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Synthesis of metastable silver-nickel alloys by a novel laser-liquid-solid interaction technique

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Metastable silver-nickel alloys have been synthesized by chemical wetness and laser-liquid-solid interaction techniques from nitrate and acetate precursors of silver and nickel. Ethylene glycol and 2-ethoxyethanol were used as reductants in the synthesis reactions. Rotating niobium substrates immersed in the liquid precursor were irradiated by a continuos wave CO_2 and Nd-YAG laser ($\lambda = 1064$ nm). The powders were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM). Two-phase alloys containing silver, nickel, and oxygen were fabricated, and the shape of the particles was found to be dependent on laser parameters and the chemical composition of the precursor solution. The synthesis mechanism of non-equilibrium Ag-Ni alloy nanoparticles has been 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 electronic, catalytic, metallurgical, ceramic, and automotive industry [1]. In particular, alloys of nickel and silver are used for making electrical contacts and switches. Recently, there has been renewed interest in the synthesis of metals, alloys, and composites by non-conventional techniques such as sputtering, evaporation, ion beam mixing, and laser ionization [2–7]. These nontraditional methods facilitate the synthesis of particles in the nanometer size range, and allow the fabrication of alloys from immiscible metals. Alloys consisting of particles with dimensions in the range of 1–100 nm are often referred to as nanocrystalline alloys. Nanocrystalline 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 the bulk miscibility. Certain theories have predicted that the temperature at which phase separation occurs is lowered or phase separation is suppressed in very small particles [8–11]. For small enough particles, there may be no nucleation barrier to form surface segregated species because the energy to be gained on moving weakly bonded atoms from the interior to the exterior of the particle is negligible. For the smallest of aggregates, surface segregation and phase separation are indistinguishable. Thus, nanocrystalline alloys could permit the mixing of metals that are immiscible in the molten state.

Alloys of miscible metals can be fabricated by traditional methods like chemical wetness, spray pyrolysis, and high energy ball milling; however, alloys and composites of immiscible metals have to be manufactured by non-conventional methods such as thermal evaporation, vacuum deposition, sputtering, ion-beam mixing and laser ionization [2–7]. For example, nanocrystalline alloys of miscible metals (Ni-Cu), and composite powders of immiscible metals (Co-Cu, Fe-Cu, Co-Ag, Ag-Pt) were produced using chemical wetness technique [12–20]. The spray pyrolysis technique was used to produce spherical, submicron sized alloy particles from metals that immiscible in all compositions (Ag-Pd) [21]. Binary cluster ions of immiscible metals (Fe-Ag, Fe-Ni, and Co-Ag) were fabricated by evaporation, sputtering, and pulsed laser ionization methods [3, 4, and 7]. All these methods seek to extend the binary phase diagram by attacking the synthesis of the alloy at the atomic level.

The objective of our study was to examine whether the laser-liquid-solid interaction technique, developed in our laboratory for the synthesis of metal and metal oxides from liquid precursors, could be extended to the fabrication of alloys and composites. Silver and nickel were systems of interest because both metals are insoluble in the liquid and solid state. It would be interesting to examine how non-equilibrium conditions at the laser-liquid-solid interface could help the mixing of immiscible metals and suppress the tendency for phase separation. Clusters of silver, nickel and nickel oxide have been synthesized by the laser-liquid-solid interaction technique and the correlation between laser parameters and particle characteristics have been studied [22]. The comparison of these results with those obtained from

synthesis of silver-nickel alloys and composites could shed light on the nucleation and growth processes in these systems.

2. Experimental

Metastable alloys were synthesized by laser irradiation of a metallic substrate immersed in a solution prepared by dissolving nitrate or acetate precursors of silver and nickel in ethylene glycol (99% Alfa Aesar), diethylene glycol (97% Alfa Aesar) and 2-ethoxyethanol (99% Alfa Aesar). The liquid was vigorously mixed to eliminate any concentration gradients in the reactor. A cooling coil was used to maintain the solution temperature at 25 °C. The reactor was constantly purged with nitrogen to prevent oxidation of the organic and powders. The precursor solution was irradiated either by a continuous wave CO_2 laser ($\lambda = 10640$ nm) or a pulse YAG laser ($\lambda = 1064$ nm) with powers ranging from 150–300 W, and the interaction time varying from 1–3 minutes (Fig. 1). Typical volume of solution processed was 200 cc and the height of the liquid was kept constant at 8 mm. The metallic disc was rotated at 5–100 rpm and care was taken to minimize vortex formation. The rotation of the substrate facilitated regular cooling of the irradiated spot, redispersion of the synthesized particles into solution, and prevented particle agglomeration by repeated interaction with the laser beam. The reaction was repeated several times under similar processing conditions to synthesize sufficient powders for characterization. The particles were separated using a centrifuge for 15 minutes, washed with distilled water for another 15 minutes, then dispersed in ethanol using an ultrasonic bath, and allowed to settle overnight.

The shape of particles was analyzed using the JEOL JSM-6300F high-resolution scanning electron microscope equipped with a field emission gun. The microchemistry of the particles was determined by energy dispersive spectroscopy. The crystalline phases of particles were determined by powder x-ray diffraction, and the bragg diffraction angles were compared with standard diffraction profile corresponding to Cu K_α radiation. The particles were supported on holy carbon copper TEM grids, and were studied using a Hitachi HRTEM. Bright-field imaging was performed to reveal the morphology of the powders. The chemical composition and crystallinity of the phases were identified using energy dispersive spectroscopy and selected area electron diffraction.

