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Distribution of concentration of gold in the process of laser alloying of the nickel surface layer

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The paper presents the results of studies on the mechanism of laser alloying of nickel with gold. From the investigations carried out, it has been found that thermocapillary phenomena play a predominant role in the alloying process. Experiments have satisfactorily confirmed the distribution area of the capillary motion velocity obtained by theoretical calculations. The paper contains examples of the actual distribution of the alloying material concentration in the areas alloyed with a single laser pulse.

1. Introduction

An effective method of modification of the physical properties of the surface layer of metals is laser alloying with foreign atoms. This can be done by means of a pulse laser in which successive microareas of the layer are alloyed by single pulses. In the case of a laser of continuous action, a laser flux moves over the sample surface at a constant speed.

If the surface layer of the sample is alloyed with atoms of another metal, the alloying material is usually deposited on to the surface of the base (fundamental) metal in the form of a layer. These layers are formed in different ways: by vacuum evaporation, in the form of colloidal suspension (metal powder in a colloidal liquid) or in the form of a very thin foil joined adhesively with the base metal surface.

In the present paper the results of investigations into alloying of the nickel surface layer (base metal) with gold as an alloying material by means of a pulse laser of the YAG: Nd type, have been presented. In the experimental investigations, samples of nickel with a layer of gold vacuum-evaporated on to the nickel surface and samples of nickel with a layer in the form of a gold foil 20 μm thick joined adhesively with the sample surface have been used.

A diagram of layer formation with the pulse laser is presented in Fig. 1. The alloying was done using laser radiation pulses of the parameters: $E_p = 7.5$ J, $D_0 \approx 600$ μm, $\tau_p = 4$ ms, $\Delta D_m \approx 1/3 D_0$.

2. Analysis of the alloying mechanism

The aim of alloying the base metal with foreign atoms is the formation of a surface layer of modified functional qualities: mechanical (microhardness, abrasion resistance), chemical (anticorrosive) or electrical (resistivity, resistance to an electric arc). The stability of the parameters of the modified layer depends on the uniformity of the alloying concentration distribution in the whole area alloyed. Thermocapillary phenomena are "responsible" for the transport of the alloying material from the free surface of the melted metal, heated with a laser flux. These problems are dealt with in a number of theoretical papers, e.g. [1–4] and experimental works, e.g. [5–7].

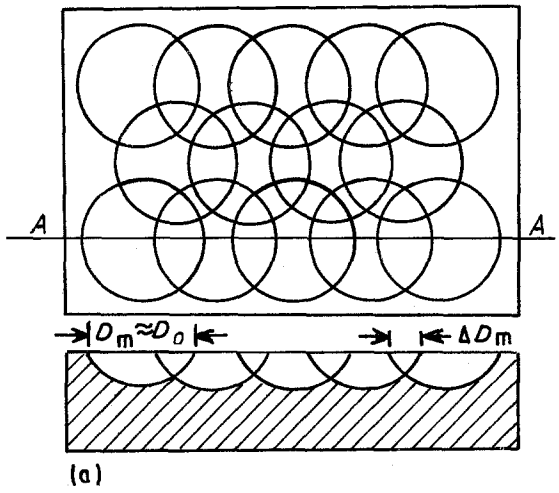

Figure 1 Image of the section of the nickel layer alloyed with gold by means of a pulse laser.

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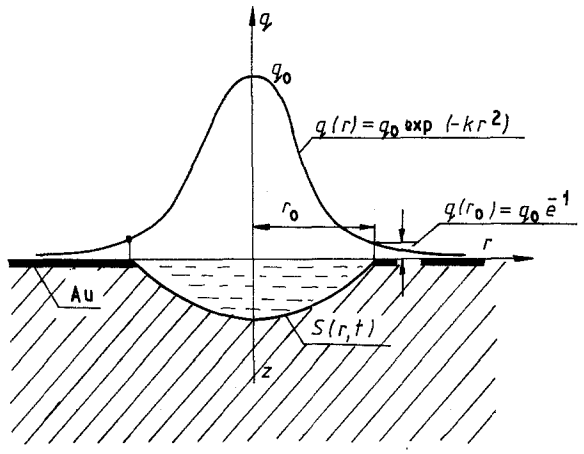

Figure 2 Diagram of the alloying process.

