Laser Surface Alloying of Gold

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In many technological applications specific material surface properties are required, which are satisfied by depositing a layer of, for example, gold on a component. Laser surface alloying can modify a surface uniquely to produce a wide range of structures and properties.

Laser alloying is a material processing method which utilizes the high power density available from focussed laser sources to melt metal coatings and a portion of the underlying substrate (1,2). Since the melting occurs in a very short time and only at the surface, the bulk of the material remains cool, thus serving as an intimate heat sink. Large temperature gradients exist across the boundary between the melted surface region and the underlying solid substrate. The result is rapid self-quenching and resolidification. Quench rates as great as 10^{11}K sec^{-1} and concomitant resolidification velocities of 20 m sec^{-1} have already been realized.

What makes laser surface alloying both attractive and interesting is the wide variety of chemical and microstructural states that can be retained because of the rapid quench from the liquid phase. These include chemical profiles where the 'alloyed' element is highly concentrated near the atomic surface and decreases in concentration over shallow depths (hundreds of nanometers), and uniform profiles where the concentration is the same throughout the entire melted region. The types of microstructures observed include extended solid solutions, metastable crystalline phases, and metallic glasses.

This review will be concerned with the subject of the surface alloying of gold by means of laser irradiation. The concept of laser surface alloying is schematically pictured in the sequential cross section views in Figure 1.

Principles of Laser Surface Alloying

In the upper-left view the metal substrate (B) coated with a thin metal film (A) is irradiated with a laser pulse. A fraction of the incident laser light is absorbed by free carriers within the electromagnetic skin depth (10^{-6} to 10^{-5}cm). For metal surfaces

and most laser wavelengths a significant fraction of the incident light will be specularly or diffusely scattered away (the reflectance process is not shown in the schematics). The absorbed energy is 'instantaneously' (10^{-12}sec) transferred to the lattice. The near surface region very rapidly reaches the melting point and a liquid/solid interface starts to move (solid arrows) through the film as indicated by the second view. In the third view the liquid/solid interface has swept through the original thin film/substrate interface. Interdiffusion of the film (solid circles) and substrate (open circles) elements starts. The laser pulse is nearly terminated and the surface has remained below the vaporization temperature. In the fourth view the maximum melt depth has been reached. Interdiffusion continues. The resolidification interface velocity is momentarily zero and then rapidly increases. In the fifth view, the resolidification interface has moved approximately halfway back to the surface from the melt depth. Interdiffusion in the liquid continues, but the resolidified metal behind the liquid/solid interface cools so rapidly that solid state diffusion may be neglected. In the final view the material is completely resolidified and a 'surface alloy' of A in B has been produced. What makes laser surface alloying both attractive and interesting is the wide variety of chemical and microstructural states that can be retained because of the rapid quench from the liquid phase, allowing one to form extended solid solutions, metastable crystalline phases and in some instances metallic glasses. The technique is quite unique for tailoring surfaces and thereby surface properties.

There is presently a large number of commercially available laser sources used to induce the melting needed for surface alloying. Of these a relatively small group, including carbon dioxide (CO_2), neodymium doped yttrium-aluminium garnet (Nd:YAG), neodymium doped glass (Nd:glass) and chromium doped aluminium oxide (Ruby), account for nearly all surface alloying work. The laser characteristics — wavelengths, output power, beam diameter, output mode, pulse length and repetition rate — are important processing factors that come into play when considering the choice of laser source. In addition the laser source may be modified as in the use of harmonic generators to double the frequency of Nd:YAG and Ruby lasers so that they emit in the green and ultraviolet respectively, or the use of acousto-optical modulation to 'Q-switch' a solid state laser source. Table I compares the various laser sources and typical parameters used in surface alloying.