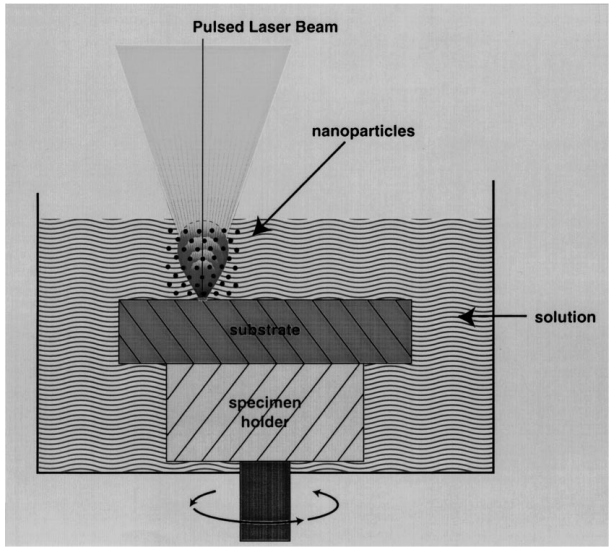


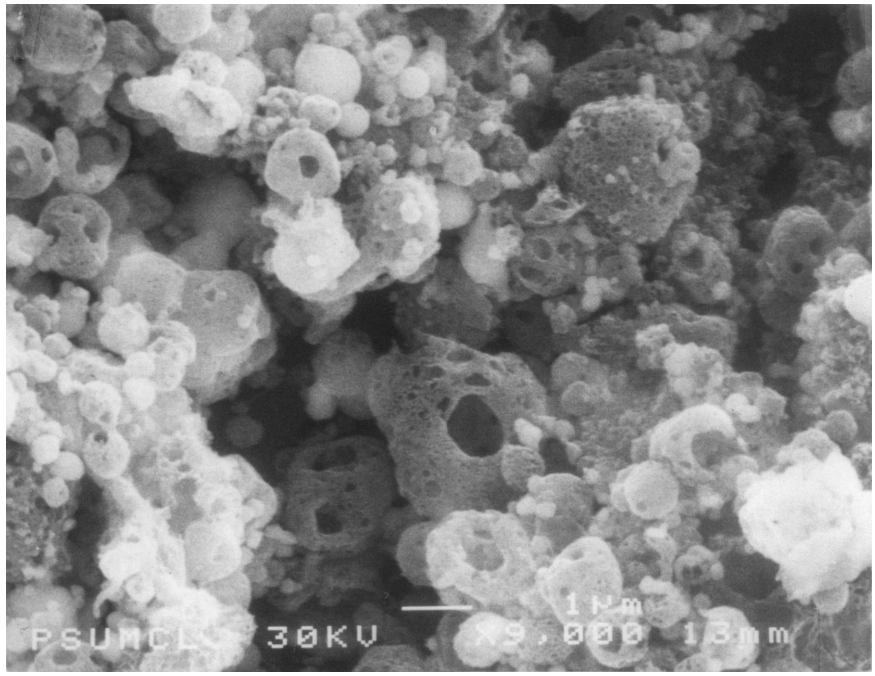
Figure 1 Schematic diagram of the laser-liquid-solid interaction technique was used in the synthesis of Ag-Ni alloy.

3. Results

Nanoparticles of various materials including silver, nickel, nickel oxide, and tin oxide have been produced from liquid precursors by the LLSI technique [22–25]. During the course of this investigation, it was found that no product was produced from the nickel nitrate salts dissolved in water or ethylene glycol by the LLSI technique. This investigation motivated in producing nano-products from the nickel nitrate salts dissolved in ethylene glycol by using silver (*exitu*) or silver nitrate (*in situ*) as a seeding media.

A solution containing silver nitrate, nickel nitrate and 2-ethoxyethanol was boiled at 195 °C, in order to determine the solubility of silver, nickel and oxygen in powders prepared using the chemical wetness technique. XRD of these particles indicated that Ag, Ni and NiO were present, which separated into three distinct crystalline phases. 2-ethoxyethanol, ethylene glycol or a mixture of ethylene glycol and diethylene glycol were chosen as solvents for the synthesis of metastable silver-nickel alloys by laser-liquid-solid interaction technique. Silver acetate and nickel acetate were sometimes used as inorganic precursors for the polyol reaction. Extremely fine silver particles were produced at room temperature by mixing diethylene glycol to a solution containing silver nitrate, nickel nitrate and ethylene glycol. The initial formation of the silver particles could be due to the metastable condition of the starting solution.

Silver particles were added to a liquid mixture of nickel nitrate and ethylene glycol, and the solution mixture was processed using the CO_2 laser. SEM and XRD analysis indicated that the particles were spherical, porous and were actually composites of silver and nickel (Fig. 2). The reduction of nickel nitrate by ethylene glycol was reported to be extremely difficult [23]. The addition of silver particles catalyzed the decomposition of nickel nitrate and reduced the activation energy for nickel synthesis. Thus, the synthesis of nickel and nickel oxide was enhanced by addition of foreign nuclei. This motivated us to try *in situ* reduction of silver nitrate in a nickel nitrate solution. The SEM micrograph and x-ray diffraction pattern of particles synthesized from a precursor solution composed of silver nitrate, nickel nitrate and ethylene glycol using a CO_2 laser are shown in Fig. 3. Diffraction peaks corresponding to FCC Ag structure were detected (Fig. 3b). However, several additional peaks (as marked by X) were also present which could not be attributed to nickel or nickel oxide. The alloy particles were extremely fine with spherical morphology and roughly of the order of 100 nm.



