Structure features of the composite materials Inconel 625/TiC, produced by LMD method

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Abstract. In this paper, the metal composite material Inconel 625/TiC with 20 % carbide content produced by laser metal deposition (LMD) method was investigated. The initial powders were in three various states: they were fed from single flasks; they were previously mixed in a gravitational mixer or in a planetary ball mill. It was shown that only composites obtained from the powders previously mixed in a planetary ball mill had no cracks. At usage the powder in another states, grown composites had magistral cracks. When cracks did not arise, the carbide particles TiC had initial spherical shape and initial composition. In those cases when cracks appeared, the carbides have dendritic shape, and their composition are changed. Investigation of the powder materials showed that during mixing the individual particles of the Inconel powder are covered with layer of titanium carbide. As a result, the thermophysical properties of Inconel powder are changed, and an energy required for recrystallization of the Inconel powder is increased.

1. Introduction

Recently, the application area of composite materials, which contain ductile metal matrix reinforced with hardening particles, is expanding.

One of the perspective ways to manufacture these objects is laser metal deposition (LMD) [1, 2]. This method is based on the formation of a local melt bath in a metal substrate under the influence of laser action and the coaxial feeding of the powder materials into the bath of the melt. The recrystallized powder forms a microregion of the whole construction. Scanning along the surface of the substrate, the laser with powder forms the profile of the construction. Then the next higher profile of the construction is formed. And the process ends by the layered synthesis the whole volume of the construction [3].

However at the using of LMD method the macrodefects (cracks, porosity) can arise in the melting composite. The quality of the formed objects depends on many parameters of LMD process, namely, a
laser power, a scan speed, a laser spot diameter, a melting strategic, a protective atmosphere etc. Besides the powder state – its size, shape and microstructure have a great influence on structure and properties of melting objects. There is an opinion that mixing powders in a planetary ball mill results to more homogeneous distribution of the reinforced particles over the matrix and decreasing of macrodefect concentration [4-6]. However the nature of positive influence mixing in a planetary ball mill has not been studied enough. From this point of view, investigation of influence of the powder initial state on the recrystallized object quality is very important.

2. Material and experimental methods
In this paper, composite material grown by LMD method was a matrix from the nickel alloy Inconel 625 reinforced with titanium carbide TiC. The composition of the nickel alloy is shown in Table 1. The nickel alloy powder was obtained by gas atomization and the carbide powder TiC – by self-propagating high-temperature synthesis. The dispersibility of the powders of the nickel alloy and titanium carbide was 50-140 and 20-50 μm, respectively. At the formation of composite Inconel 625/TiC, powders were used in ration of 80 % Inconel and 20 % TiC carbide; this ration is recommended in the literature as optimal [7].

| Table 1. Chemical composition of Inconel 625 alloy |
|-----------------------------------------------|
| Concentration of elements, mass.%            |
| Cr   | Mo  | Fe  | Nb  | Co  | Mn  |
| 20.0-23.0 | 8.0-10.0 | <5.0 | 3.2-4.2 | <1.0 | ≤0.5 |
| Si   | Al  | Ti  | C   | Ni  |     |
| ≤0.5 | ≤0.4 | ≤0.4 | ≤0.1 | basis |

The powders in the three different states were used for melting samples:
1) the initial powders Inconel 625 and TiC were fed from single flasks;
2) the initial powders Inconel 625 and TiC were previously mixed in a gravitational mixer with a rotation speed of 60 rpm for 4 h;
3) the powders were mixed in a planetary ball mill with a rotation speed of 200 rpm using balls from the steel Fe-1%Cr-1%C; a milling time was 8 h.

The samples were prepared using the following parameters of the process LMD: the scan speed was 500 mm/min; the laser spot diameter was focused at 1 mm; the laser power were varied at 400, 600, 800 and 1000 W; parallel melting strategic was used; powder was carried by argon; powder feeding rate was 3 g/min; carbon steel Fe-0.2%C was a substrate.

The structure of both powders in the different states and the recrystallized composites were studied by methods of metallographic and X-ray analysis, scanning electron microscopy and microspectral X-ray analysis. X-ray phase analysis was carried out in Co Kα radiation in the range of diffraction angles 20=125. The parameters of the crystal lattices were determined from the diffraction maxima Ni (311) and TiC (420) with ± 0.0003 Å the error of determination.

