), (Diamond type)
(OR): orthorhombic
*** hex.:hexagon, oxt.:oxtagon, squ.:square
poly.:polygon, glo.:globule
**** Pulsed YAG laser; E_I=33 J/p, τ=3.6 ms, f_d=10 mm (f=130 mm)

Types of UFP (Lattice structure**) Morphology of UFP*** Median size (Max. size)****	Color of powder

the TEM photo of particles made from Ti by the laser process in O_2, the electron diffraction rings from the particles, particle size distribution and X-ray diffractometer results. According to the result of Fig. 2 (d), particles consisted of mainly Anatase-type TiO_2 oxides and partly Rutile-type TiO_2 oxides. From Fig. 2 (a) and (c), TiO_2 oxide particles, which were spherical in shape, ranged in size from 15 to 125 nm.

The oxide particles produced from the other metals were further studied, and the results are summarized in **Table 1**. Ultra-fine particles of Fe_2O_3, NiO, Al_2O_3, TiO_2, ZrO_2, Cr_2O_3, MoO_3, Ta_2O_5 and WO_3 type oxides were produced from Fe, Ni, Al, Ti, Zr, Cr, Mo, Ta and W sheets, respectively. All Si oxides produced were amorphous. It was found that one or two kinds of oxide particles were formed from metallic sheets by the laser process in O_2 atmosphere. Oxide particles had slightly larger sizes and broader size distribution than metal ones. They showed respectively different characteristic colors of white, gray, brown and green.

Subsequently, a feasibility of the production of ultra-fine nitride particles was studied by irradiating the laser on metal targets in N_2 atmosphere. **Figure 3** shows the results of particles from Ti sheets in N_2. It is apparent

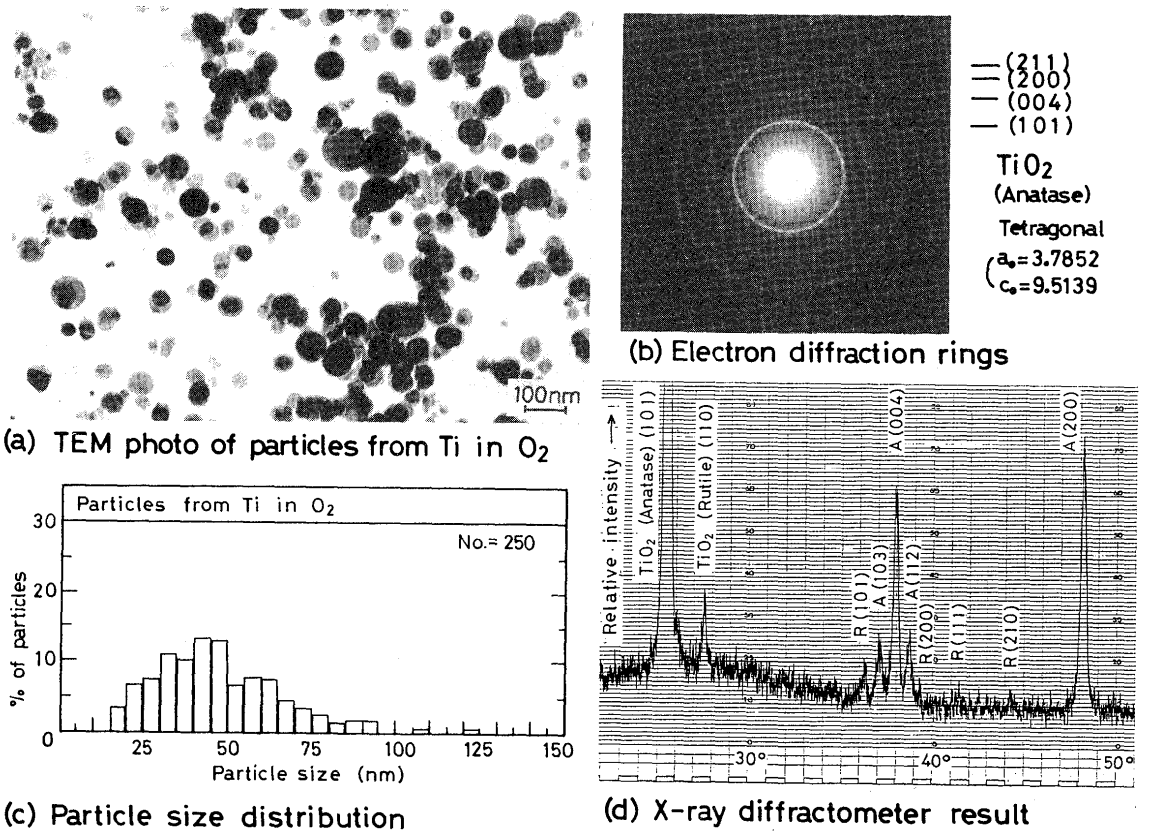

Fig. 2 TEM photo of particles produced from Ti by laser in O_2 (a), electron diffraction rings (b), particle size distribution (c) and X-ray diffractometer result (d), showing formation of ultra-fine TiO_2 oxide particles.