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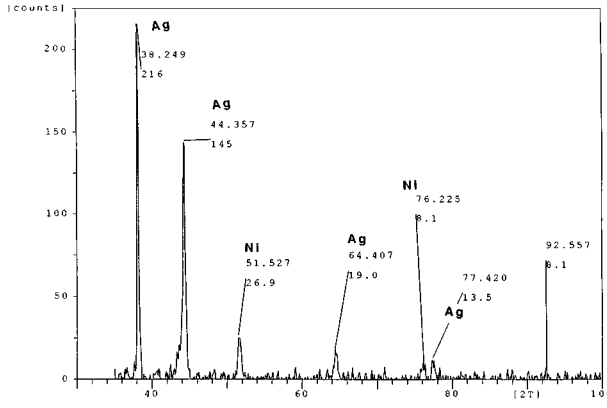


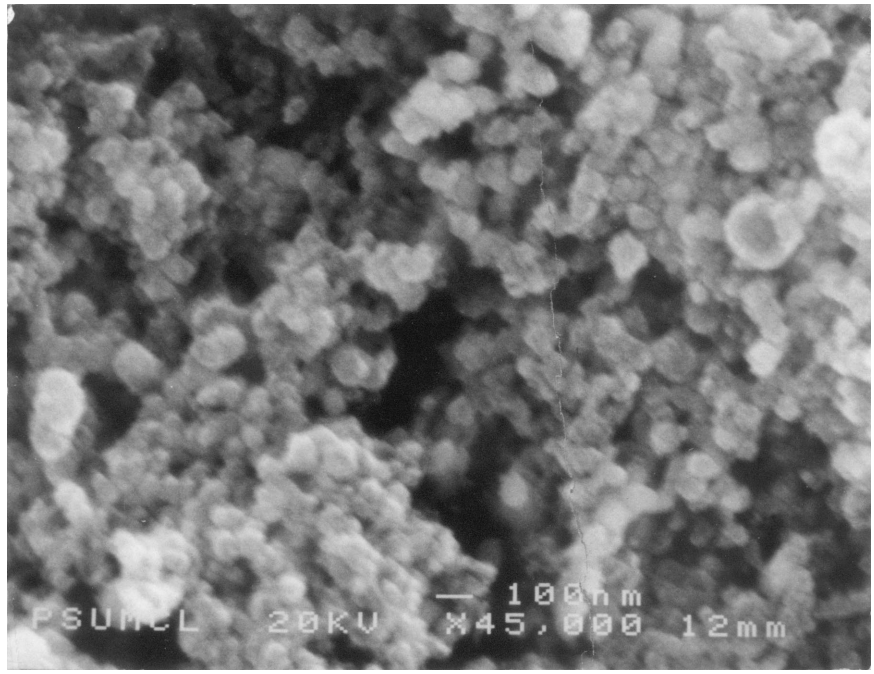
(b)

Figure 2 (a) SEM micrograph of particles synthesized from a 0.6 M nickel nitrate + ethylene glycol solution and "seed" silver particles using a CO_2 laser. (150 W, 3 mm defocus and 3 min irradiation time). (b) X-ray diffraction profile obtained from particles from a 0.6 M nickel nitrate + ethylene glycol solution and "seed" silver particles using a CO_2 laser. (150 W, 3 mm defocus and 3 min irradiation time).

Particles with different shapes, sizes and brightness were formed when a mixture of silver nitrate, nickel nitrate, ethylene glycol and diethylene glycol was irradiated by a CO_2 laser (Fig. 4a). The XRD pattern shows the presence of crystalline silver and some additional peaks that did not correspond to Ni or NiO (Fig. 4b). The additional peaks attributed to the formation of metastable Ag-Ni alloy. The size, shape and crystallinity of the powders were altered when the same solution was processed using a YAG laser. The corresponding SEM micrograph and XRD pattern are shown in Fig. 5. Diffraction peaks corresponding to Ag. Additional peaks again could be due to formation of metastable phases composed of Ag-Ni alloy.

A liquid mixture of silver nitrate, nickel nitrate and 2-ethoxyethanol was irradiated by a CO_2 laser for powers ranging from 150–400 W and irradiation times varying from 1–3 minutes. The morphology of the particles was examined in the SEM, the crystallinity determined by XRD and the chemical composition was analyzed using energy dispersive spectroscopy (Fig. 6). The precipitated powders contained a higher concentration of nickel as compared to those synthesized using ethylene glycol as a reductant. 2-ethoxyethanol has been reported to be a better reductant of nickel nitrate than ethylene glycol [23], which would explain the presence of larger amounts of nickel in these samples. Dual-phase alloys containing particles of different shapes, brightness and compositions were produced. EDS analysis indicated that the brighter particles (large blocky morphology) were rich in silver (Fig. 6b) and darker phase (small nm sized particles) were having higher concentration of nickel (Fig. 6c). The Ag-rich particles were irregular shaped and highly agglomerated. The size of the Ag-rich particles ranged from 1 μm to 2 μm, while the Ni-rich phase was composed of much finer particles.

The morphology of the particles was significantly altered by changes in precursor composition and laser parameters. Fig. 7 shows the SEM micrograph of powders precipitated from solutions containing very small concentrations of silver nitrate. Spherical and rod-shaped



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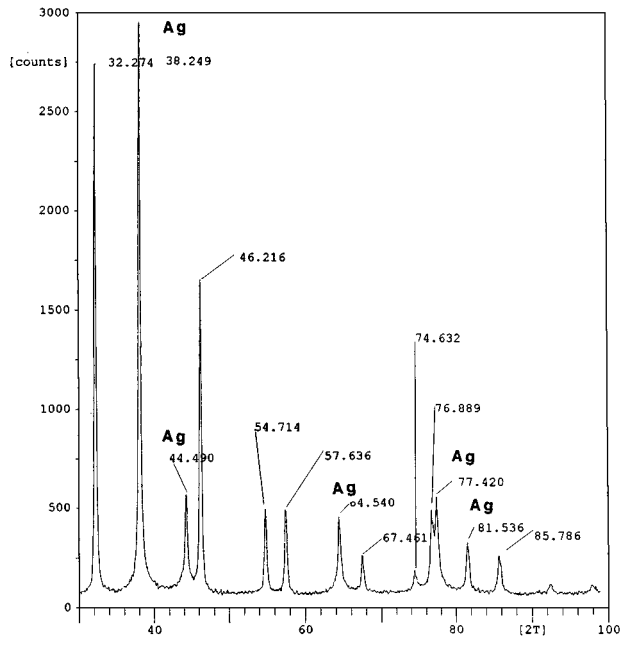