3. Results and discussion
Figure 1 shows the structure of composite material grown by the LMD method from powders in different states (laser power P = 800 W). In composite structures, there is a light matrix consisting of a nickel alloy, and dark gray TiC particles. In the structures of samples of composite materials obtained with a separate feed of powders and mixing of powders in a gravitational mixer, there are magistral cracks (Fig. 1 (a, b)). In the case of mixing powders in a planetary ball mill, they are absent (Fig.1(c)). At other values of laser power (P = 400, 600 and 1000 W), the same results can been observed: the melting layer does not have cracks only when using a powder that was previously mixed in a planetary ball mill.
Two zones can be identified in the observed structures: a zone with spherical dark gray TiC particles and a zone without them (zones I and II in Fig. 1 (b)). Figure 2 shows the structures of these zones. It can be seen from the figure that in zone I there are partially dissolved initial agglomerates with a highly branched surface and high porosity, as well as small (micron) carbide crystals uniformly distributed over the matrix (Fig.2(a)). In zone II, dark grey TiC carbides have dendritic shape (Fig.2(b)). It can be seen from Figure 1(a, b) that in the samples obtained with a separate feed of powders and mixing of powders in a gravitational mixer, zone I is of short length, it adjoins directly to the substrate. Samples obtained using mixing of powders in a planetary ball mill consist entirely of zone I (Fig.1(c)).

In addition, Figure 1 shows that cracks propagate only along the zone of dendritic carbide crystals, when the transition to the zone with carbides of the initial spherical form, the propagation of cracks is
suppressed. In samples obtained by mixing powders in a planetary ball mill in which there is no zone of dendritic carbide crystals, there is no tendency to crack. The same result was observed in the experimental work [7], in which the structure of a composite material based on nickel and WC was investigated. The authors of the article observed the zones with carbide particles of different shapes. Except the morphology of the TiC particles, their composition also changes during recrystallization. Figure 3 shows the microstructures of Inconel 625/TiC composites, for the preparation of which powders were used in various initial states, and the experimental points at which microspectral X-ray analysis was performed, the results of microspectral X-ray analysis are shown in Table 2. According to the microspectral X-ray analysis, it was shown that when using a separate feed of powders, the carbide composition, in addition to Ti and C, includes the dissolved elements of the matrix Mo and Nb (point A, Table 2). In the case of mixing powders in a planetary ball mill, titanium carbide had its original composition (point F). In composite materials obtained by mixing powders in a gravitational mixer, both types of carbides are present in the structure - the initial composition (point C) and with dissolved elements from the Inconel matrix (point D).

**Figure 3.** Scanning electron microscopy of carbide inclusions: a) separate feed of powders; b) mixing in a gravitational mixer; c) mixing in a planetary ball mill; A, B, C, D, E, F, G – the points at which microspectral X-ray analysis was performed.

| Point | Concentration of elements, mass.% |
|-------|----------------------------------|
|       | C      | Ti     | Nb     | Mo     | Cr     | Ni     |
| A     | 26.2   | 40.7   | 13.2   | 15.9   | 2.3    | 1.8    |
| B     | –      | 7.0    | –      | 7.1    | 18.3   | 65.7   |
| C     | 21.9   | 78.1   | –      | –      | –      | –      |
| D     | 20.1   | 48.2   | 15.2   | 12.1   | 1.9    | 1.3    |
| E     | –      | 1.8    | –      | 4.1    | 14.0   | 41.0   |
| F     | 23.1   | 75.9   | –      | –      | –      | 1.0    |
| H     | –      | 2.0    | –      | 11.1   | 23.9   | 61.2   |
It can be assumed that in the spherical carbide zone, the TiC particles were not recrystallized during LMD, the initial powder particles were only ground and redistributed over the matrix. On the other hand, dendritic carbide particles were formed during laser growth under conditions of high cooling rate from the liquid state. Thus, it can be assumed that the formation of cracks in these composite materials is caused by recrystallization of the carbide phase. Perhaps the cause of the appearance of cracks are the thermal stresses arising from the simultaneous growth of crystals with different temperature coefficients of linear expansion.

To determine the nature of the influence of the powder initial state on the structure and properties of the composite material, including their tendency to form cracks, the phase-structural state of the powders was studied after different versions of their mixing. Figure 4 shows the diffractograms of a mixture of powders after different versions of their mixing.

![Diffractograms](image)

**Figure 4.** Diffractograms of mixture of powders: a) separate feed of powders; b) mixing in a gravitational mixer; c) mixing in a planetary ball mill.
Regardless of the state of the powders, the diffraction maxima of a solid solution based on Ni and TiC phase are observed on all diffractograms of the powders. However, it turned out that the quantitative ratio of the phases, determined from the intensity of the diffraction maxima, essentially depends on the variant of mixing the powders. So, after mixing the powders during the feeding from individual flasks, the amount of carbide calculated from the diffractogram corresponded to the loaded one, i.e. 20%; after mixing the powders in a gravitation mixer, the calculated amount of carbide was 50%; and after mixing in a planetary ball mill – 70%.