Figure 2 presents the normal spectral reflectance of gold (3). Annotated on the abscissa are four laser wavelengths. Of these laser

Fig. 1 Sequential cross-section schematics illustrating mechanism of laser surface alloying from arrival of laser pulse to complete resolidification

Table I
Typical Laser Parameters for Sources used in Surface Alloying

Laser Parameters	CW CO ₂	Q-switched Nd:YAG	Frequency Doubled Q-switched Nd:YAG	Homogenized Q-switched Ruby	Pulsed Ruby or Nd:YAG and Glass
Wavelength	10.6 μm	1.06 μm	0.53 μm	0.69 μm	0.69, 1.06 μm
Average power*	0.2-15 KW	0.53-3 W	50-300 mW	1-10 J	2-50 J
Focussed optical spot	0.1-10 mm	20-40 μm	10-30 μm	6 mm	0.5 mm
Focussed power density	1-10 MW cm ⁻²	80-200 MW cm ⁻²	30-100 MW cm ⁻²	10-200 MW cm ⁻²	0.5-10 MW cm ⁻²
Dwell/pulse length	10-1000 s	130 ns	120 ns	2-80 ns	2-10 ms
Repetition rate	—	11 KHz	5 KHz	0.03 Hz	0.1-10 Hz
Spatial distribution	multimode top hat or gaussian	gaussian	gaussian	top hat	multimode

*Output capabilities of low rep. rate lasers are normally measured and quoted in energy content per pulse.

sources the optimum choice is that of the frequency doubled Nd:YAG. The double exposure photograph of Figure 3 shows a frequency doubled Nd:YAG laser in a typical laboratory configuration used to produce various surface alloys. The elements of the laser system are denoted on the schematic representation.

Because focussed laser sources are so intense almost any metal surface can be melted by simply increasing the incident power density sufficiently to allow for the large reflectance losses. This approach, however, overlooks one of the practical problems in laser processing, that of defining the conditions under which melting can be achieved without vaporization. The optical micrographs in Figure 4 will help to explain this concept (4). The metal surface in this case is a cold rolled copper alloy (UNS designation C72500, 88Cu/10Ni/2Sn per cent) with spectral reflectance characteristics very similar to gold. In the left hand view melting has been caused by raster scanning of a Q-switched Nd:YAG laser (1.06 μm wavelength), while in the right hand view the same surface has been treated with a frequency doubled Q-switched Nd:YAG laser (0.53 μm). The incident power density at the fundamental wavelength is 30 times that for the frequency doubled case. In both instances melting is achieved. However, for the fundamental laser this surface cannot be area scanned without locally vaporizing some fraction of the surface as shown by the line of deep craters in the left hand micrograph of Figure 4. This selective area vaporization is a common problem in laser treatment of surfaces with local non-uniformities in their reflectance characteristics, particularly when using incident energy densities well above the required absorbed energy densities. At the shorter wavelength the excess energy is significantly less, and thus when a local strong coupling centre is scanned, there is insufficient energy to reach the vaporization point. The result is a much more uniform and reproducible laser surface treatment.

In general the output of a laser source must be focussed on a spot

Fig. 3 (left) A typical laboratory set-up of a frequency doubled Nd:YAG laser used to produce gold and other surface alloys

Fig. 4 (below) Optical micrographs of surface of cold rolled copper alloy (88 Cu/10 Ni/2 Sn per cent) following laser surface melting with Q-switched Nd:YAG (left) and frequency doubled-Q-switched Nd:YAG (right). The vertical rolling texture has a periodic spacing running left to right of the order of 1 micrometer per line

in order to achieve sufficient energy density to induce melting of a metal surface. This focussed spot is characterized by its optical spot size. The size of the melted spot (effective spot size) resulting from the laser exposure will generally be smaller than this optical spot size. For a continuous-wave laser source, a melt strip will be produced as the focussed beam and metal surface are moved relative to one another. As is shown in Figure 5, individual melt strips must be partially overlapped to produce area coverage. The effective spot size, degree of overlap, and relative scanning speed will thus determine the areas per unit time which can be produced.

