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A novel laser-liquid-solid interaction technique for synthesis of silver, nickel and immiscible silver-nickel alloys from liquid precursors

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Silver, nickel, nickel oxide and silver-nickel alloys have been produced from their inexpensive liquid precursors using CO_2 and Nd-YAG lasers. Ethylene glycol, diethylene glycol and 2-ethoxyethanol were used as reductants in the synthesis reactions. Spherical and faceted silver particles of high purity were formed by laser interaction between the precursor solution and a rotating substrate, while porous dual phase nickel and nickel oxide particles were produced when nickel nitrate was used as a precursor. The composition and morphology of the alloy particles was dependent on laser parameters and chemical composition of the precursor solution. The product composition was dependent only upon the chemistry of the precursors used. The mean particle size was dependent upon the temperature generated by irradition and the duration of exposure to the laser beam. The synthesis of nano-particles and metastable alloys is proposed to occur primarily at the laser-liquid-solid interface by a nucleation and growth mechanism.

1. Introduction

Powders of silver, nickel, nickel oxide, gold, cobalt, copper, palladium, platinum and their alloys have important applications in the micro-electronic, catalytic, and automotive industry [1, 2]. Traditional techniques for producing nano-particles include mechanical milling, spray pyrolysis, chemical precipitation and vapor-phase synthesis [3, 4]. Each of these techniques has advantages and disadvantages (Table I). A novel laser-liquid-solid interaction (LLSI) technique developed in our laboratory offers an attractive alternative to conventional methods because the synthesis reaction takes place in a localized area. In addition, particle morphology, size, and production rate can be controlled processing parameters including laser energy and wavelength, liquid precursor composition and concentration, substrate and interaction time [3].

Nanocrystalline particles and alloys can exhibit properties different from those of the same materials made of larger particles, because of size confinement effects and the large volume fraction of interfaces. Another attractive feature of nanocrystalline alloys as compared to conventional powder metallurgical alloys is that chemically different atoms are mixed in the interfaces irrespective of their bulk miscibility. Silver and nickel were systems of interest because both metals are insoluble in the liquid and solid state. The objective of this study was to determine the correlation between silver and nickel particle size and process parameters, and to probe how non-equilibrium conditions at the laser-liquid-solid interface could help the mixing of immiscible metals and suppress the tendency for phase separation.

2. Experimental

The schematic line diagram of the laser-liquid-solid interaction technique is shown in Fig. 1. Sub-micron and nm-sized particles and alloys were synthesized by laser irradiation of a metallic substrate immersed in a solution prepared by dissolving nitrate precursors of silver and nickel in ethylene glycol (99% Alfa Aesar), diethylene glycol (97% Alfa Aesar) and 2-ethoxyethanol (99% Alfa Aesar). Three types of metallic substrates (nickel, copper and niobium) were used for the synthesis of nickel nanoparticles. The objective was to examine the thermal conductivity effect of the substrates on the particles size produced during the LLSI process. The liquid was vigorously mixed to eliminate any concentration gradients in the reactor. The precursor solution was irradiated either by a continuous wave CO_2, ($\lambda = 10640$ nm) or a pulse YAG laser ($\lambda = 1064$ nm) with powers ranging from 150–1100 W, and the interaction time varying from 1–3 minutes. At the conditions used, plasma was observed to form within the liquid solution for both the continuous wave CO_2 and the pulsed YAG lasers. This plasma was not observed at lower powers and no product was yielded under conditions where the plasma did not form. The particles were separated using a centrifuge for 15 minutes, washed with distilled water for another 15 minutes, then dispersed in ethanol bath, and allowed to settle overnight.