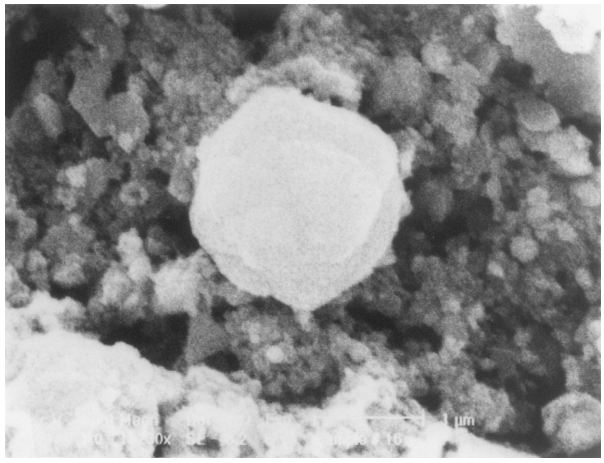
(b)

Figure 3 (a) SEM micrograph of particles synthesized by laser irradiation of a solution containing 16.6 g silver nitrate, 6.9 g nickel nitrate and 200 cc ethylene glycol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time). (b) X-ray diffraction profile obtained from particles synthesized by laser irradiation of a solution containing 16.6 g silver nitrate, 6.9 g nickel nitrate and 200 cc ethylene glycol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time).

particles were formed. XRD analysis of the product is shown in Fig. 7b. Additional peaks are due to the presence of metastable phases. The HRTEM analysis of the rod or viscous fiber morphology is shown in Fig. 7b. Two important features were observed. First, the rod is appeared as a hollow tube with diameter 40 nm and length is ranging 2–5 μm. EDS from the different regions in the tube revealed that the inner shell of the nanotube were actually composed of silver crystallites and were surrounded by an amorphous phase containing a higher concentration of Ni as shown in Fig. 7c-inset.

4. Discussion

The thermodynamic phase diagram indicates that Ag and Ni are insoluble in both the liquid and solid state. The mutual solubility of Ag and Ni is only of the order of 2 to 3 atomic percent at the melting point of Ni and the solubility is of the order of 0.2 atomic percent at the melting point of Ag. The atomistic and energetic causes for this miscibility gap are not known; however, it has been postulated that differences in atomic radii and bonding conditions of the metal atoms can play a significant role [1]. The mixing of such immiscible metals has been reported to be enhanced in



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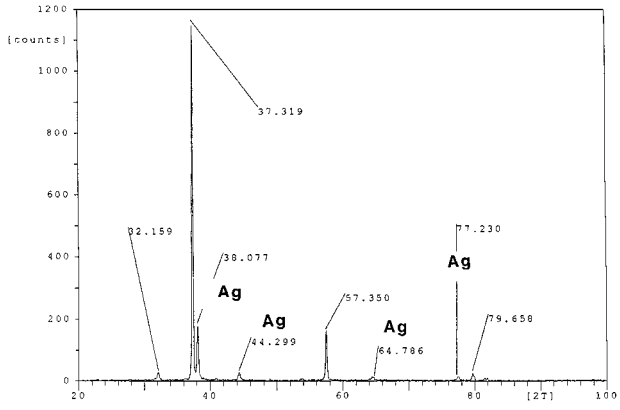
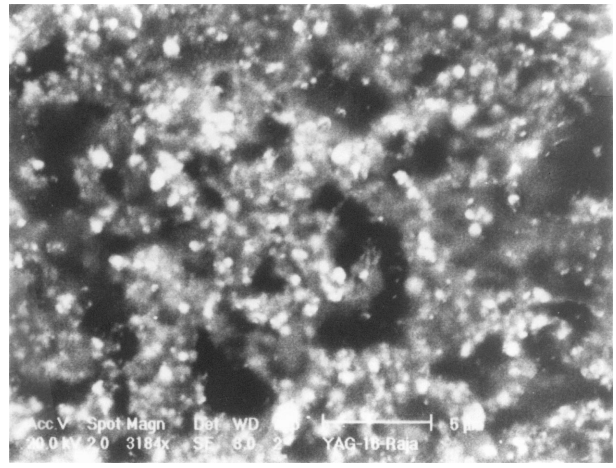


(b)

Figure 4 (a) SEM micrograph of particles synthesized by laser irradiation of a solution containing 75 g silver nitrate, 75 g nickel nitrate, 200 cc ethylene glycol, 40 cc diethylene glycol and 200 cc water (CO_2 laser: 150 W, 3 mm defocus and 3 min irradiation time). (b) X-ray diffraction profile obtained from particles synthesized by laser irradiation of a solution containing 75 g silver nitrate, 75 g nickel nitrate, 200 cc ethylene glycol, 40 cc diethylene glycol and 200 cc water (CO_2 laser: 150 W, 3 mm defocus and 3 min irradiation time).