For a pulsed or Q-switched laser (high-power, short-pulse laser) source, the 'pulse length' is the time of exposure. The laser pulses are emitted in a train of pulses characterized by a repetition rate. As is shown in Figure 6, this train of pulses is raster-scanned across the metal surface to produce area coverage. For these lasers, the effective spot size, degree of overlap, and repetition rate determine the area per unit time which can be produced.

For all the laser sources (continuous-wave, pulsed, and Q-switched) the exposure time (dwell time or pulse length) strongly influences the depth that will be melted. Longer exposure times result in deeper melting. Since deeper melting means a longer total time in the molten state, that means more time available for diffusion of the one or more alloying elements into the molten

portion of the substrate. Deeper melting and longer melt times therefore result in more dilute surface alloys, while shallow melting and shorter melt times result in more concentrated surface alloys.

An appreciation of the order of the melt depth and the scale of the melt time is necessary to determine mass transfer. Consider, as an example, a thin deposited film where short melt times are required. Q-switched laser sources, with pulse lengths (t_p) of tens to hundreds of nanoseconds, will produce melt times (t_l) on the order of 50 to 500 nanoseconds. Liquid phase diffusion coefficients (D_L) for metal solutes in metal melts are nearly all in the range of 10^{-4} to $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. Thus the diffusion length or mixing range ($D_L t_l$)^{1/2} for this short melt time-simple diffusion case will be of the order of 70 to 700 Å, which is significantly less than the maximum melt depth calculated for metals. Thus we would expect that the solute depth profile ($A_x B_{1-x}$) in the last frame of the sequence in Figure 1 would show a concentration peak at the surface, dropping off sharply over a depth of the order of the diffusion length, to a low (near zero) value at about the melt depth, and a zero value beyond this.

Gold Alloy Systems

A gold depth profile appears in Figure 7 for the case of a gold surface alloyed into nickel following irradiation by a Q-switched laser source (5) (see footnote overleaf). Profiles such as this have been successfully reproduced with straightforward models incorporating little more than known liquid state diffusion coefficients and heat

flow estimates of the melt time (6). The case of relatively thin films and deeper melting (pulsed or continuous laser sources) is illustrated by the gold-in-nickel depth profiles (5) in Figure 7 for a melt time greater than 50 μs (CW- CO_2 laser). The melt depth and melt time are much greater than those of the Q-switched lasers. The greatly increased melt time allows diffusion of the gold over much greater depths. Over the depth range analyzed the gold profile in Figure 7 is completely flat.

In order to establish the structural relationship of the Au-Ni surface alloy to the parent base metal, single crystal nickel substrates were coated with gold films of 500-5000 Å thickness and capped with 250 Å of nickel. The Ni <110> /Au/Ni 'sandwiches' were laser alloyed with Nd-YAG radiation and examined with Rutherford backscattering and channeling (5). Figure 8 shows, for example, the aligned and random spectra for a 960 Å gold film with a 250 Å nickel cap following Nd-YAG irradiation. The gold surface concentration is 21 atomic per cent. The fact that the Au <110> and random yields are in the same ratio as the Ni <110> and random yields indicates that the gold atoms are substitutional. If the Au-Ni alloy was a perfect single crystal with no defects we would expect a ratio of 3 per cent or so. The measured ratio of 60 per cent is a measure of the high degree of disorder in the lattice.

In this series of constant fluence Nd:YAG laser alloying experiments on Ni/Au/Ni samples where the intermediate gold layer was varied from 500 to 5000 Å, the melt depth increased significantly with increasing thickness of the gold. This behaviour can be understood in terms of the effective thermal diffusivity which determines the rate of heat propagation in transient state processes, and for thin gold is approximately that of nickel; while for thick gold it is more closely that of gold, and a factor of six times greater than the value for nickel.

Similar experiments on sandwich type multilayers of Cu/Au/Cu have been performed by Wang, *et al.* (7) using a Q-switched Ruby laser and Rutherford backscattering spectroscopy (RBS) for analysis. As in the case of Au-Ni the Au-Cu intermixing can be readily understood, even predicted, based on gold solute diffusivities in molten copper and estimated melt times. Structural analysis was not performed, however the RBS data suggest that extended solid solutions (like Au-Ni) are formed rather than intermediate compounds.