TABLE I Advantages and disadvatanges of methods making nanocrystalline particles

Method	Advantages	Disadvantages
Mechanical milling	High production rates	contamination, limited-multicomponents
Thermal E-Beam	Simple system limited reactive	Nonreactive, limited low production rates,
Gas phase Precursor	High production rates, reactive, multicomponent materials produced	Complex system (control of reaction and particle size, in series difficult), precursor choice, no quenching, vacuum unit required
Laser Ablation	reactive, quenching complex mutlicomponent materials produced	low production rates, vacuum unit required
Flame Pyrolysis	same as above	same as above
Laser Pyrolysis	same as above	low production rates, otherwise same as above
Colloidal	high production rates, reactive, multicomponent materials produced	solvent extraction (contamination)

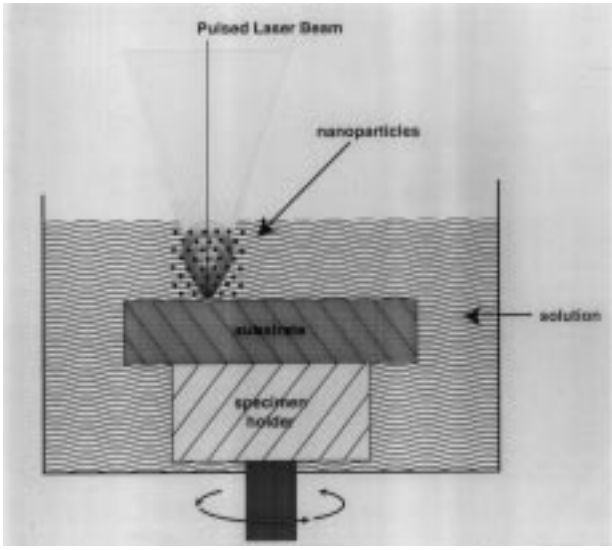


Figure 1 Schematic diagram showing the laser-liquid-solid interaction setup for making nanoparticles and nanotubes.

The shape and size of particles were analyzed using the JEOL JSM-6300F high-resolution scanning electron microscope equipped with a field emission gun. The crystalline phases of particles were determined by powder x-ray diffraction. The particles were supported on holy-carbon copper grids and were studied using a high-resolution transmission electron microscopy (HRTEM). The chemical composition and crystallinity of the phases were identified using energy dispersive spectroscopy and selected area electron diffraction.

3. Results and discussion

Fig. 2 is the SEM micrograph showing the silver nano sized particles produced by the laser-liquid-solid interaction (LLSI) technique. The size of the silver particles was ranging from 50 nn to 0.1 μm. The silver particles size also depends upon the laser processing conditions such as laser energy, and wavelength (Fig. 3). Silver particles size produced by chemical wetness technique (i. e., precipitation process) at room temperature were relatively larger than those obtained by LLSI [3].

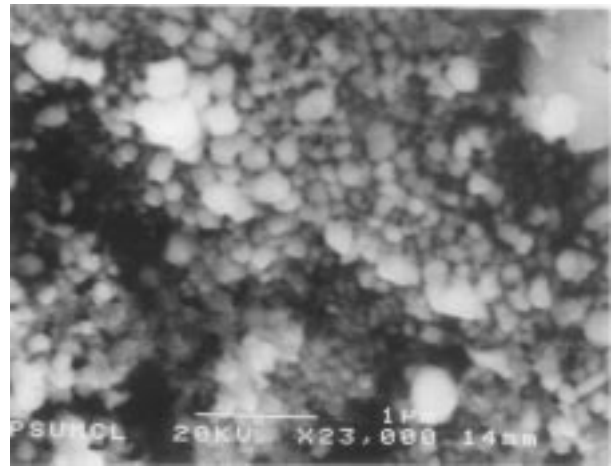


Figure 2 SEM micrograph showing silver nanoparticles produced by LLSI technique.

