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Formation of Aluminium Surface Layers' Structure during Laser Alloying with Copper and Cobalt Powders

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Possibility of quasi-crystal decagonal phase formation in the surface layers of aluminium during laser alloying is demonstrated. Alloying is carried out by mixture of copper and cobalt powders with atomic ratio 1:1. The phase state of laser alloying zone is thermally stable up to the temperatures close to the matrix melting point.

Показано можливість одержання квазикристалічної декагональної фази в поверхневих шарах алюмінію при лазерному леґуванні. Леґування виконувалося сумішшю порошків міді і кобальту з атомним відношенням 1:1. Встановлено, що структурно-фазовий стан зони леґування характеризується термічною стійкістю аж до температур, близьких до температури топлення матеріалу матриці.

Показана возможность получения квазикристаллической декагональной фазы в поверхностных слоях алюминия при лазерном легировании. Легирование выполнялось смесью порошков меди и кобальта с атомным отношением 1:1. Установлено, что структурно-фазовое состояние зоны легирования характеризуется термической устойчивостью вплоть до температур, близких к температуре плавления материала матрицы.

Key words: annealing, laser treatment, aluminium alloys, phase diagram, quasi-crystals.

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1. INTRODUCTION

The wide use of aluminium and its alloys is limited by inconsistency of some of its technical properties (such as hardness, wear resistance, etc.) with high technological requirements. The imperfection of construction properties of investigated materials can be compensated by formation of particular structures in surface layers.

Quasi-crystalline (QC) alloys are characterized by complex of special physical (mechanical, thermal, *etc.*) and chemical properties. These properties determine possible applications of such materials. There is a number of methods (thermal and electron beam deposition, *etc.*), which allow to produce the quasi-crystalline coatings [1]. The resulting coatings are characterized by high brittleness and relatively low adhesion to the matrix material.

Most known QC-phases are formed in alloys of the Al–Cu–TM (TM — transitional metals: Fe, Co, Cr, Mn), where Al is the basic element of chemical compound. The formation of most of these alloys occurs in the process of non-equilibrium crystallization. In this regard, the wide prospect has the method of laser surface alloying of aluminium and its alloys by a mixture of transition metals powders. This method allows to produce the coatings with high adhesion to the matrix material.

The authors of Refs [2, 3] have already demonstrated that the method of aluminium laser alloying by copper and iron powders mixture can be used to obtain wear-resistant coating. It is known [4] that quasi-crystal decagonal phase (D-phase) can be formed in the ternary Al–Cu–Co alloys in a narrow range of component concentrations.

2. MATERIALS AND METHODS

The commercially pure aluminium (99.80 at.% Al, 0.12 at.% Fe, 0.10 at.% Si, 0.01 at.% Cu, 0.04 at.% Zn, 0.02 at.% Ti) samples with size $10\times5\times5$ mm^3 have been used for laser alloying. Chemical ratio between components in the mixture for alloying was approximately 1:1 (in at.%), which corresponds to stoichiometry of the decagonal phase $Al_{65}Cu_{15}Co_{20}$. Fraction size of alloying powders did not exceed 50 μm. Laser alloying was carried out by the method described in Ref. [5]. A Nd:YAG pulsed laser was used ($\lambda = 1.06$ μm, pulse duration $\tau = 3$ ms, laser power density $q = 330$–850 MW/m^2). Alloying layer depth was 130–140 μm. Phase composition of the laser-alloying zone was studied by X-ray diffraction (CoK_α), metallographic and micro-hardness analyses. Indexing of the diffraction patterns, which correspond to D-phase, was performed using three indices, according to the method proposed in Ref. [6].

3. RESULTS

According to Ref. [7], non-equilibrium crystallization conditions at extremely high cooling rates can promote formation of QC-phases. However, the narrow range of homogeneity and mainly peritectic type of reaction complicate the formation of these phases [8–10]. Pulsed laser alloying is accompanied with the formation of highly dispersed structures in laser alloying zone due to high cooling rate of the melt (~ 10^4 K/s for this laser [11]). The structure of the surface layer of the samples has a quite heterogeneous chemical composition. That is caused by the following factors: high temperature gradients arising in the process of quenching of the melt, the Marangoni–Gibbs capillary effects in the laser alloying zone [12] (Fig. 1). These features of the structure obtaining during the laser alloying can contribute to the creation of time–concentration conditions necessary for the formation of QC-phase in some parts of the laser-alloying zone.

X-ray diffraction data show that three phases exist in the laser-alloying zone: aluminium-based f.c.c. solid solution (α-phase), monoclinic phase $Al_{13}Co_4$ and quasi-crystalline D-phase (depending on different laser power density). However, the reflections corresponding to the D-phase were fixed at values $q = 330$ MW/m^2 (Fig. 2). A further increase of the values did not result in a significant change of the phase composition. We noted a certain increase in the intensity of the diffraction patterns of monoclinic and quasi-crystalline phases with the rise of q values. According to metallographic analysis, inhomogeneous heterophase disperse structure was actually formed in the laser alloying zone. It was difficult to identify precisely the phase components with optical microscopy method.