Glassy or amorphous metal surfaces can be readily formed at the very high quench rates associated with laser alloying. A number of amorphous gold surfaces have been prepared. The Au-Si system was the first metallic glass reported by Duwez (8) who pioneered the

The polycrystalline samples (10 x 20 mm) were prepared from strip stock (0.64 mm thick) of commercial grade nickel 200. Thin gold films (1500 Å, or 3500 Å) were vacuum deposited onto this strip at room temperature and at pressures of 10×10^{-7} torr. The surface alloys produced by the various laser systems were analysed using Rutherford backscattering spectroscopy.

Fig. 8 Backscattering spectra of a sandwich structure after Nd:YAG irradiation. The random and channeling spectra show that the Au is substitutional, has a peak surface concentration of 21 at.% and is alloyed to a depth of approximately 3400 Å

mechanical melt quench methods. The Au-Si system was a natural choice for early experiments in glass formation via laser alloying and has been investigated in a rather large number of laboratories. The work of von Allmen and colleagues (9, 10) has been quite extensive. Glass formation was described (9) over the entire range from 9 to 91 silicon atomic per cent for 30 ns Nd:YAG laser radiation. This greatly exceeds the limits established for glass formation by earlier melt quench methods, which were restricted to near the deep eutectic at 17 silicon atomic per cent. The Au-Si metallic glass surface 'alloys' were reported to crystallize at temperatures near 370K. An intermediate metastable hexagonal gold silicide phase was also reported to form upon careful annealing with phase separation to gold and silicon occurring around 420K. The optical and electrical properties of the Au-Si glassy surface alloys were investigated and found to exhibit wide variability. Figure 9 shows the normal spectral (1.4-5.4 eV) reflectance of the Au-Si surface as a function of composition. The optical behaviour can be described with a Lorentz-Drude model with a free-electron and single resonance bound-electron term. Physically, this may be interpreted as the silicon switching between the metallic and semiconducting states at a composition of 30 silicon atomic per cent, while gold switches from metallic to dielectric at 85 silicon atomic per cent.

A number of other binary Au-X glassy systems have also been made by laser alloying. These include Au-Ge, Au-Bi and Au-Ti. Au-Ge is a glass forming system similar to Au-Si and, not surprisingly, the results reported are similar to those discussed above

for the latter, and are in line with what one would expect based on other experience with melt quenching of easy glass-forming systems.

The superconducting transition temperature (T_c) and electrical resistivity of laser alloyed $Au_{(1-x)}Bi_x$ thin films have been investigated by Wolthuis and Stritzker (11). Gold and bismuth multilayers with average values for x ranging from 0.2 to 0.9 were laser quenched (KrF laser, 20 ns pulses) into an amorphous phase exhibiting a T_c of 5.4K. A typical T_c dependence on laser fluence is given in Figure 10 for a composition of $x=0.65$. With increasing laser fluence three separate T_c regions are observed. Up to about 40 mJ cm^{-2} there is no change in T_c indicating the fluence is below the melting threshold. Between 40 mJ cm^{-2} and about 80 mJ cm^{-2} the surface is melting and with increasing fluence the depth of melting and thus volume fraction of high T_c material produced is increasing. Above 80 mJ cm^{-2} the entire volume of $Au_{35}Bi_{65}$ has been quenched from the liquid with the SiO_2 substrate at 4.2K acting as an effective quench medium. The annealing behaviour of the amorphous laser-produced samples was found to be similar to that of earlier investigated vapour-quenched and ion bombarded amorphous Au-Bi layers.