The present publication reports analysis of the alloying process of the nickel surface layer with gold which covers the sample surface in the form of a layer. The alloying was carried out with a pulse laser whose pulse energy, $E_p \leqslant 15$ J, and pulse duration, $\tau_p \leqslant 4$ ms. The power density distribution in the cross-section of the focused laser flux is described by the Gauss function: $q(r) = q_0 \exp(-kr^2)$ in which the concentration coefficient $k \approx 10^7$ m^{-2}.

It is assumed that the parameters of metals: thermal conductivity, λ; specific heat, c; density, ρ and coefficient of radiation energy absorption, A are not temperature dependent. The duration of the whole alloying process, which is equal to $t = \tau_p$, can be divided into two stages. During the first stage, which lasts in the time interval $0 < t < t_m$, the sample surface is heated and, at the instant $t = t_m$, the temperature in the centre of the area heated ($r = z = 0$) reaches the value of the melting point T_m. The melting time, t_m, can be determined from the dependence [7]

$$t_m = \frac{1}{4\alpha k} t_g^2 \left(\frac{\pi^{1/2} \lambda k T_m}{q_0} \right) \tag{1}$$

in which the temperature diffusivity, $\alpha = \lambda/c\rho$, and t_g is the glass transition temperature.

Although in the time interval $0 < t < t_m$ the process of diffusion of gold atoms to the nickel surface layer occurs, due to a short diffusion time ($\sim 10^{-5}$ s), the depth of penetration of gold atoms is small (< 0.1 μm). Phenomena occurring in the second stage of alloying, $t_m \leqslant t \leqslant \tau_p$, are decisive in determining the depth of penetration of the alloying material into the surface layer of the sample. At the instant $t = t_m$, the process of melting in the local area (Fig. 2) and the displacement of the interface $z = S(r, t)$ begin. The Gaussian distribution of the power density on the surface of the melted area results in appearance of the surface tension gradient $\partial\sigma(r, t)/\partial r = \partial\sigma/\partial T \partial T/\partial r < 0$. The existence of this surface tension gradient is the fundamental cause forcing out thermocapillary motion of the melted metal. Treating the liquid metal as a viscous liquid of a dynamic viscosity, μ, and density, ρ (according to the principles of the fluid mechanics [8]) the thermocapillary motion can be described by the Navier–Stokes equation

$$\rho \frac{\partial \bar{v}}{\partial t} = -\nabla p + \mu \nabla^2 \bar{v} + F \tag{2}$$

along with the conditions

$$\operatorname{div} \bar{v} = 0 \tag{3}$$

$$\left.\frac{\partial v_r}{\partial z}\right|_{z=0} = \frac{\Omega}{\mu} \left.\frac{\partial T}{\partial r}\right|_{z=0} \tag{4}$$

where ∇ is the nabla, ∇^2 is the Laplacian, p is the pressure in the liquid metal, F is the volume force exerted on the fluid, $\Omega = |\partial\sigma/\partial T|$ and v and v_r are the velocity and radial components of the velocity of motion of the liquid metal.

For relatively small velocities of the liquid metal (~ 1–3 m s^{-1}), an assumption that $F = 0$ is justifiable. For small values of v_r, the Reynolds number $\mathrm{Re}^* = v_r r_0/\Omega(S/r_0)^2 \ll 1$.

The Navier–Stokes equation (Equation 2) along with conditions (Equations 3 and 4) describes thermocapillary motion in an area limited by stationary walls.

