Laser alloying in innovative intermetallic compounds making

I. Smurov, C. Dupuy, R. Flamand, M. Ignatiev, L. Covelli

► To cite this version:

I. Smurov, C. Dupuy, R. Flamand, M. Ignatiev, L. Covelli. Laser alloying in innovative intermetallic compounds making. Journal de Physique IV Proceedings, 1994, 04 (C4), pp.C4-143-C4-146. 10.1051/jp4:1994431 . jpa-00252694

HAL Id: jpa-00252694

<https://hal.science/jpa-00252694>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Laser alloying in innovative intermetallic compounds making

I. SMUROV, C. DUPUY*, R. FLAMAND*, M. IGNATIEV** and L. COVELLI***

Ecole Nationale d'Ingénieurs de Saint-Etienne, 58 rue Jean Parot, 42023 Saint-Etienne cedex, France

** Institut de Science et de Génie des Matériaux et Procédés, CNRS, 66125 Font-Romeu cedex, France*

*** Institute of Metallurgy, Russian Academy of Sciences, Leninsky Prospect 49, 117334 Moscow, Russia*

**** Istituto di Tecnologia Industriali e Automazione, CNR, viale A. Lombardia 20 A, 20131 Milano, Italy*

I. INTRODUCTION

Concentrated energy fluxes, such as laser, electron beam, etc, have unique possibility for fast melting and intensive remixing of alloying elements (for example, [1,2]), these processes are characterized by extremely high cooling rates that are able to quench the melt. As a result nonequilibrium and metastable phases could be obtained. For example, composition of Ni-Hf alloys produced by laser cladding process exceeds the equilibrium solid solubility limit [3].

Usually, the following ways are used to insert alloying elements into the zone of laser beam interaction with base material: from pre-deposited coatings; by powder flow; from gas phase; from the layer of transparent fluids. As a rule, these methods are not efficient for laser alloying when components with big differences in physical properties need to be remixed.

In the present article several original solutions are proposed to solve this problem, among them: (a) combined action of the different types of lasers (for example, pulse-periodic and continuous wave lasers); (b) using of shielding covers to avoid the destruction and evaporation of alloying element from the surface of base metal; (c) initial preparation of thick (more than 100 μm) multilayers coatings ("puff-pastry") of alloying elements.

The following system "base metal-alloying element" are considered: Al-Sn(In), Fe-Sn(In,Pb), Al-Fe. Here base metal is indicated on the first position, alloying element - on the second, alternative alloying element - in the brackets.

2. EXPERIMENTAL PROCEDURE

2.5 kW carbon dioxide ($\lambda=10.6 \mu\text{m}$) and Nd:YAG pulse-periodic ($\lambda=1.06 \mu\text{m}$, pulse duration 0.1-15 ms, pulse energy 1-30 J) lasers were used in the experiments. During laser treatment Ar gas was used to protect metal surface from oxidation. The samples have been specially prepared before treatment by the methods which were mentioned above. The pure metals including less than 0.1% of impurities were used. Cross-sections of the treated samples were metallographically polished and etched to allow microstructural examination and microhardness measurements. The distribution of elements in the laser treated regions was examined using CAMEBAX X-ray microprobe.

Simultaneously with continuous wave laser the pulse-periodic laser was involved in combined action processes [4]. Irradiation of solid state laser was delivered through an optical fiber. CO₂ laser beam was oriented normally to the surface, Nd:YAG to the angle of 45°. The main idea of combined laser-laser action in alloying is to use high power CO₂ laser (power $P \approx 2.5 \text{ kW}$, energy density flux $q \approx 10^3 \text{ W/cm}^2$) for melting and pulse-periodic Nd:YAG laser (average power $P \approx 200 \text{ W}$, energy density flux $q \approx 10^5 \text{ W/cm}^2$), with high energy density flux, for melt remixing. By this method it is possible to reduce the destruction of alloying elements on the irradiated surface, intensify melt convection and, as a result, obtain higher and more uniform concentration of alloying elements in the molten pool. From a general point of view this is an opportunity to separate and control independently both the melting process and the remixing one.

