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POSSIBILITIES AND LIMITATIONS OF LASER SURFACE ALLOYING BY MELTING OF PREDEPOSITED LAYERS

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Abstract: A brief overview of the different phenomena and problems which occur during laser surface alloying is presented in this study, for example the physical description of the different stages (melting, interdiffusion, solidification); attention is payed on limitations (especially concerning the realization of thick and strongly alloyed surface layers).

I - Introduction:

It is well known that for many technological applications surface treatments have to be performed, in order to improve, for example, tribological properties or corrosion resistance. Laser surface treatments have been extensively studied in the last decade (see for example 1-4), and two main methods have been reported:
- solid phase treatments; they require the possibility of a significant phase transformation during the heat cycle produced by the laser-material interaction. So only allotropic or martensitic transformations are involved, and consequently this possibility has been applied to transformation hardening in iron base alloys.
- laser surface alloying or cladding: various substrates (Al, Cu, Fe, Ti... base alloys), as well as different coating materials (Fe, Ni, Al, Co ... base alloys) were used.

In the present work, we try to give a brief overview of the different problems and phenomena which occurs during this last processing. Schematically, three stages may be distinguished during laser surface alloying:
- melting (partial or total) of the deposit and part of the substrate,
- interdiffusion of the various elements,
- solidification.

II - Melting:

During the laser treatment, a heat cycle is induced in the specimen (5). The maximum temperature obtained during the processing depends on laser irradiance (I(W/cm2)), interaction time (τ(s)) and on distance (z) from the surface. In given processing conditions, two temperatures have to be considered: Ts, the surface profile and Ti, the temperature at the interface between the substrate and the predeposited surface layer. Two situations may occur, depending on the relative values of melting temperatures of substrate (Tmμ) and deposit (Tμd):
- Tμd > Tμs: melting starts always at the outer surface and both depth and composition of the melted layer may be easily controlled. A typical example is given by an electroless nickel layer (Ni-P) (Tμd = 1000°C) on a mild steel substrate (Tμs = 1535°C).
- Tμs < Tμd: in some conditions (for example low thermal gradient, small deposit thickness...), melting may start in the substrate and then progress towards the surface layer; this phenomena is more difficult to control. This situation may also be observed with multilayers with different thermophysical properties. For example, fig. 1 shows a Cr - (Ni-P) bilayer on a mild steel; as Tμs > TμNi,P (=1860°C and =1000°C respectively), the electroless nickel layer is fully melted, while the surface chromium layer remains in the solid state. Due to the thermal expansion of liquid nickel, this component goes into the cracks of the hard chromium deposit and induces a progressive dissolution of this element. Control of this phenomenon is very difficult to achieve and thicknesses smaller than 200-250 μm cannot be obtained.
A similar situation is sometimes observed in laser surface alloying on materials with low melting temperature, especially aluminium alloys (6). However, due to the existence of large thermal gradients, especially in rapid processing conditions or with thick layers, melting generally begins on the specimen surface and progresses towards the bulk. Various models (5, 7) have been proposed to calculate the temperature evolution, either analytical or numerical models, either 1D, 2D or even 3D descriptions. A rough estimation of the surface temperature $T_S$ gives:

$$T_S = \frac{q}{k} \sqrt{\frac{4 \alpha \tau}{\pi}}$$

with:
- $q$: absorbed laser power density,
- $k$: thermal conductivity,
- $\alpha$: thermal diffusivity,
- $\tau$: laser-material interaction time.

Taking into account the values of these parameters and of the absorptivity coefficient for a CO2 laser ($\lambda = 10.6 \mu m$)(8), we obtain the following results for the incident irradiance $q_0$ (for a given interaction time $\tau = 100ms$):

- for nickel: $q_0 = 10^5$ W/cm$^2$
- for chromium: $q_0 = 10^5$ W/cm$^2$
- for tungsten: $q_0 = 2.2 \times 10^5$ W/cm$^2$

So a typical value of $10^5$ W/cm$^2$ may be retained as an order of magnitude. Let us mention that an increase of the irradiance generally induces a plasma formation above the sample; this plasma modifies very significantly the laser-material interaction and consequently the temperature profile within the sample. A precise control of the laser surface alloy requires a precise control of the interaction, especially of its stability.

III - Interdiffusion of the elements:

A good homogeneity of the surface alloy requires a complete interdiffusion of the various elements. This phenomenon depends on time, temperature and nature of the elements.