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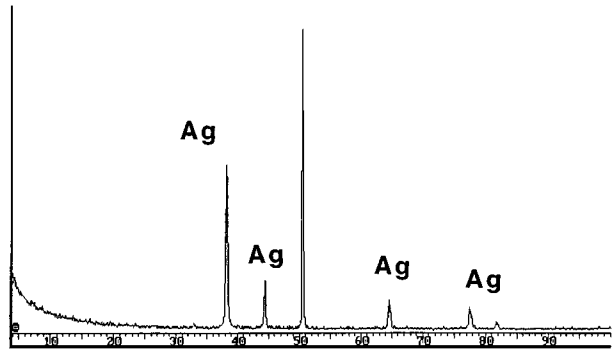
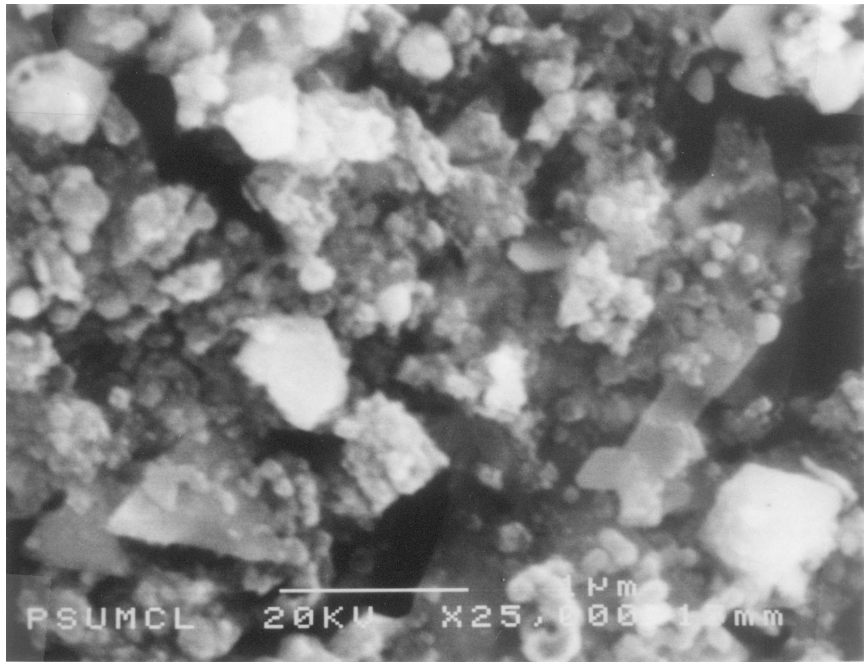


(b)

Figure 5 (a) SEM micrograph of particles synthesized by laser irradiation of a solution containing 75 g silver nitrate, 75 g nickel nitrate, 200 cc ethylene glycol, 40 cc diethylene glycol and 200 cc water (YAG laser: 1100 W, 3 mm defocus and 3 min irradiation time). (b) X-ray diffraction profile obtained from particles synthesized by laser irradiation of a solution containing 75 g silver nitrate, 75 g nickel nitrate, 200 cc ethylene glycol, 40 cc diethylene glycol and 200 cc water (YAG laser: 1100 W, 3 mm defocus and 3 min irradiation time).

nanometer-sized particles [7]. If the crystallite size is small, the surface energy contribution to the free energy becomes large enough that the free energy is reduced by forming a solid solution [4, 7]. Alloying of metals with large miscibility gaps (Ag-Co, Cu-Fe, Fe-Ag, Ag-Ni, Ag-Cu) has been demonstrated using synthesis techniques with ultrahigh heating, irradiation and quenching rates like sputtering, laser ionization, ion-beam mixing, ion-beam implantation, and thermal evaporation [2–7]. In the ion implantation and ion beam mixing methods a solid is bombarded by beams of highly energetic particles. New structures or metastable derivatives produced in the energized region are frozen during extremely rapid de-energization [2]. Vapor and sputter deposition techniques involve condensation on a surface maintained at a temperature well below that of configurational freezing [2, 7]. The favored positional configuration of the condensing atom is that with short range positional correlations which assemble to topologically and compositionally disordered or structures. This tendency towards disorder would be countered by rearrangements on the surface limited by surface diffusion [2]. Thus, the formation of disordered metastable structures is favored at high deposition rates and lower surface temperatures.

Nanocrystalline Ag-Fe, Cu-Sn, Cu-Ag, Au-Co and Fe-Cu have been produced by simultaneously evaporated or sputter co-deposited in amorphous solid forms [7, 23–26]. Mossbauer spectroscopy of Ag-Fe alloys revealed that in the strained lattice in the vicinity of the Ag-Fe interphase boundaries, the solubility of Ag in Fe and Fe in Ag was enhanced. In addition, boundary segregation of Ag and Fe was also postulated to occur at the grain boundaries [7]. Co-Ag composite metal films with nanometer sizes of Co and Ag crystallites were prepared by magnetron sputtering [3]. The mutual solubility of Ag and Co under equilibrium conditions is very low in both the solid and liquid form; however, Co-Ag alloy films were formed under fast quenching conditions. Subsequent annealing of these films at high temperatures resulted in phase separation into distinct Co and Ag fcc structures [3]. Composite powders of immiscible metals like Co-Cu, Fe-Cu and Fe-Co were prepared using the chemical wetness technique [16, 17]. Submicron-size particles were made by adding foreign nuclei or forming foreign *in situ* nuclei [18]. A “metastable” solid solution of Fe-Cu and Co-Cu was formed by reduction of constituent salts