Under the conditions of laser alloying, the boundary separating the liquid phase from the solid phase, $z = S(r, t)$, changes its position (Fig. 3). As a result, the Navier–Stokes equation must be supplemented with the equation of conductivity with the Stefan condition and adequate boundary conditions

$$\frac{\partial T_1}{\partial t} = \alpha_1 \nabla^2 T_1; \quad \frac{\partial T_2}{\partial t} = \alpha_2 \nabla^2 T_2 \tag{5}$$

$$\lambda_2 \frac{\partial T_2}{\partial z} - \lambda_1 \frac{\partial T_1}{\partial z} = \rho L_m \frac{\partial S(r, t)}{\partial t} \tag{6}$$

$$-\lambda_1 \left.\frac{\partial T_1}{\partial z}\right|_{z=0} = q_0 \exp(-kr^2) \tag{7}$$

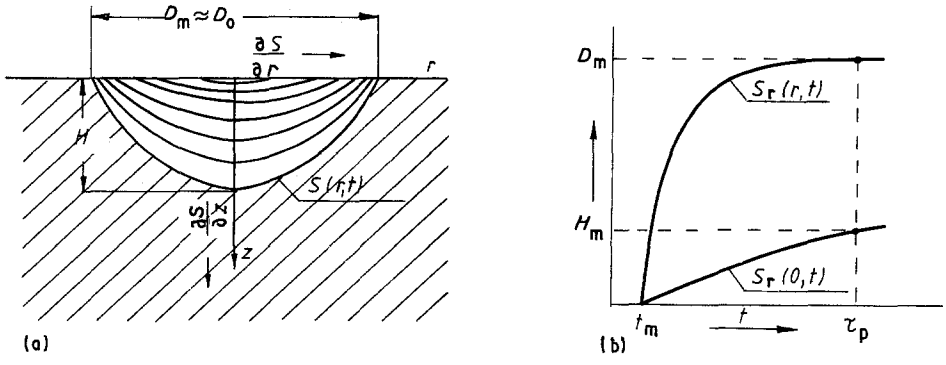

Figure 3 Diagram of a gradual increase in the fusion dimensions.

$$T_2(r, z, 0) = T_2(r, \infty, t) = T_2(\infty, z, t) = T_0 = 0 \quad (8)$$

where λ is the thermal conductivity, α is the temperature diffusivity, L_m is the specific heat of melting, and subscripts 1 and 2 represent the liquid and solid phases, respectively.

An analysis of the formation process of fusion [9] shows that in the initial period ($t \geqslant t_m$) the interphase $S(r, t)$ displaces quickly in the radial direction and then $\partial S/\partial r \gg \partial S/\partial z$. As the fusion diameter, D_m, approaches the value of $D_m \approx 2r_0$, the interphase displacement velocity increases, $\partial S/\partial z > \partial S/\partial r$.

To determine the functions $z = S(r, t)$, $T(r, 0, t)$ and the components v_r and v_z of the thermocapillary motion velocity of the liquid metal, the system of Equations 2–8 must be solved. It is virtually impossible to perform this task using analytical methods, without making considerable simplifications and without making use of numerical methods.

Numerical solutions to this problem have been presented in the works [1–6] in which a number of simplifications are made and inertial components in the Navier–Stokes equations as well as convection components in the conductivity equations are neglected. The introduction of simplifying assumptions into Equations 2–8 and the use of numerical methods allowed the determination of an image of the velocity field of the melted metal [2, 4] and a theoretical distribution of the alloying material concentration [10]. A typical theoretical image of the stationary velocity field of motion of the melted metal in the fusion is shown in Fig. 4. Such a theoretical shape of the velocity field first results in the displacement of the alloying material (melted gold) in the radial direction (at $v_z \sim 0$) to the boundary of the fusion, and then along the boundary $S(r, t)$ into the sample (at $v_z \approx 0$).