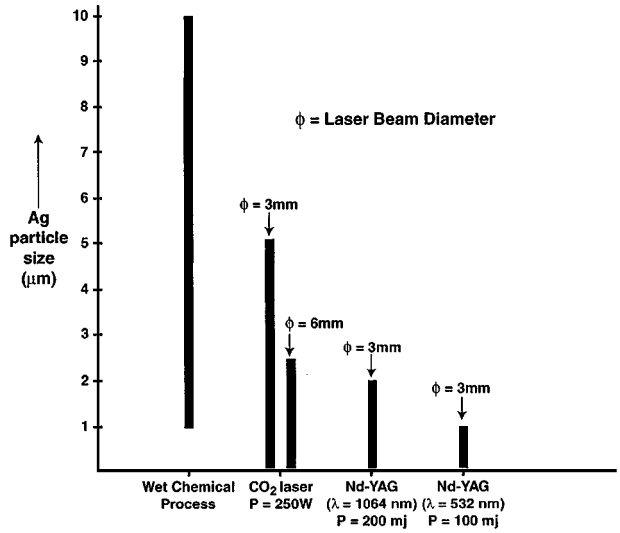
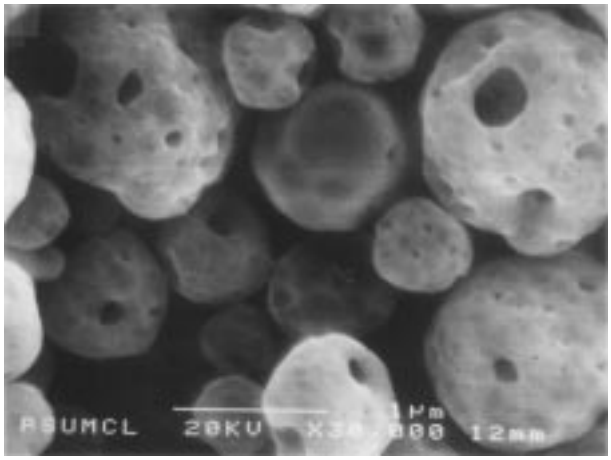


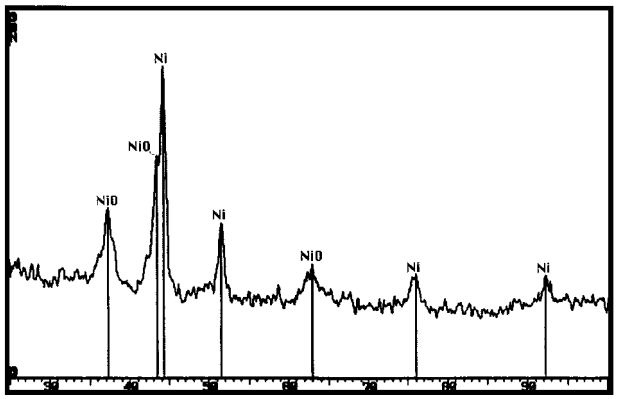
Figure 3 Size distribution of silver particles produced using CW CO_2 and YAG laser.

Large particles size variation in the precipition process was due to non-controllable reaction rate resulting in secondary nucleation and inhomogeneous particle size. Particle size also varied with CO_2 laser parameters like defocusing condition. The particles tended to be finer when the laser was operated in a pulse rather than a continuos mode. Also, silver particle size decreased when the beam was defocused to a larger beam diameter (Fig. 3).

Highly porous dual phase nickel-nickel oxide composite powders were synthesized by LLSI process at laser powder densities of 37.5 kW/cm^2, 50.0 kW/cm^2 and 87.5 kW/cm^2 (Figs 4 and 5). The porous powder morphology could be explained with few assumptions. Burst of clusters is formed during thermal dissociation of the liquid at the laser–liquid-solid interface. These



(a)



(b)

Figure 4 (a) SEM micrograph showing submicron sized porous nickel and nickel oxide composite particles produced by LLSI technique; (b) X-ray of the Fig. 4a showing the presence of Ni and NiO phases in the synthesized product.

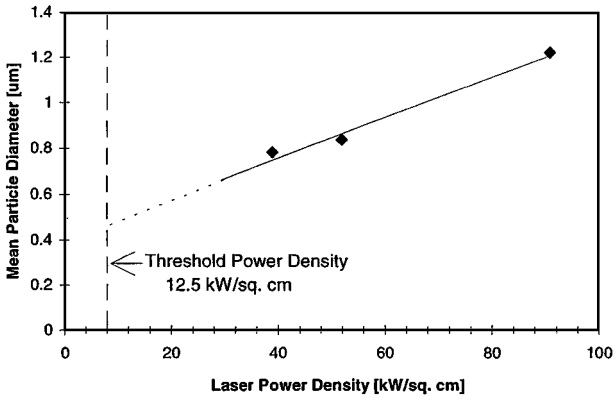


Figure 5 Variation of dual phase nickel-nickel oxide particle diameters with laser power intensity using a copper substrate, 0.6 moles/liter nickel nitrate solution, and irradiation time of 3 minutes.