Diffusion in the liquid state is much more efficient than in the solid state, generally by several orders of magnitude. So one of the most important parameters is the lifetime of the melted pool; this duration may be increased by:

- increasing either irradiance or interaction time. However an increase of the irradiance is often to be avoided, because of the plasma formation (see above) and a too large interaction time induces a pronounced melting of the substrate and therefore a large dilution of the addition element. So for a given solute-solvent system, an optimization of the laser processing conditions is necessary. For example the existence of undissolved pieces of deposit (fig.2) may be suppressed by an increase of interaction time (fig.3).

- a decrease of the liquidus temperature. Let us for instance consider the case of laser surface alloying on aluminium alloys; for pure Al, $T_f \approx 660^\circ C$. An addition of 10 at.\% Ni leads to a liquidus temperature $T_i \approx 800^\circ C$, while the addition of 10 at.\% Ti gives $T_i \approx 1200^\circ C$. So nickel will be a more favourable element than titanium for the realization of surface alloy on aluminium substrates.

For many applications, a thick surface alloy is required. This may be obtained only by using a thick initial predeposit. But then two problems occur:

- the interdiffusion is more difficult to achieve, since the required diffusion lengths are longer and need an increase of the melted pool duration.
- the increase of the solute element concentration in the melted pool may induce an increase of the liquidus temperature and therefore a decrease of the temperature range allowed for diffusion.

So a limitation occurs and therefore thicknesses of the surface alloys reported in the literature are generally lower than $500 \mu m$. This phenomenon is less pronounced in electron beam processing, since the vacuum environment avoids the plasma formation effect.

In the liquid state, diffusion is enhanced by convection movements, induced by the Marangoni effect. Various authors have simulated this effect. Morvan et al (9) have for example shown that a decrease of the scanning velocity of the sample under the laser beam induces a large increase of the geometrical features of the convection movements (length, depth). So a beneficial effect on interdiffusion of the elements may be induced. Unfortunately, a recent study of the stability of a free surface of a liquid submitted to large temperature gradients (10) has shown that the existence of these movements generally induces a
deformation of the surface and therefore the apparition of ripples after the solidification and hence a deleterious effect on surface roughness is achieved. So an optimum has to be found.

IV - Solidification :

Solidification microstructure depends, for a given system, on two main parameters: solidification rate (Vs) and thermal gradient (G) (11). A slow solidification rate gives:
- a good homogeneity of the surface alloy,
- a low level of residual stresses and then a beneficial effect on, for example, fatigue lifetime;
- sometimes the existence of a plane front growth at the interface between surface alloy and substrate.

This phenomenon, which occurs for high values of (G/Vs) and in homogeneous conditions of nucleation, leads to a very regular composition. Its presence may sometimes act as a barrier against the propagation of a crack in aggressive conditions (fig.4).

In opposition, a rapid solidification induces:
- higher thermal stresses (deleterious effect),
- but a finer microstructure and therefore a larger improvement of mechanical properties (Hall and Petch’s law).

So, depending on the application, laser processing conditions have to be adapted. In many cases, phases formed induce an improvement of the surface properties; as they are generally equilibrium phases, a good thermal stability is expected (6, 12).

V - Conclusion :

The conclusions are as follows:
- limitations of laser surface alloying concerns mainly the realization of:
  - thick layers, with a large solute content,
  - large areas, since only localized treatments are carried out,
- but large possibilities are offered; after an optimization of laser processing conditions, surface layers are obtained without imperfections (cracks, porosity...) and their formation may induce an improvement of different surface properties (mechanical properties, corrosion resistance...). Depending on the considered application, nature of the addition elements, thickness of the deposit, interaction time and irradiance have to be adapted.

References:

Fig. 1: partial melting of an intermediate electroless nickel layer between an electrolytic chromium coating and a mild steel substrate (laser processing conditions: $P = 1640 \text{ W}; V = 20 \text{ mm/s}$).

Fig. 2: example of defects observed in laser surface alloy; Al - 5% Si + Ni electrolytic layer (50μm) + laser melting ($P = 2200 \text{ W}; V = 2 \text{ cm/s}$).

Fig. 3: same system, but after optimization of the laser processing conditions ($P = 2000 \text{ W}; V = 1 \text{ cm/s}$).

Fig. 4: plane front growth.