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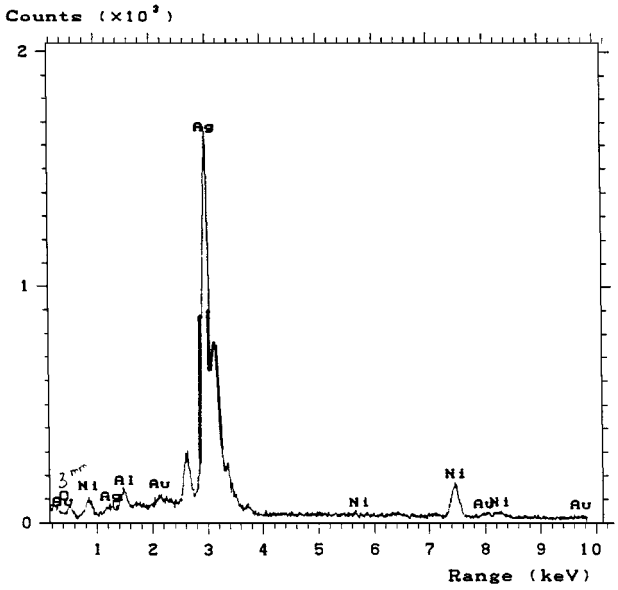

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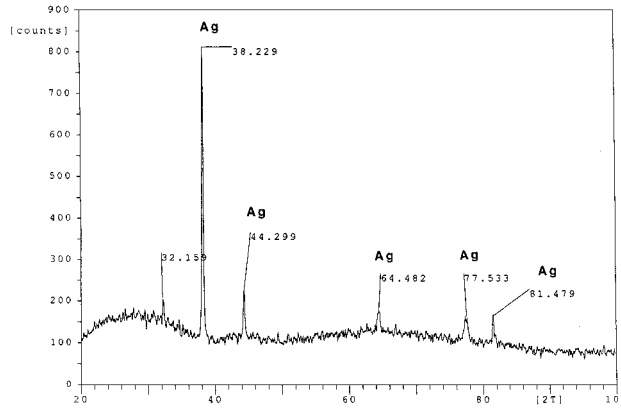

(c)

Figure 6 (a) SEM micrograph of particles synthesized by laser irradiation of a solution containing 9.6 g silver nitrate, 20 g nickel nitrate and 200 cc 2-ethoxyethanol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time). (b) EDS obtained from particles synthesized by laser irradiation of a solution containing 9.6 g silver nitrate, 20 g nickel nitrate and 200 cc 2-ethoxyethanol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time). (c) X-ray diffraction profile obtained from particles synthesized by laser irradiation of a solution containing 9.6 g silver nitrate, 20 g nickel nitrate and 200 cc 2-ethoxyethanol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time).

using a polyol or borohydride solution [16, 17]. The precipitated powders were subsequently heat-treated causing phase separation. This yielded a composite; however, alloying of constituent components did not occur.

Dahlgren and co-workers succeeded in sputter co-depositing at room temperature forming homogeneous fcc Ag-Ni solutions with up to 13 atom percent Ni in Ag and 8 percent Ag in Ni [5]. Because of the small solid state solubilities the morphology of the precipitate dispersion of one of these elements in the other, once formed, should remain frozen to quite high temperatures. Ag-Ni alloys were also synthesized by sequentially depositing alternate layers of Ag and Ni using an electron gun and then bombarding the resulting film with heavy ions, e.g., Xe^+ [2]. The present study represents the first attempt to synthesize "metastable" Ag-Ni alloys by liquid-phase chemical reaction using lasers as an energy source. The general procedure in the synthesis of "metastable" structures is to energize and then quench the material. In the LLSI technique, the energization step would involve irradiation of the precursor solution. Quenching or condensation would occur in solution and the cooling rate could be of the order of 10^{13} K/s [2]. It was theorized that rapid evaporation and quenching rates in the laser-irradiated area could facilitate the mixing of Ag and Ni clusters and result in the formation of "metastable alloys". Also,