clusters are diffused together forming initially nanoparticles. Due to sufficient energy available at the interface, these nanoparticles again diffused together forming porous submicron size particles. The dual phase nickel-nickel oxide composite formation could be due to incomplete reduction of the chemical compounds used under these processing conditions. The average composite particles diameter increased as a function of laser power density (Fig. 5). There was a threshold laser power density (12.5 kW/sq. cm), below which particles

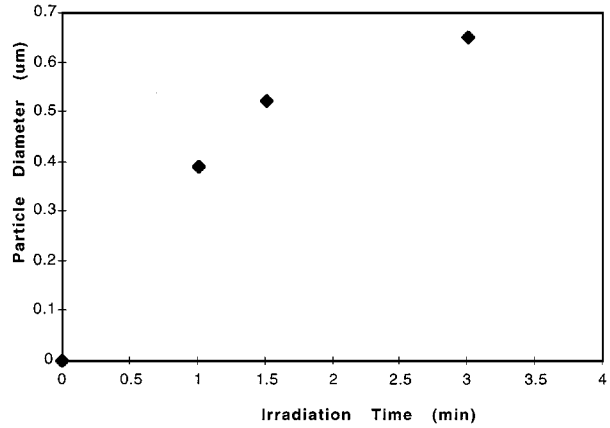


Figure 6 Plot of particle diameter versus total irradiation time for dual-phase powders synthesized from nickel nitrate in 2-ethoxyethanol solution, with laser powder intensity of 50 kW/cm^2 and a copper substrate.

were not synthesized. Laser power densities below this threshold are unable to form the plasma in the liquid solution. Fig. 6 shows a graph of mean nickel-nickel oxide particle diameter as a function of total irradiation time at a laser power intensity of 50 kW/cm^2. Nucleation could occur by diffusion of ions across the boundary layer and particle growth is assisted by elevated solution temperature. Fig. 7 graphically shows the effect of substrate thermal conductivity on mean nickel-nickel oxide particle diameter. The mean particles diameter decreased as the thermal conductivity of the substrates increased. The disc substractes served two purposes. First, the substrate is the source of thermal energy by interacting with the laser beam. Second, the substrate will also dissipate energy of the localized hot spot through conduction. Therefore, the thermal conductivity of the substrate plays an important role in controlling the synthesis reaction, i.e., temperature of the reaction zone. It is important to mention here that copper is a highly reflective material for the laser beam whereas nickel and niobium materials are reported to have relatively better absorption characteristics. Laser

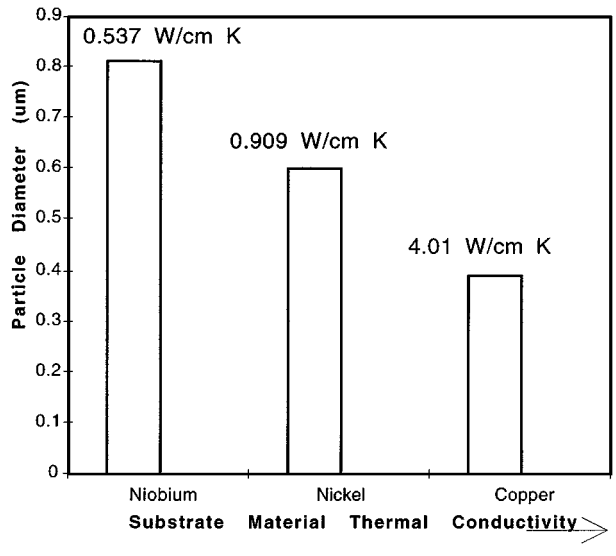


Figure 7 Particle size as a function of substrate thermal conductivity processed using 0.6 moles/liter nickel nitrate, irradiation time of 1 minute and laser power intensity of 50 kW/cm^2.