As a conclusion, the main steps to make innovative materials by laser alloying [5] are the following: (a) to melt and to remix the materials in an optimum way to obtain the required composition (or required range of compositions) of elements in a molten pool; (b) to cool (quench) the melt quick enough to fix nonequilibrium and metastable phases.

3. RESULTS AND DISCUSSION

3.1. SYSTEM Al-Sn(In)

According to equilibrium phase diagram for Al-Sn these elements are not miscible in solid state. The attempt to mix Al with Sn is interesting for: (a) investigations of peculiarities of mass transfer in laser making of advanced alloys; (b) from practical point of view to make alloy with high performance properties.

The typical modified zone, obtained in our experiments, is sufficiently uniform. There are small (0.7-1.5 μm) Sn-rich precipitations ("white" regions) in matrix of melted pool. Most of these inclusions have practically spherical shape at the top and middle part of molten pool. The elongate needles of Sn-rich regions (directed along the temperature gradient) are observed at the bottom of alloyed zone. The presence of Sn-rich precipitations is explained by full miscibility in liquid state in total range of concentrations (at temperature higher 930K) and full immiscibility in solid state. The combined action of CO₂ laser and Nd:YAG pulse-periodic laser sharply intensify the convective mass transfer. It leads to uniform distribution of alloying element in the molten pool. The fast cooling of the melt leads to formation of Sn-rich precipitations. The average Sn concentration was measured on the square 10x10 μm by X-ray microprobe analysis. It varies in the range 19-23 wt.%. The presence of Sn (2-3 wt.%) was also found in the matrix itself. SEM examinations did not reveal any nonhomogeneity of matrix at magnification up to 8000. Unconditionally, it is most interesting part of alloyed zone for more detail investigations to clarify up the possibility of formation of nonequilibrium solid solution of Sn in Al.

Sn was not found inside the treated zone when only CO₂ laser was used. In case of action of pulse-periodic laser only, the distribution of Sn was strongly nonuniform. In some regions the average Sn concentration have reached 31 wt.%. and, as a rule, the size of Sn-rich precipitations was smaller (about 0.7 μm).

Al and In are also not miscible in solid state, but in comparison with Al-Sn system, there exist the region of immiscibility in liquid state (between 930K and 1180K). The structure of alloyed zone is different from the structure of Al-Sn alloys discussed before. It consists of two strongly contrasted regions that for convenience could be named as "white" and "black" areas. The size range of the first ones is 0.8-4 μm , the second ones are smaller: 0.4-1.5 μm . Black areas are strongly chemically etched. The average concentration of In varies from 1 up to 7 wt.%. Maximum concentration is observed at the top part of melted pool, minimum - at the bottom. There are a lot of spherical pores, probably as a result of gas bubbles solidification inside the molten pool. At the pool's bottom In was found (about 1 wt.%) only near these pores.

Using only CO₂ laser leads to the decrease of total amount of In: only 3 wt.% are observed near the surface of treated layer.

Big difference between the results of laser alloying for systems Al-Sn(In) may be explained by the presence, in one case, of immiscibility domain in liquid phase (Al-In) and full miscibility in liquid phase in the other case (Al-Sn). Note, that the observed maximum of In concentration in the alloyed zone is not far from the lower limit of mutual (Al-In) immiscibility in liquid phase.

3.2. SYSTEM Fe-Sn(In,Pb)

The proposed method concerns with using Cr as a shielding cover to avoid the destruction and evaporation of soft metals coatings. Two systems have been chosen for investigations: (1) 50 μm Cr layer on 70 μm Sn layer; (2) 50 μm Cr layer on 50 μm Sn

layer. Pure iron was used as a base material. The energy and pulse duration of pulse-periodic laser were varied from 5 to 8 J and from 6 to 14 ms, respectively.