Because $v_z < v_r$ for the whole process, the melted base metal (nickel) with the alloying material (gold) moves along a "flattened spiral" forming a "whirl". The centre of this whirl is approximately determined

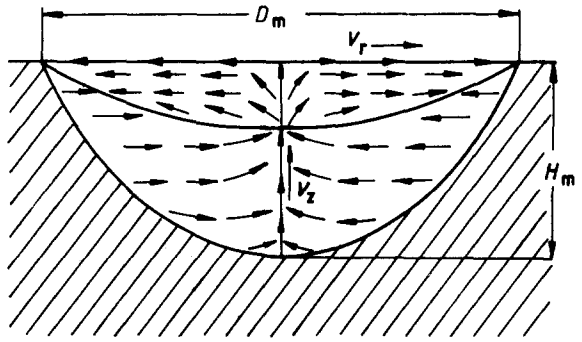

Figure 4 Velocity field (directions and senses of the velocity vectors) of the liquid phase of metal in the fusion $D_m > H_m$.

by the following coordinates: $r_c \approx \frac{1}{2}r_m = \frac{1}{4}D_m$, $z_c \approx \frac{1}{3}H_m$.

It results from calculations that, in the fusion, $D_m \approx 600$ μm and $H_m \approx 60$ μm at a velocity of the whirl, $v \approx 2\,m\,s^{-1}$. A complete rotation of the whirl which introduces the alloying material takes place in the time $t \approx 2.5$ ms. A case is possible where, in the process of alloying, the dependence $v_z < \partial S/\partial z$ occurs, which leads to the detachment of the whirl from the interphase (see Fig. 7). It is obvious that uniformity of the concentration distribution of the alloying material will be greater if, during the whirl, the alloying material makes more than one complete rotation. It can be easily obtained by using lasers of continuous action.

3. Experimental results

Experimental investigations were carried out for the samples in which nickel was the base (fundamental) material and gold was the alloying material. Two kinds of samples, which differed from each other in the manner of formation of a gold layer on the nickel surface, were tested. In the first series of samples, a gold layer was deposited by the method of vacuum evaporation. In the other, a gold foil 20 μm thick was pressed into the nickel surface. The alloying was carried out in air, by means of a YAG:Nd pulse laser of

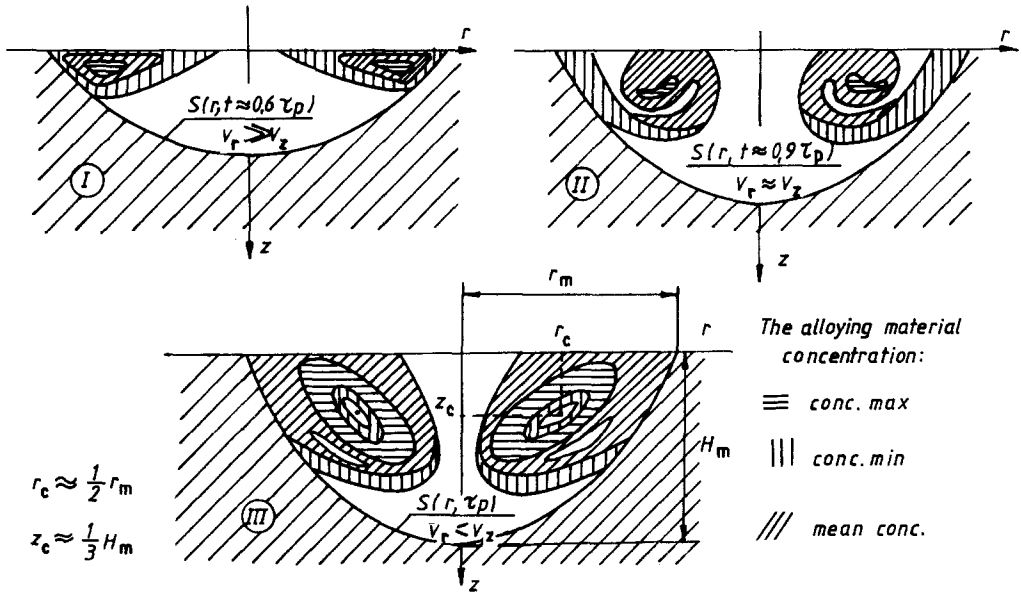

Figure 5 Graphic image of the change in the alloying material concentration in the alloying process ($t_m < t \leqslant \tau_p$). Pulse duration $\tau_p \approx 4$ ms.