absorption characteristics appeared to be similar for these substrate materials (nickel, niobium and copper), when they were immersed in the liquid precursor. The mean particle diameter in product powders decreases as the substrate thermal conductivity increases (Fig. 7). Fig. 8 shows the SEM micrograph of rod-shaped and spherical particles precipitated from solutions containing a small concentration of silver nitrate, i.e., silver nitrate, nickel nitrate and 2-ethoxyethanol. The morphology of the product was found to be dependent upon various processing conditions including laser energy, interaction time (i.e., rotation speed of the disc), and precursor composition. X-ray of the product showed diffraction peaks corresponding to Ag and several additional peaks, which could not be attributed to Ni or NiO (Fig. 9). Both Ag and Ni were detected using energy dispersive spectroscopy. These results suggest a possible alloy formation. This analysis was reconfirmed by microanalysis of the rod and nanoparticles in the high resolution TEM (Fig. 10). Two interesting features were observed. First, nanoparticles or rods were actually composed of small crystallites rich in Ag and surrounded by an amorphous phase containing a higher concentration of Ni. Second, the interior core of the rod appeared to be hollow with some helical ring or chain patterns. These rings were found to be rich in Ag whereas the outer wall of the rod was rich in Ni (Fig. 10).

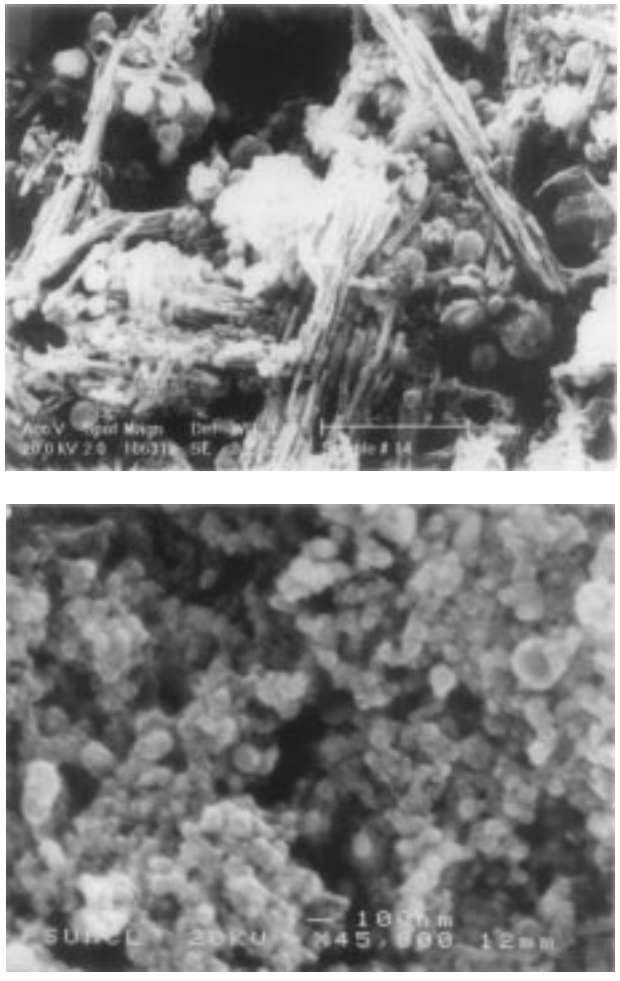


Figure 8 SEM micrograph showing rod-shaped and spherical particles synthesized by laser irradiation of a solution containing silver nitrate, nickel nitrate and 2-ethoxyethanol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time).

It is important to mention here that very little or no silver was produced when the silver nitrate solution was laser irradiated in the absence of the substrate, indicating that the photolytic component was minimal. The thermal energy absorbed by the substrate could facilitate the synthesis of metal atoms in the liquid medium by three processes:

i) Heat transfer from the substrate to the liquid causes an increase in temperature of the liquid close to the irradiated area; consequently, the rate of "chemical" reduction of the precursor compound increases [5]. For example, the rate of silver nitrate ($AgNO_3$) reduction by ethylene glycol (EG) would be increased due to heating of the solution at the laser-liquid-substrate interface.

$$(AgNO_3 + EG \Longrightarrow Ag \text{ particles})$$

ii) The thermal energy causes the "pyrolytic decomposition" of the precursor molecule resulting in the production of metal atoms and nuclei. For example, thermal decomposition of $AgNO_3$ yields silver particles.

iii) A local increase in substrate temperature develops an electromotive force (emf), and induces a migration of metal ions to the illuminated area. The concentration of metal ions in this region continues to increase until a critical value is reached, following which nucleation of ionic clusters starts to occur [6].