Analysis of cross sections of treated zones have shown the sharp influence of: (a) pulse energy, (b) pulse duration, and (c) thickness of Cr and Sn layers, on the depth of melting pool and concentration of alloying elements. Laser alloying is practically absent at 8 J pulse energy and 14 ms pulse duration for system $50\text{ }\mu\text{m Cr}+70\text{ }\mu\text{m Sn}$. In this case, Cr shielding cover was partially destroyed and overheated Sn melt have flowed out. Only thin layer (about $30\text{ }\mu\text{m}$) of Fe was melted. Laser alloying of required quality could not be reached at any variations of treatment parameters (inside the above mentioned range) for given thickness of the coatings. Two typical situations were observed: (1) destruction of shielding cover and expulsion of overheated Sn melt; (2) formation of alloyed zone with strongly destroyed top part.

A small decrease of Sn coating thickness (from 70 to $50\text{ }\mu\text{m}$) allows to optimize the alloying process. The distribution of Sn and Cr becomes enough uniform (fluctuations of concentrations less than 0.5 wt.%) except for individual comparatively large inclusions of pure Sn. Note, that the fluctuations of alloying elements concentration sharply increase up to 5 wt.% at lower pulse energy and shorter pulse duration; microhardness in remelted zone varies from 330 to 450 Hv. One of the advantages of pulse and pulse-periodic laser alloying is the opportunity to vary easily the concentration of alloying elements and the dimensions of melted pool by the parameters of laser pulses. For example, it is possible to obtain maximum Sn concentration up to 30 wt.% at $150\text{ }\mu\text{m}$ depth (maximum equilibrium solubility of Sn in Fe is 18 wt.% at 900°C and 7 wt.% at 600°C). The corresponding microhardness can reach 600 Hv.

In case of CO_2 laser alloying of Fe with In, the molten pool consists of two alternating strongly contrasted regions (size $1\text{-}2\text{ }\mu\text{m}$). The average In concentration varies from 3 up to 7 wt.%. The equilibrium miscibility of In in Fe is less than 1 wt.% in solid state. Intensive remixing of Fe and In in the molten pool, that is followed by fast cooling, leads to exceeded solid solution of In in Fe. The main feature of equilibrium phase diagram for these system is wide range of immiscibility in liquid state (from 6.5 wt.% up to 95 wt.% in temperature range 1770-2050K). The maximum In concentration in alloyed zone is close to its lower limit of immiscibility with Fe in liquid state. The same situation was also observed for system Al-In (see previous chapter) which zones of alloying have the similar structure.

The Fe and Pb are not miscible both in solid and in liquid phase. The conventional methods (including traditional laser action) are inefficient to remix Fe and Pb. The forces of chemical nature on the atomic level prevent the remixing of these elements in the melt. The above mentioned methods were used to solve this problem. As a result, cross section of the alloyed zone consists of an elliptical shape region of pure Pb surrounded from all the sides by pure Fe. Small alloyed Fe-Pb regions were found in the different parts of their boundary. It is, as a rule, thin ($20\text{-}30\text{ }\mu\text{m}$) layers with 4-7 wt.% of Pb concentration. For example, this layer is located near the bottom of treated zone and Pb concentration fluently varies from 100 wt.% (top region) to 7 wt.% (near the border with base material). SEM investigations at 8000 magnification did not reveal any nonhomogeneity of the above mentioned layer. Probably, remixing of Fe and Pb was reached inside the metastable overheating melt (in spite of thermodynamic barrier of mutual immiscibility of Fe and Pb in liquid phase at equilibrium conditions) which was produced inside the bulk of base material by our method. Later the composition was fixed by extremely high cooling rates, that realised inside the bulk of base material.