The laser surface alloying results reported by von Allmen and colleagues (12) on a series of binary X-Ti multilayers include a rather unusual observation in the case of Au-Ti. They report at the composition investigated ($Au_{35}Ti_{65}$) the formation of a glassy matrix in which a small quantity of crystalline titanium exists as a 'precipitate'. Upon annealing the surface alloys, the 'precipitates' disappear into the glass at about 620K before the system crystallizes irreversibly at 670K. This type of behaviour has since been reported by von Allmen to occur in non-gold binary systems as well (13). It will probably require extensive investigation before it is satisfactorily understood.

Other 'Laser-Improved' Gold Processing Applications

Although the focus of this article has been on laser alloying of gold there are two other ways that lasers have been used in relation to gold coating methods. The first is laser surface finishing of copper alloys prior to conventional electroplating of gold. The second is laser-enhanced electroplating wherein the laser beam defines the track of gold deposited from the electrolyte. Laser surface melting of copper alloys has been demonstrated (14, 15) to produce an ultrasmooth finish on a microscopic scale. The right hand photomicrograph in Figure 4 shows the surface finish on a copper alloy before (top) and after (bottom) laser surface melting achieved with Q-switched frequency doubled Nd:YAG laser (Figure 3) scanning. The scanning of the surface is pictorially described in Figure 6. The 'before' surface finish is that of a high quality cold rolled surface. The rolling marks stand out at this magnification because of the use of Nomarski interference contrast microscopy. The 'after-laser melting' finish literally converts the surface finish to one of mirror-like quality. These surfaces were found to result in

Fig. 9 Optical reflection spectra of the glassy Au-Si films. Also included are spectra of evaporated amorphous Si (...) and pure crystalline Au (---)

Fig. 10 The superconducting transition temperature T_c of a $Au_{35}Bi_{65}$ film versus energy density of the laser pulse

superior quality gold electroplates with significantly reduced porosity (14). In addition it was found that these surfaces exhibited improved resistance to both sulphur and chlorine corrosive atmospheres (15). The use of lasers for spatial definition of gold deposition from solution has been receiving considerable attention since it was first reported by von Gutfeld (16). Those interested in details of the process and the mechanisms should consult a review article by von Gutfeld in the IBM journal (17). It has been reported at CLEO meetings in 1984 and 1985 that the process is being used to make product in IBM's Endicott, New York plant.

The highly competitive forces in the electronics and telecommunications market place great pressure on the R & D sector to produce reliable contact finishes that reduce or eliminate, where possible, the need for gold which, historically, as a result of its ultra-reliable contact surface properties, has held an unchallenged position in its application at the upper end of the market. One of the more recently introduced contact finishes which still requires the use of gold but in diminished quantities, is the so called 'diffused gold' surface (18). Very thin films of gold are diffused into palladium or palladium-silver inlays, or into palladium electrodeposits. In 1985 the savings realized in AT & T on batches of a few types of components finished with gold-flashed palladium electrodeposits instead of electroplated gold amounted to more than \$12 million (19). Diffused gold surfaces can be prepared by two different methods. In the first method the thin gold layer and a portion of the palladium underlayer are melted on a nanosecond timescale with Q-switched laser radiation (20). The intermixing is quenched during the resolidification process so that a graded distribution of gold in palladium results. In the second method the thin gold layer is diffused into the underlying palladium or palladium-silver alloys during an elevated temperature inlaying process (18). In this the solid state interdiffusion of the metals occurs over times that are long compared to the laser liquid state method, but sufficiently rapid to make it a viable production method. This is possible in the case of gold and palladium because interdiffusion is measurable even at room temperature and is quite extensive at only 550K (21). In either method the gold distribution in the palladium or palladium-silver layer is much like that of gold in nickel (open circles) presented in Figure 7 above.

Summary

Laser surface alloying of gold has been investigated as an alternative means for producing surface coatings of high gold content. In some cases, the high quench rates have been found to result in the formation of extended solid solutions and metastable alloys as well as metallic glasses in the treated surfaces. The continued high price of elemental gold and concern over waste disposal throughout the conventional electroplating industry will continue to put pressure on R & D organizations to come up with novel methods such as laser surface alloying as alternative coating methods.

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