Not only stable but also metastable phases can be formed in laser alloying zone due to ultra-high cooling rate of the melt. Hence, it is nec-

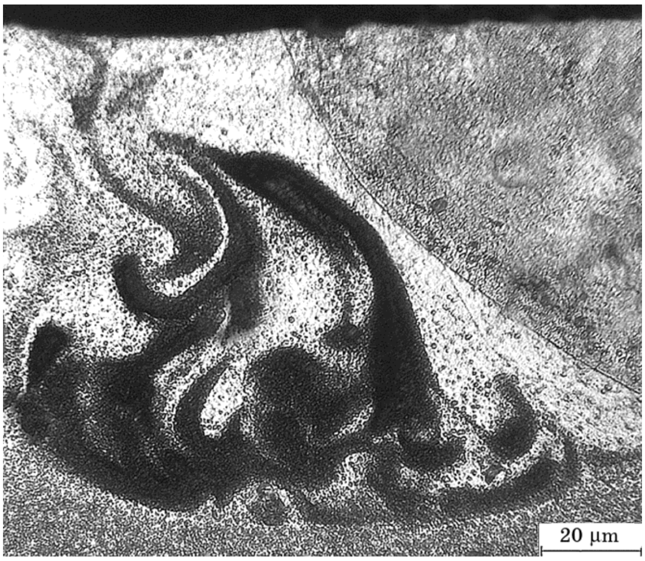


Fig. 1. General view of laser alloying zone (alloyed depth $d = 130–140$ μm, power density $q = 850$ MW/m^2).

essary to investigate thermal stability of phase composition of the laser-alloying zone. It is important, because decomposition of metastable components may lead to changes in physical and mechanical properties of the alloyed surface layers. Thermal stability of phase composition is checked by isothermal annealing between 573 and 873 K. The higher limit of the temperature range was approximated to the melting temperature of the matrix.

X-ray data demonstrate that after annealing at 573 K phase composition is following aluminium-based f.c.c. solid solution (α-phase), monoclinic phase $Al_{13}Co_4$, quasi-crystalline D-phase, and small amount of Al_3Cu_2 and Al_7Cu_2Co phases (Fig. 3, *b*–*e*). No significant changes in the phase composition with increasing of annealing temperature are not observed. Only redistribution of the intensities of lines for α-phase and some increase of the diffraction maximums intensity of QC-phase was detected. Evidently, it is caused by the relaxation processes in the laser alloying zone structure and gradual decrease of its texturing. Probably, it is caused by the intensification of diffusion processes dur-

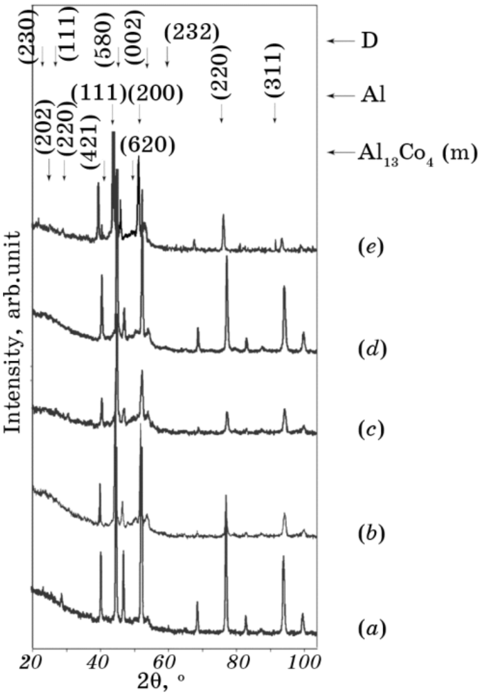


Fig. 2. Diffraction patterns of the samples after laser alloying with the laser power density: 330 MW/m^2 (*a*), 400 MW/m^2 (*b*), 630 MW/m^2 (*c*), 750 MW/m^2 (*d*), 850 MW/m^2 (*e*).