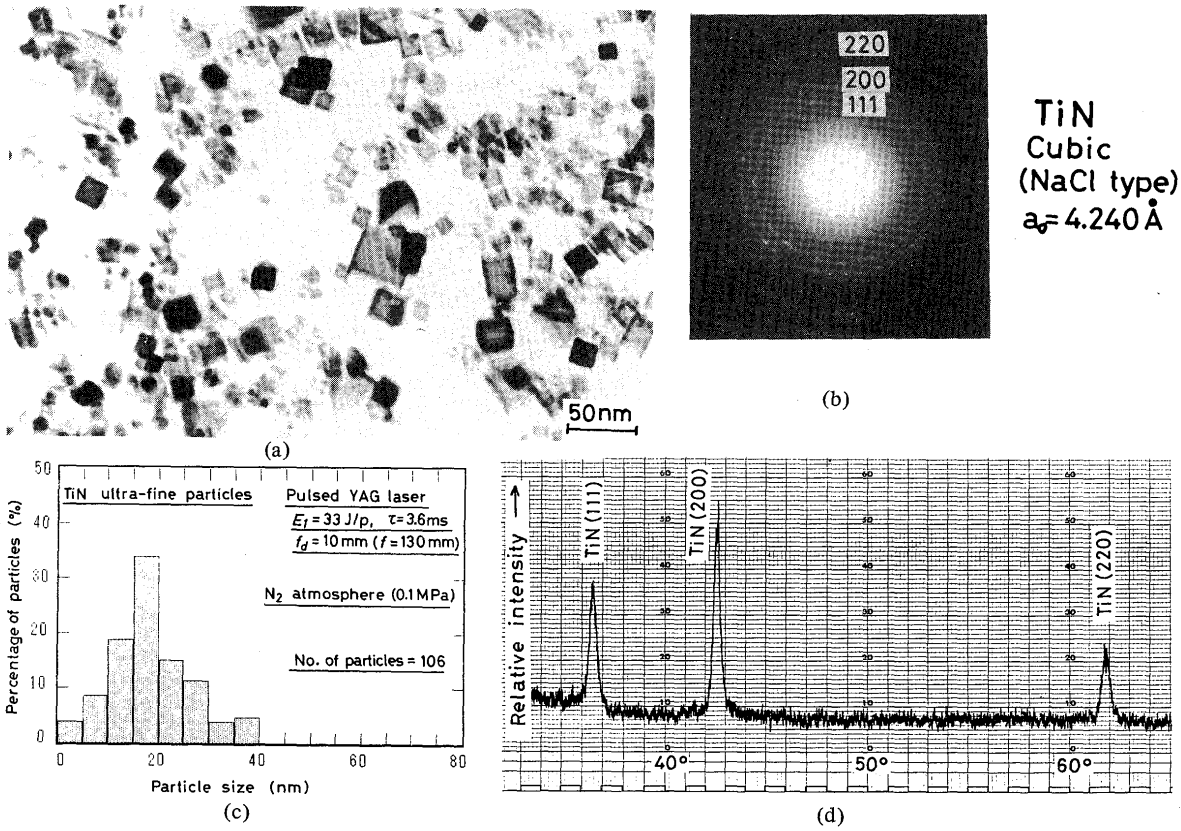

Fig. 3 TEM photo of particles produced from Ti by laser in N_2 (a), electron diffraction rings (b), particle size distribution (c) and X-ray diffractometer result (d), showing the formation of ultra-fine TiN nidtride particles.

from the electron diffraction rings and X-ray diffractometer result that NaCl-type TiN nitride particles were formed. They were cubic or rhombus in shape in the size range of less than 40 nm.

As a summary of particles made in N_2 atmosphere is given in **Table 1**, ultra-fine particles of TiN, ZrN, Cr_2N and Ta_2N type nitrides were made from Ti, Zr, Cr and Ta sheets, and ultra-fine particle mixtures of Al metal and AlN nitride were formed from Al sheet, but from Fe, Ni, Cu, W and Mo their ultra-fine nitride powders could not be produced.

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