About Wave Nature of the Formation of Gradient and Microcomposite Zones Near Non-Metallic Inclusions During Laser Processing of the Steels

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Abstract: The goal of this investigation was to research the wave nature of the formation of gradient and composite zones near non-metallic inclusions during laser treatment of the steels. The materials for investigation were commercial steels containing different non-metallic inclusions. The specimens of different steels were exposed to laser beaming on the installations GOS-30M. The research methods were applied: petrography, X-ray microscopy (MS-46 Cameca, "Nanolab - 7") and optical microscopy (Neophot-31) to study steel matrix near non-metallic inclusions and to identify of the inclusions. Nanohardness of the steel matrix near inclusions ("Nano Indenter II") was analyzed. Peculiarities of wave saturation of the steel matrix by chemical elements of non-metallic inclusions during laser action were investigated. It was shown the role of wave relaxation of stresses in the formation of cascade type structure of steel matrix near non-metallic inclusions. The features of the formation of gradient and micro composite saturation zones of cascade type in a steel matrix under conditions of abnormal mass transfer from nonmetallic inclusions during laser processing are discussed. It has been established that the formation of gradient saturation zones with a cascade and "spot" distribution of elements and nanohardness is due to the wave nature of the relaxation of thermal and deformation stresses near non-metallic inclusions at the time of laser exposure. The difference in the rates of abnormal mass transfer of chemical elements of non-metallic inclusions into a steel matrix at the moment of laser melting is shown, which is associated with different solubility and mobility of the atoms of alloying elements in liquid iron.

Keywords: Non-metallic inclusions, Steel, Microcomposite zones, Abnormal mass transfer, Laser treatment, Stresses, Wave relaxation, Strengthening, Nanohardness.

INTRODUCTION

Laser processing is widely used for surface strengthening of steels and steel products [1-5]. It is known that the mechanism of laser strengthening of steels is associated with a number of factors that create a total strengthening effect [1-6]. First of all, these are high-speed phase transformations, thermoplastic stresses, microchemical heterogeneity, partial or complete dissolution of carbides and non-metallic inclusions, etc. High-speed shear phase transformations in the steel matrix generate stresses from high-temperature and phase hardening during rapid heating and cooling, including the local influence of inclusions on these transformations.

Non-metallic inclusions that are present in any steel affect the local processes occurring during laser treatment. Under conditions of pulsed laser exposure, due to high-speed heating to high temperatures, non-metallic inclusions melt, high-speed mass transfer develops, which leads to mutual saturation of inclusions and the steel matrix with chemical elements that make up their compositions [7, 8]. In the vicinity of non-metallic inclusions due to microalloying, areas appear that are supersaturated by inclusion elements solid solutions [8-10]. The level of the strengthening of steels near non-metallic inclusions depends on some factors: chemical composition of steel and non-metallic inclusion and also character of speed structural and phase transformations which flow in steel matrix, phase, deformation and high temperature hardening. It was found that the strengthening zones of the steel matrix near non-metallic inclusions have different structures and phase compositions [9-11]. At the same time, the nature of the formation of these zones is not always clear. The goal of this investigation was to research the wave nature of the formation of gradient and composite zones near non-metallic inclusions during laser treatment of the steels.

MATERIALS AND METHODS

Samples of different steels were laser treated by GOS-30M installation with parameters: an excitation voltage of 2,5 kV, pulse energy of 10…30 J, heating rate of 10^5 °C / s, cooling rate of 10^6 °C / s, action time of $(1{,}0\ldots6{,}0)^{\cdot}\ 10^{-3}$ s. Identification of non-metallic inclusions was carried out by metallographic (Neophot-31), X-ray microspectral and petrographic methods [1]. Distribution of the elements by X-ray microanalysis (MS-46 "Cameca", "Nanolab - 7") and nanohardness of

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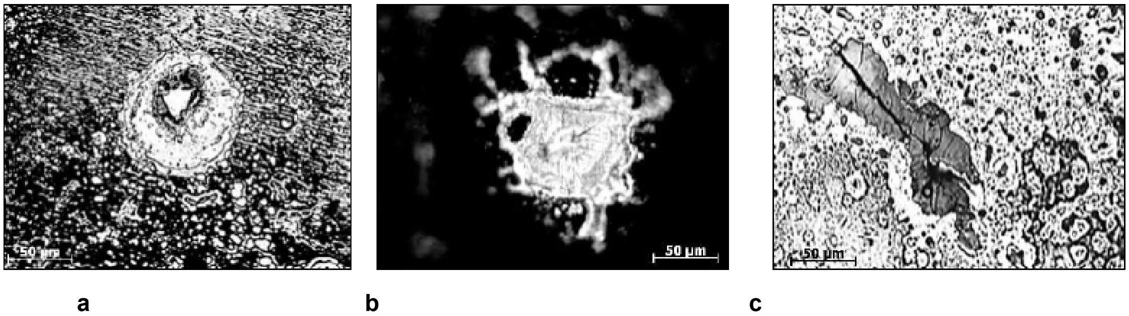
the steel matrix near non-metallic inclusions ("Nano Indenter II") were analyzed.