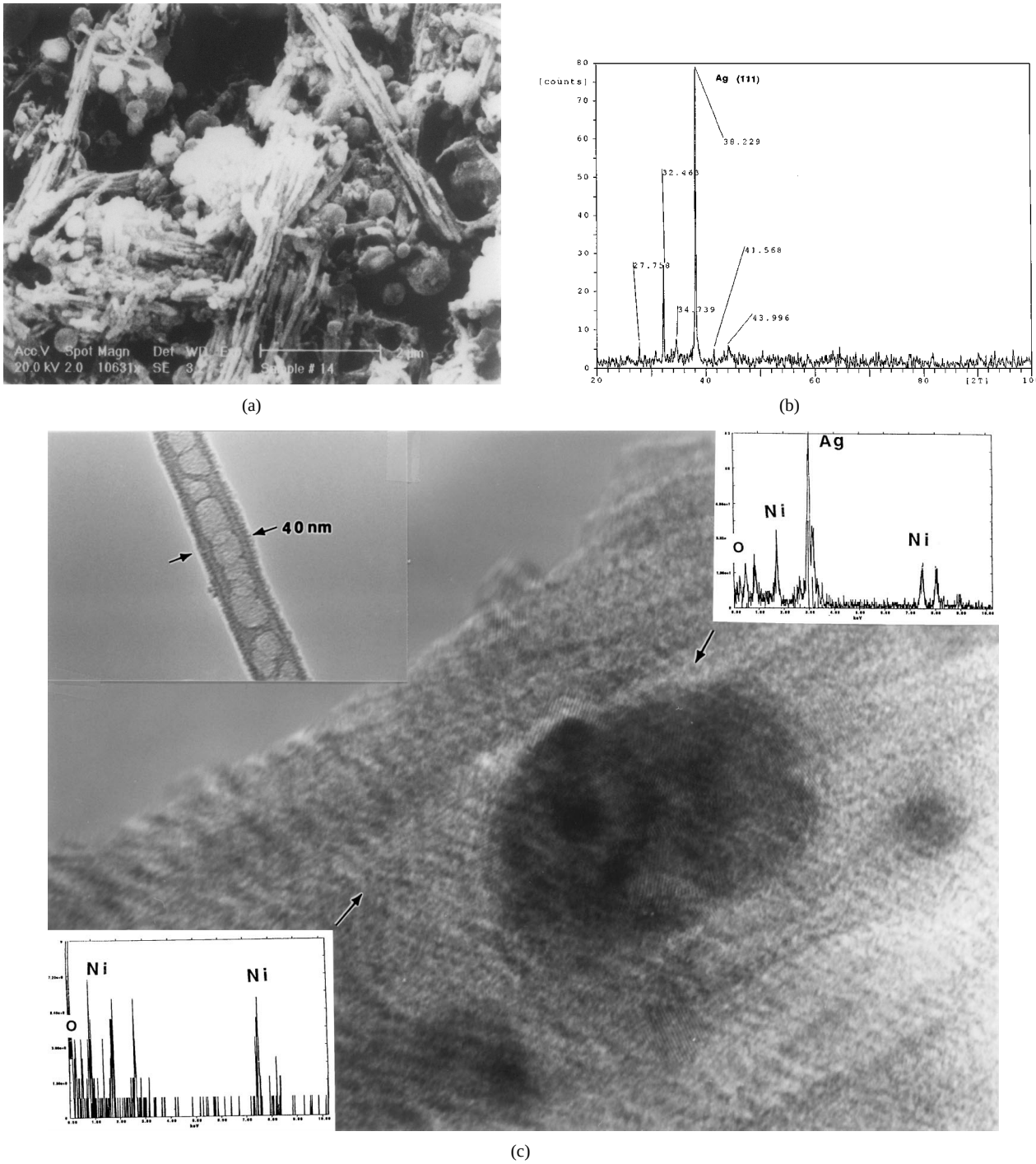

Figure 7 (a) SEM micrograph of particles synthesized by laser irradiation of a solution containing 9.6 g silver nitrate, 20 g nickel nitrate and 200 cc 2-ethoxyethanol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time). (b) X-ray diffraction profile obtained from particles synthesized by laser irradiation of a solution containing 9.6 g silver nitrate, 20 g nickel nitrate and 200 cc 2-ethoxyethanol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time). (c) HRTEM and of rod shaped particles synthesized by laser irradiation of a solution containing 9.6 g silver nitrate, 20 g nickel nitrate and 200 cc 2-ethoxyethanol (CO_2 laser: 300 W, 3 mm defocus and 6 min irradiation time).

nanometer-sized particles produced by this method could permit the increased solubility of Ag and Ni.

A mixture of silver nitrate, nickel nitrate, and 2-ethoxyethanol was heated on a hot plate with an objective of determining the Ag-Ni-O phases that could be formed. X-ray diffraction of the precipitated powders revealed that Ag, Ni and NiO separated into three distinct phases and no alloy was formed. Very little nickel or nickel oxide was produced when a solution containing nickel nitrate and ethylene glycol was irradiated by a laser beam; however, composites containing silver, nickel and nickel oxide were generated in detectable quantities when silver was added to the same precursor solution. This implied that the silver particles acted as "seeds" over which the Ni-rich phase started to grow. *In situ* reduction of silver nitrate in a solution containing nickel nitrate and a polyol produced 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. Both Ag and Ni were detected in the product powders using energy dispersive

spectroscopy. These results suggested a possible Ag-Ni alloy formation.

In the LLSI technique, the substrate gets heated due to absorption of photon energy from the laser beam. The thermal energy absorbed by the substrate is proportional to the laser intensity at the substrate surface, and can be controlled using laser power and laser beam diameter. The photon energy absorbed by the substrate is also dependent on the laser wavelength and irradiation time. The thermal energy absorbed by the substrate could facilitate the production of metal atoms by chemical reduction, pyrolytic and ionic processes. The production of clusters or particles could go through three distinct stages. In the prenucleation step, the starting compound undergoes reduction in solution (Stage I). The concentration of atoms continues to increase to a value that facilitates nucleation (Stage II). This is followed by the growth process, where in the nuclei grow by supply of atoms in solution (Stage III). It is postulated here that the laser irradiation of a solution containing silver nitrate, nickel nitrate, and a polyol results in the synthesis of Ag, Ni, and NiO_x atoms simultaneously. These atoms would have little mutual solubility in the bulk solution which is at room temperature; however, their miscibility could be higher in the hot plasma region at the laser-liquid-solid interface. Mixing of silver, nickel and oxygen atoms in the plasma region would yield a metastable Ag-Ni alloy, which on rapid quenching could undergo phase separation into Ag-rich and Ni-rich phases.

The morphology and composition of alloy particles synthesized by LLSI technique could also be influenced by interfacial tension, temperature and concentration gradients in solution, convective flow fields, and gravity induced sedimentation effects. The vigorous agitation of the liquid and the use of the cooling coil helped eliminate temperature and concentration gradients in the reactor. The size of dual-phase NiO-Ni particles synthesized by this technique was reported to increase linearly as a function of time suggesting that the growth of particles was not diffusion controlled [22]. The convective flow fields and sedimentation effects might play a role in phase separation; however, since the volume of liquid and the convective liquid turbulence is small, these effects are expected to be insignificant. Interfacial tension between phases of immiscible liquids is a quantity of eminent importance in phase separation and nucleation processes. Interfacial tension determines the barrier for nucleation and consequently influences the rate of nucleation. The introduction of "seeds" or foreign nuclei significantly reduces the nucleation energy and catalyses the formation of particles. Interfacial tension between different phases could play a role in determining the morphology of particles.