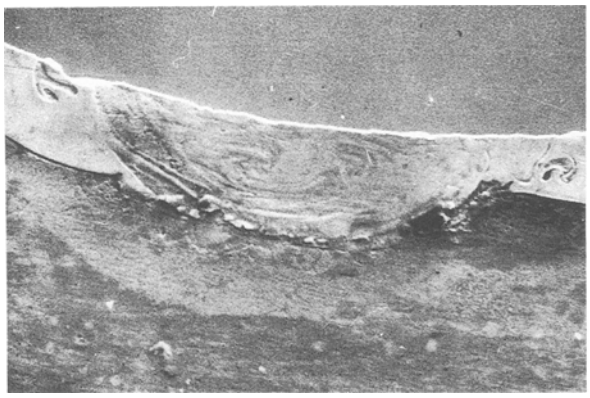

Figure 6 Image of whirl formed while alloying by a laser pulse: $E_p = 6.8$ J, $\tau_p = 4$ ms, $D_0 \approx 600$ μm.

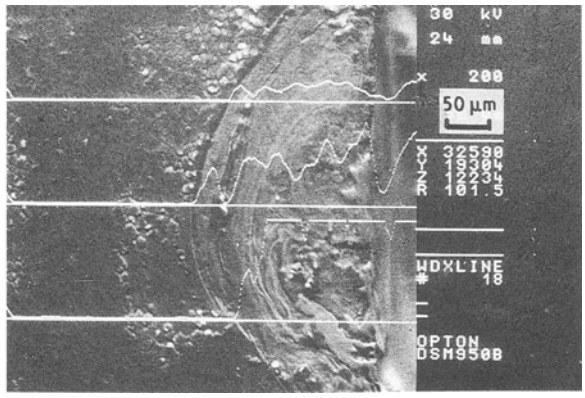

Figure 8 Relative distribution of concentration of the alloying material (gold) in the nickel sample of the dimensions $D_m \approx 600$ μm. $H_m \approx 200$ μm.

the pulse parameters: $E_p \leqslant 15$ J, $\tau_p \leqslant 4$ ms. Then the structure of the area alloyed and the alloying material concentration distribution in the area alloyed were studied. To do this, appropriate sections of particular single fusions were made and then the fusion surfaces were subjected to mechanical working and chemical treatment.

Microscopic studies of the sample sections confirmed high conformity of the real image of the area alloyed (Figs 6 and 7) with the theoretical one (Fig. 5). In the alloyed area (Fig. 6) of the dimensions $D_m/H_m \approx 5$, the centre of the whirl ($v = 0$) is at the point whose coordinates have the following values: $z_c \approx 0.4H_m$, $r_c \approx 0.15D_m$. The discrepancy between the experimental values of z_c and r_c and the theoretical values ($z_c \approx 0.33H_m$, $r_c \approx 0.25D_m$) is fully justifiable considering the simplifications made for the theoretical analysis.

The image of the section of the alloyed area observed in an optical microscope (Fig. 7) reveals areas of different degrees of concentration of the alloying material. This image is very similar to the theoretical image (Fig. 5c). It also reveals the case when $\partial S/\partial z > v_z$, which occurred in the final phase of alloying. As a result, the whirl of the liquid metal (with the alloying material) detaches from the interphase (from the fusion bottom). An X-ray analysis of the concentration distribution of the alloying material shows, in numerous cases, occurrence of asymmetry in the concentration distribution. A frequent case of asymmetry is shown in Figs 8 and 9. Determination of the causes of this phenomenon requires additional studies. It can be supposed that its primary cause is the temperature distribution in the area heated other than the Gaussian distribution assumed for the theoretical analysis.