Silver and nickel nano-particles were produced in very minute quantities when the precursor compound was dissolved in water; however, silver and nickel production rate was significantly increased when ethylene glycol and 2-ethoxyethanol were used as reductants [3]. These results suggest that silver and nickel production occurs predominantly by a chemical reduction reaction. The starting compound (silver nitrate and nickel nitrate) undergoes dissolution in the solvent, as a first step of the synthesis process. The formation of metal atoms from the precursor compound could go through an intermediate phase. The concentration of metal atoms in solution continues to increase up to a value that facilitates nucleation. The metal nuclei form through clustering of atoms by diffusion in liquid phase and the nuclei grow by supply of metal atoms in solution.

In the LLSI technique, the silver and nickel particle size was found to vary with laser mode, laser energy, defocusing condition, and laser wavelength. The increase in particle size of dual phase nickel-nickel oxide with increasing laser intensity of CW CO_2 laser could be attributed to the excessive absorption of photon energy, which triggered the growth of particles by sintering (Fig. 5). For the same laser power (250 W) and interaction time (1 min), the average size of silver particles decreased when the laser beam was defocused to a larger beam diameter. Finer particles were obtained when the laser was operated in a pulse rather than a continuous

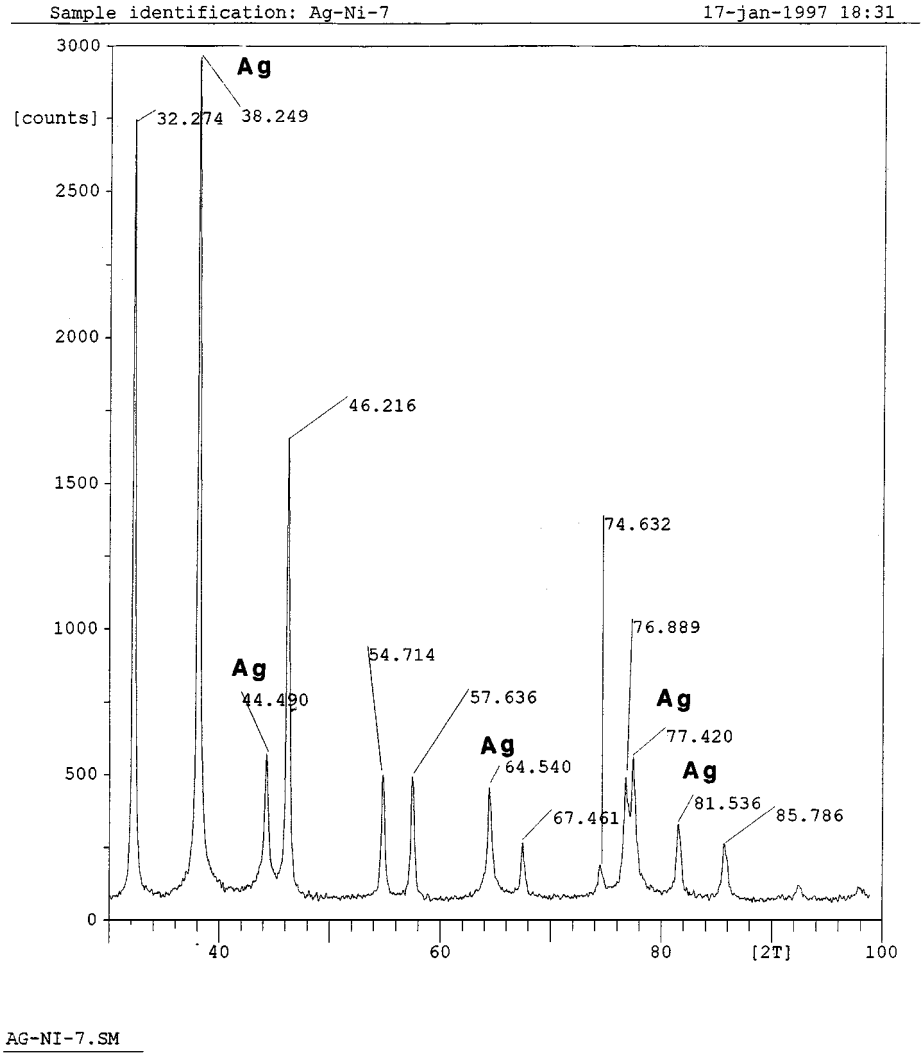


Figure 9 X-ray diffraction profile of the product produced synthesized by laser irradiation of a solution containing silver nitrate, nickel nitrate and 2-ethoxyethanol.