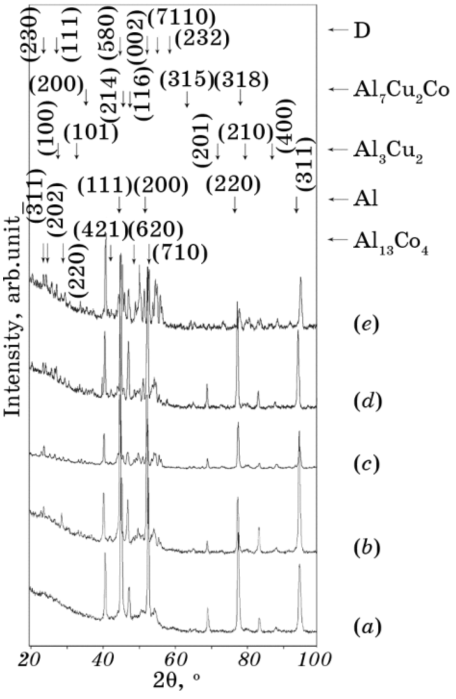


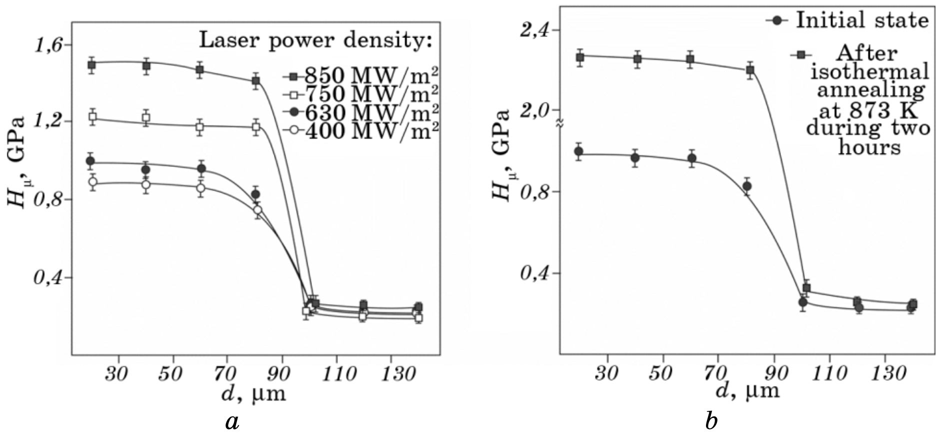
Fig. 3. Diffraction patterns of the samples in initial state after laser alloying (*a*) and after annealing during 2 hours at: 573 K (*b*), 673 K (*c*), 773 K (*d*), 873 K (*e*).

ing the annealing, and, as a consequence, by redistribution of chemical elements in the laser-alloying zone. Hence, the concentration area can arise in the surface layer which stoichiometry is close to the stoichiometry of decagonal phase $Al_{65}Cu_{15}Co_{20}$.

It should be noted that the view of phase diagrams could significantly change at ultra-high cooling rate of the melt. Therefore, the formation of solid solutions with a high degree of supersaturation is possible. Indeed, in such conditions the solubility of cobalt and copper in aluminium can reach 7 at.% and 35 at.%, respectively [13]. Precision measurements of α-phase lattice parameter ($a = 0.40450$ nm) show that it decreases compared with the lattice parameter of the matrix ($a = 0.40498$ nm). Evidently, this decrease is caused by supersaturating with copper. Isothermal annealing at different temperatures resulted in the decomposition of supersaturated solution, which accompanied by copper segregation. This fact can be the cause of formation of additional intermetallic phases.

Microhardness values H_μ in laser alloying zone in the initial state (immediately after laser alloying) were higher as compared with microhardness values of the matrix (Fig. 4, *a*). This may be caused by several factors: a) high dispersivity of structure (accompanied by increase of the total length of grain boundaries), b) existence of intermetallic dispersed phases and QC-phase.

After annealing, the dependence $H_\mu(d)$ is not fundamentally different from those in the initial state. However, the values of H_μ after annealing were 1.5 times higher than those in the initial state (Fig. 4, *b*). Significant contribution to the rise of H_μ values can give: a) additional intermetallic dispersed phases, which were formed as a result of α-



a *b*

Fig. 4. Microhardness distribution along depth of laser alloying zone end after treatment with different laser power densities (*a*) and after thermal treatment (*b*).

phase decomposition; b) some increase of amount of QC-phase.

So, laser-alloying method can be used to form heterophase structure in the surface layers of matrix material. One of the components of laser alloying zone is a D-quasi-crystalline phase. This phase state is characterized by thermal stability of laser alloying zone up to melting point of the matrix material.

4. CONCLUSIONS

1. Aluminium laser alloying by mixture of copper and cobalt powders with atomic ratio of 1:1 leads to the formation of dispersed heterogeneous structure in surface layers of matrix. One of the components of laser alloying zone is the quasi-crystalline decagonal phase.
2. Quasi-crystalline decagonal phase is formed by laser alloying method and it is thermally stable at the temperatures close to the melting point of aluminium matrix.

The decomposition of supersaturated α-phase during annealing leads to formation of dispersed intermetallic phases. The presence of intermetallic phases causes the rise of the average values of H_μ in the laser-alloying zone.

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