3.3. SYSTEM Al-Fe

In our experiments typical modified zone consists of two regions: (a) upper part of melted pool which has the usual shape; (b) down part - narrow and deep as if in case of deep penetration welding. Al distribution is practically uniform (13-14 wt.%) in the region (a). Its structure corresponds to Al-Fe solid solution plus AlFe_3 ; microhardness varies in the range 400-450 Hv. Fe distribution in the region (b) is nonuniform and varies from 4 to 12

wt.%. There are a lot of Fe-rich inclusions inside of zone (b) : small "needles" at the top part and large "drops" near the bottom. Probably the needles at the top part of zone (b) are the result of the movement of large drops from the region (a) into the bottom of region (b). The high cooling/solidification rates fixed these needles inside the melt. The microhardness of the region (b) is also quite nonuniform and varies in the range 700-1400 Hv (it depends on the process parameters). Maximum value of microhardness (1400 Hv) correspond to the maximum value of Fe concentration (12 wt.%) and was found in the strongly contracted with the surrounding material areas of "white" colour : or in the above mentioned "drops", or near melted pool boundaries in zone (b). The dimensions of these areas can reach up to 70x100 μm . The behaviour of Al-Fe alloy from the above mentioned areas, during annealing at temperature 730K associated with small (about 10%) increase of microhardness and did not reveal any other changes. Probably, the main reason of a little microhardness increase was the formation and slow growth of the particles of metastable FeAl_6 phase. Note that this region could not be etched metallographically by Keller's reagents. The results of these preliminary investigations have shown that it is, probably, a supersaturated solid solution of Fe in α -Al formed in macro-volume (up to 70x100 μm).

4. CONCLUSIONS

1. Mixing of immiscible elements (Al and Sn) with small (0.7-1.5 μm) Sn-rich precipitations was observed inside of melted zone after combined action of two laser beams on Al-Sn system. The average Sn concentration in 10x10 μm region varies in the range 19-23 wt.%. Sn was also found in matrix itself (2-3 wt.%).

2. Pulse-periodic laser treatment of system "Cr shielding cover-Sn powder coating-Fe substrate" allows to reach extremely high depth with high uniformity of chemical composition of modified zone due to convective heat-and mass transfer by overheated Sn melt. Uniform Sn and Cr concentrations reach 10 wt.% and 10.9 wt.%, respectively, at optimum parameters of laser treatment. Maximum Sn concentration can reach 30 wt.% (maximum equilibrium solubility of Sn in Fe is 7% at 600°C).

3. Continuous CO_2 laser alloying for Fe-Sn system leads to formation of practically uniform alloyed zone. Preliminary observation indicates that it consists of metastable intermetallic crystals (Fe 59 wt.-%-Sn 41 wt.%) distributed in α -Fe solid solution of Sn (8 wt.%). Small (about 1-2 μm) inclusions of pure Sn are also observed in melted zone.

4. Laser alloying of Fe-In system forms in Fe substrate the composition consisting of two small (1-2 μm) alternating strongly contrasted regions with In concentration of 7 wt.% and 3 wt.% respectively (equilibrium miscibility less than 1 wt.%).

5. Remixing of Fe and Pb can be realized in spite of thermodynamic barrier (immiscibility in liquid phase at equilibrium conditions). Pb concentration can reach 7 wt.%.

6. For Al-Fe system laser remelting can lead to the formation of Al-base composition (Fe concentration 4-12 wt.%) with very slight response to etching and extremely high microhardness (800-1400 Hv). Probably it indicates on formation of supersaturated solid solution of Fe in Al.

7. For the systems with a region of immiscibility in liquid phase (for example, Al-In, Fe-In), maximum concentration of alloying element (In) in the melted zone is close to its lower limit of immiscibility. Zones of alloying have the similar structure for both systems.

References

1. G.Herziger and E.W.Kreutz, Phys. Scripta T 13 (1986) 139.
2. C.W.Draper, J.M.Poate, Int. Met. Rev., 30 (1985) 85.
3. A.Kar and J.Mazumder, Acta Metall., 36 (1988) 701.
4. I.Smurov, L.Covelli, Proc. of the IVth European Conference on Laser Treatment of Materials (ECLAT-92), Göttingen, 1992 (DGM, Oberursel, 1992), p. 251.
5. I.Smurov, G.Flamant, L.Covelli, M.Ignatiev, E-MRS 1993 Spring Meeting, Final Book of Abstracts, F-11/P25.