In the LLSI technique, the quenching process opens up several thermodynamic permissible courses of structural evolution including that to the most stable state. The metastable alloy synthesis can occur only when the kinetically preferred course differs from the one most favored thermodynamically. It was noted that systems seemed generally to transform to a metastable rather than to their most stable phase [2]. It was argued that if the initial system is far out of equilibrium, nucleation of the metastable phase would be preferred because the interfacial tension with the initial phase should be lower than that formed by the more stable phase. Paths favored kinetically were generally those requiring lesser correlations of atomic positions and motions. Thus short range order, whether compositional or topological, was suggested to develop more rapidly than long range order [2]. During the quenching step in the LLSI process, the Ag-Ni alloy also may go through a metastable intermediate states, which might be amorphous or crystalline. Two distinct phases with different crystallinities were observed in several Ag-Ni samples. The Ag-rich phase was usually crystalline while the Ni-rich phase was amorphous.

Spherical, fibrous and irregularly shaped particles of different compositions and crystallinity were detected in powders prepared by the LLSI technique. The precipitated powders had a higher concentration of nickel when 2-ethoxyethanol was used as a reductant, which could be attributed to the better reducing ability of 2-ethoxyethanol. The reduction of nickel nitrate was reported to be more difficult than silver nitrate, under similar synthesis conditions [23]. Based on these results, it can be inferred that the Ag-rich phase would nucleate and form crystallites. These Ag-rich particles could serve as nuclei upon which Ni-rich phase starts to grow. This explanation is in agreement with that proposed for the fabrication of Co-Cu nanocomposites by the polyol technique. During the synthesis of Co-Cu powders, Cu nucleated first to form nanocrystallites since it is more easily reducible than Co. Cu nanoparticles subsequently served as nuclei upon which less reducible Co was formed. Heterogeneous reduction of $Co(OH)_2$ to Co on foreign Ag and Pd nuclei using ethylene glycol as a reductant has also been reported. The addition of 'seeds' significantly decreased the barrier for nucleation, separated the nucleation and growth steps, and facilitated the synthesis of sub-micron sized particles. The crystallographic structure of 'seed' particles have been postulated to induce preferential growth of certain planes in the secondary phase which grows over the nuclei. For example, bulk Co has a hcp structure below 417 $^{\circ}$C; however, formation of metastable fcc Co was observed in Co-Cu sputtered film and chemically prepared powders. The formation of metastable fcc Co below the phase transformation temperature was explained by the stabilization of fcc Co by already formed fcc Cu particles. Similarly, the Ag-rich phase could induce preferential growth of certain planes in the phase containing a higher concentration of nickel.

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 the silver nitrate concentration in the precursor solution was reduced to a very low value. The equilibrium eutectic phase diagram for Ag-Ni-O is not available; however, the eutectic point is expected to be significantly suppressed due to rapid quenching rates at the laser-liquid-solid interface.

Eutectic phase transformation could occur at compositions other than the eutectic point, and the silver content in the "metastable" alloy would determine whether rod-shaped or irregularly shaped particles are formed. Rod-shaped particles or fibrous microstructures would be expected when the silver content in the alloys is small. Rod-shaped or fibrous microstructures have been detected in experiments involving heterogeneous nucleation of Ag on Pt nuclei. The aligned fibrous structures in these systems, which is due to "monotectic" growth of Ag (majority phase) on Pt (minority phase), can be affected by solution composition, interfacial energy and convective fields. The Ag-Ni particle morphology was also dependent on the inorganic precursor used in the synthesis reaction, and alloy particle shapes, composition and crystallinity were different when acetate rather than nitrate precursors were used. Laser wavelength, laser beam diameter and laser power would determine heating and quenching rates in the irradiated area, and thereby affect the suppression of the eutectic point, nucleation and growth processes at the laser-liquid-solid interface. Thus, the morphology of Ag-Ni particles could be altered by variations in laser parameters as well.

The complete reduction of nickel nitrate and nickel acetate to nickel was seldom achieved using the LLSI technique and dual phase nickel oxide-nickel particles were typically formed [22]. A finite amount of oxygen was detected in several Ag-Ni samples synthesized by the LLSI technique, and can be attributed to the incomplete reduction of NiO_x to Ni under operating conditions. Metastable alloys of Fe and Cu prepared by borohydride reduction of ferrous chloride and cupric chloride also contained oxygen in sizable quantities. For samples with low concentrations of iron, considerable amount of copper atoms formed an oxide. Boron, sodium and chlorine were other impurities that were incorporated into these powders. Similarly, Fe-Co and Cu-Co powders formed by reduction of inorganic salts in a borohydride or polyol medium also contained detectable amounts of oxygen, boron and sodium.

Further research is necessary to understand the mechanistic correlation between particle size, shape and composition and process parameters, and to fully establish the alloy synthesis mechanism at the laser-liquid-solid interface. The LLSI technique is unique because it seeks to extend the miscibility of immiscible metals by providing rapid evaporation and quenching rates at the laser-liquid-solid interface.

5. Conclusion

Metastable alloys of silver and nickel were synthesized using a novel laser-liquid-solid interaction technique. The effect of process parameters on the size, shape and composition of alloy particles was studied by varying the chemical composition of the solution and the laser parameters. 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. Based on LLSI experiments for synthesis of Ag, Ni, and NiO powders, it can be inferred that the Ag-rich phase would nucleate and form crystallites. These silver rich particles serve as nuclei upon which nickel rich phase starts to grow. Trace amounts of oxygen, detected in several Ag-Ni samples synthesized by the LLSI technique, can be attributed to the incomplete reduction of NiO_x to Ni under operating conditions. Spherical, fibrous and irregularly shaped particles were formed depending on the chemical composition of the precursor solution and the laser parameters that were used. HRTEM of the fibrous or rod shaped particles revealed that they 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 and mixing Ag, Ni and NiO_x species has been proposed to occur in the plasma region at 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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