Investigation of the structure of individual powder particles, carried out by the SEM method and microspectral X-ray analysis, made it possible to explain the overestimated concentration of the carbide phase fixed in the diffractograms after preliminary mixing of the powders in a gravitation mixer and a planetary ball mill. Figure 5 shows the microimage of the cross section of the Inconel 625 powder particle after mixing in a planetary ball mill and the distribution of chemical elements along the depth of the surface layer of this particle. The results of microspectral X-ray analysis allow us to assert that on the surface of the Inconel particle there is a layer of titanium carbide several microns thick. It is possible that, during mixing in a planetary ball mill, dispersed TiC particles were incorporated into a softer Ni-based alloy powder. Since X-ray radiation penetrates into the metallic material to a depth of about 10-20 μm, partial adherence of carbide particles to the surface of the Inconel powder should result in a decrease in the relative intensity of the diffraction maxima of the nickel solid solution, which is observed experimentally. A similar, but weaker effect is observed when the powders are mixed in a gravitation mixer.

![Cross section of the Inconel particle](image)

*Figure 5.* Cross section of the Inconel particle (a) and the distribution of chemical elements along the depth of the surface layer of the particle (b, c).

Table 3 shows the parameters of the crystal lattice of a solid solution based on Ni and TiC $a_{Ni}$ and $a_{TiC}$, depending on the method of mixing the powders. It can be seen that the mixing of powders, especially in a planetary ball mill, results to decrease the period of the solid solution of nickel, while the lattice parameter of the carbide phase practically does not change with different methods of mixing the powders. Presumably, the decrease in the values of $a_{Ni}$ when mixing powders is associated with the redistribution of carbide-forming elements between a solid solution of nickel and TiC carbide. Atoms
Mo and Nb present in the Inconel can dissolve in the carbide in the sublattice of Ti in which perhaps there are vacancies. When atoms with a relatively large atomic radius leave the crystal lattice of nickel, its period decreases. This assumption is confirmed by the molybdenum spectrum obtained by the method of energy-dispersive microanalysis (Fig. 5(c)). Near the surface of the Inconel particle, where a layer of TiC carbide is observed, the relative concentration of Mo increases. The absence of influence of the method of mixing powders on the parameter $a_{Ni}$ is probably due to the fact that the redistribution of elements occurs only between the particles of the nickel powder and the adhered carbide layer, while the basic volume of the carbide powder retains its original composition.

| Method of feeding powders | Separate feed of powders | Mixing in a gravitation mixer | Mixing in a planetary ball mill |
|---------------------------|--------------------------|-------------------------------|-------------------------------|
| $a_{Ni}$, Å               | 3.5957                   | 3.5943                        | 3.5912                        |
| $a_{TiC}$, Å              | 4.5328                   | 4.5323                        | 4.5330                        |

Thus, the powder formed when mixed in a planetary ball mill differs significantly from the original in its structural state. Namely, the powder particles of the heat-resistant nickel alloy are partially covered with a layer of titanium carbide. In addition, with mechanical alloying, the elemental composition of the nickel matrix and carbide phase changes. Of course, these structural changes lead to a change in the physical characteristics of the powder, for example its heat capacity and thermal conductivity, which in turn will affect the energy of the laser radiation necessary for heating and melting the carbide and matrix components.

Conclusions

1. It has been established that in the synthesis of Inconel 625 / TiC composites by the LMD method using a separate feed of powders and premixing the powders in a gravitation mixer, the material tends to crack. But the mixing of powders in a planetary ball mill makes it possible to obtain a composite material without cracks.
2. It has been shown that when using a powder that has been mixed in a planetary ball mill, the carbide particles in the composite material structure have a spherical shape. When using a separate feed of powders and mixing powders in a gravitational mixer, carbide inclusions have a dendritic shape; the exception is the layer near the substrate, where the carbides are spherical.
3. It was found that the formation of cracks is observed only in the zone with the dendritic form of TiC carbides.
4. By the method of microspectral X-ray analysis, it is shown that as a result of preliminary mixing on the surface of particles of Inconel powder, titanium carbide sites alloyed with molybdenum are formed.
5. It was shown that when the powders were premixed, the period of the crystal lattice of the nickel solid solution decreased, which was due to a redistribution of the alloying elements between the solid solution and the carbide shell of the powder particles.

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