mode (Fig. 3). Trends observed in mean nickel-nickel oxide particle diameter with process parameters are consistent with the proposed nucleation and growth theory [3]. The temperature profile at the laser-substrate interface is expected to follow a gaussian peak profile typical for laser irradition of solids. However, LLSI processing parameters affected the peak temperature achieved during particle synthesis. Temperatures at the laser-substrate interface would increase with increasing irradiation time and laser powers, and decrease with increasing substrate thermal conductivity. Correspondingly, experimental results show the mean particle diameter increases with increasing irradiation time and laser power density, and decreases with increasing substrate conductivity (Figs 4–6).

The reduction of nickel nitrate was reported to be more difficult than silver nitrate, under similar synthesis conditions [7]. For example, very little nickel or nickel oxide was produced when a solution containing nickel nitrate and ethylene glycol was laser irradiated. However, Ag-Ni composites were formed in detectable quantities when Ag particles were added to the nickel nitrate solution. This implied that the Ag particles acted as "seeds" over which the Ni and NiO phase started to grow. Laser irradiation of a solution containing silver nitrate, nickel nitrate and a polyol results in the synthesis of particles of different composition and shape. X-ray diffraction of these powders showed diffraction peaks corresponding to Ag and several additional peaks, which could not be attributed to Ni or NiO (Fig. 9). Both Ag and Ni were detected using energy dispersive spectroscopy. These results suggest a possible alloy formation. It is proposed here that Ag, Ni and NiO_x atoms form simultaneously in the laser irradiated area. These atoms would have little mutual solubility in the bulk solution that is at room temperature; however, their miscibility could be higher in the hot plasma region at the laser-liquid-solid interface. Mixing of silver and nickel atoms in the plasma region would yield a metastable Ag-Ni alloy, which on quenching undergoes phase separation into Ag-rich and Ni-rich phases. Two distinct phases of different crystallinities were observed. The Ag-rich phase was usually crystalline while the Ni-rich phase was amorphous. The morphology, composition, and crystallinity of the alloy particles was dependent on laser wavelength, laser power and precursor concentration. Two-phase alloys containing irregularly shaped Ag-rich and Ni-rich phases were typically formed; however, rod-shaped particles were formed when silver nitrate concentration in the