On the other hand, no dependence of these phenomena on the manner of preparation of the surface layer (i.e. vacuum evaporation or pressing in a foil) has been found. However, a relationship has been found to exist between the maximum concentration of the alloying material and the manner of preparation of the alloying material surface. In the case of the surface of vacuum-evaporated alloying material, the alloying material concentration in the area alloyed does not exceed a few per cent. If, however, a gold foil (~ 20 μm) is pressed into the sample surface in the layer of the alloying material, then after alloying, concentration of ~ 40 % occurs in the area alloyed. The result of a quantitative microanalysis for such a case is presented in Fig. 10.

4. Conclusions

1. The thermocapillary mechanism is decisive in the determination of the concentration distribution of the alloying material in the area alloyed.

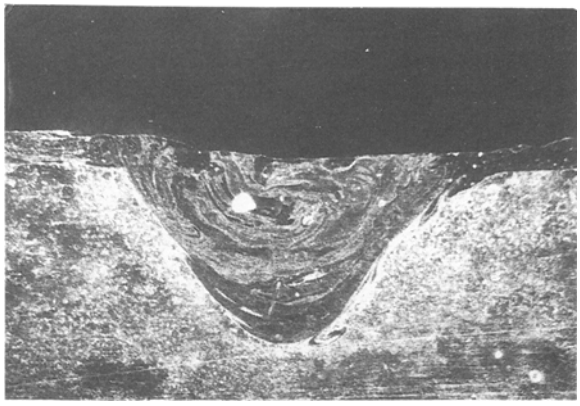

Figure 7 Image of detachment of the whirl from the interphase at $v_z < \partial S/\partial z$ while alloying by a pulse of the parameters: $E_p = 8.2$ J, $\tau_p = 4$ ms, $D_0 \approx 600$ μm.

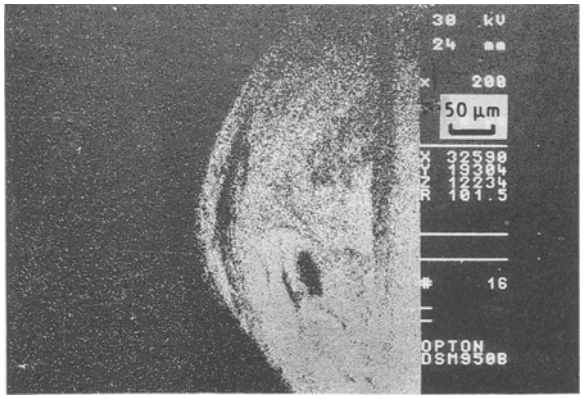

Figure 9 The mapping of concentration of the alloying material (gold) in the alloyed area of the nickel sample.

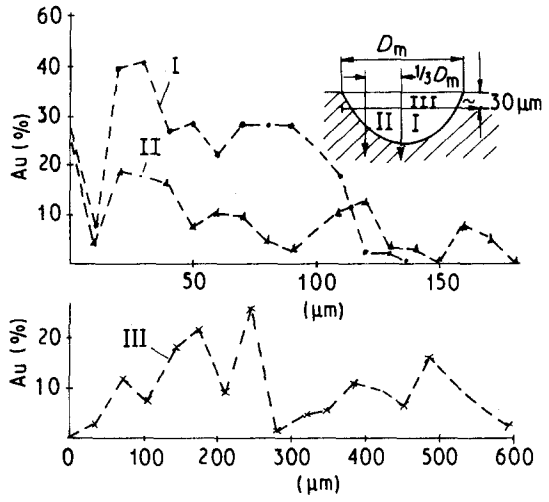

Figure 10 Results of microanalysis of the concentration distribution of the alloying material (gold) in the cross-section of the area alloyed. The alloying was achieved from the solid phase: gold foil (~ 20 μm) pressed into the nickel sample surface.

2. Theoretical analysis of the alloying process based on a simplified model yields results which are in agreement with the experimental results to a satisfactory degree.

3. Alloying with a pulse laser flux of the duration $\tau_p \leqslant 4$ ms opens up the possibility of distributing the alloying material over the whole area alloyed.

4. Relatively high concentrations of the alloying material in the area alloyed ($\leqslant 40\,\%$) can be obtained if a thin gold foil (~ 20 μm) has been pressed into the sample surface.

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