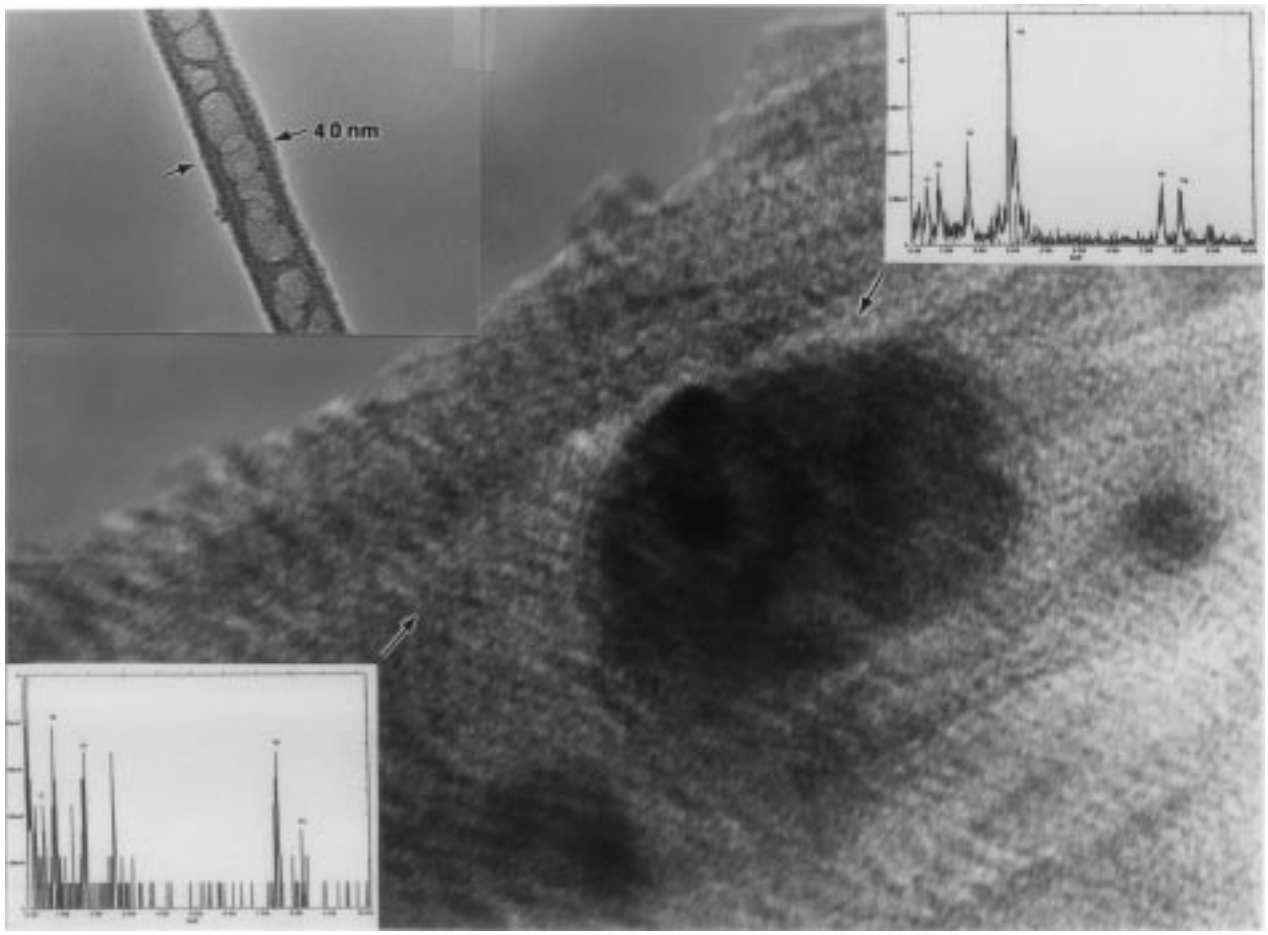


Figure 10 HRTEM showing nanotube of Ag-Ni alloy produced by the LLSI using solution composed of silver nitrate, nickel nitrate and 2-ethoxyethanol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time). The interior core of the nanotube is rich in silver and outer wall is rich in nickel with corresponding EDX micro-chemical analysis shown as inset.

precursor solution was reduced to a very low value (Fig. 10). The equilibrium eutectic phase diagram for Ag-Ni-O is not available; however, the eutectic point will be significantly suppressed due to rapid quenching rates at the laser-liquid-solid interface. Rod-shaped or fibrous microstructures would therefore be formed at a range of compositions other than the eutectic point.

4. Conclusion

Silver, nickel, nickel oxide and metastable alloy powders were synthesized from silver and nickel precursors using the laser-liquid-solid interaction technique. Silver particles produced using CO_2 and Nd-YAG lasers were equiaxed; however, porous dual phases nickel and nickel oxide particles were formed when nickel nitrate dissolved in 2-ethoxyethanol was irradiated by a CO_2 laser. It is envisioned that the synthesis of silver and nickel particles occurs by a nucleation and growth mechanism beginning with the absorption of photon energy by the substrate. The photon energy is released locally into the adjacent solution and facilitates the synthesis of nano-particles by thermally induced chemical reactions.

Spherical, fibrous and irregularly shaped silver-nickel alloy particles were fabricated depending on the chemical composition of the precursor solution and the laser parameters that were used. The concentration of nickel was higher in powders fabricated using 2-ethoxyethanol than those manufactured using ethylene glycol, which can be attributed to the better reducing ability of 2-ethoxyethanol. Trace amounts of oxygen were detected in several samples and can be attributed to the incomplete reduction of NiO_x to Ni under operating conditions. HRTEM of the fibrous or rod shaped particles revealed that were actually composed of Ag-rich crystallites aligned in the longitudinal direction and surrounded by an amorphous phase containing a higher concentration of nickel. The simultaneous synthesis of Ag, Ni and NiO, has been proposed to occur in the plasma region at the laser-liquid-solid interface. Subsequent quenching and solidification of Ag-Ni_x-O_y molecules could lead to phase separation and formation of dual-phase alloys.

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