RESALTS AND DISCUSSION

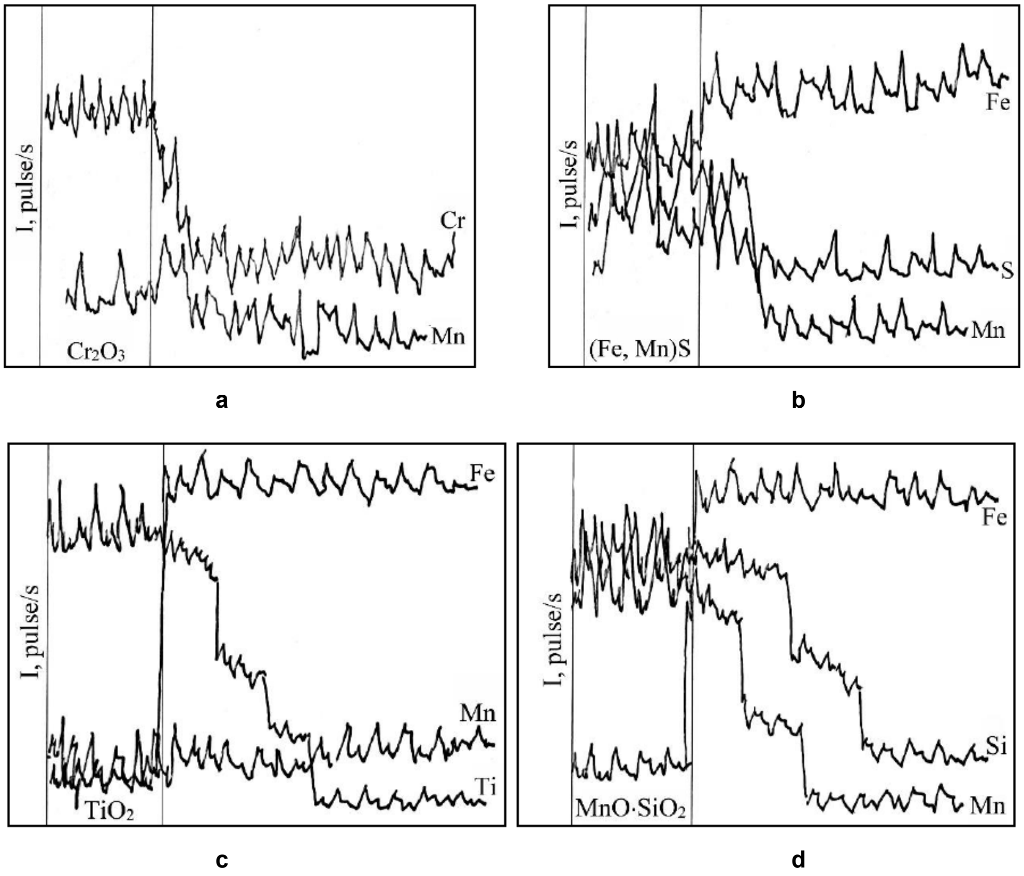
Some transformations in non-metallic inclusions and steel matrix under laser action took place. The type of inclusion determines of their behavior at the time of laser beam action. High-melting non-metallic inclusions (oxides Al_2O_3, Cr_2O_3, SiO_2, TiO, $MnO.Al_2O_3$, $MgO.Al_2O_3$, $MnO.Cr_2O_3$, TiCN) are melted or remained hard during laser treatment (Figure **1**, **a**). Some low-melting inclusions (iron-manganese silicates and sulfides) are melted under laser action and spread over a surface under shock wave (Figure **1**, **b**, **c**). Due to melting and partial dissolution of non-metallic inclusions, the steel matrix is saturated with inclusion components (Figure **2**, **a**, **b**).

In the process of laser action between a non-metallic inclusion and a steel matrix, a high-speed exchange of atoms occurs through the interface under conditions of an abnormal high mobility of the atoms that does not meet the conditions of classical diffusion (abnormal mass transfer) [12-15]. The processes of mass transfer during laser exposure are facilitated by the following factors: heating to high temperatures and



a b c

Figure 1: High-melting TiCN (**a**) and low-melting $MnO{\cdot}SiO_2$ (**b**), FeS-(Mn,Fe)S (**c**) non-metallic inclusions after laser treatment.



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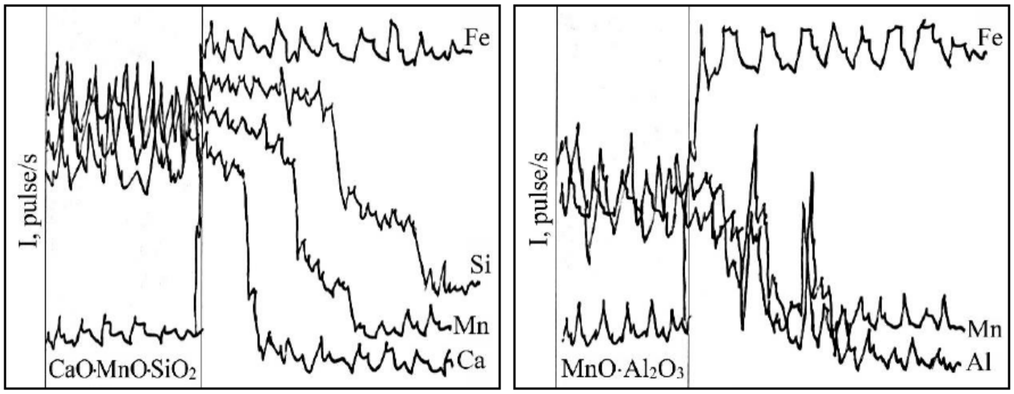


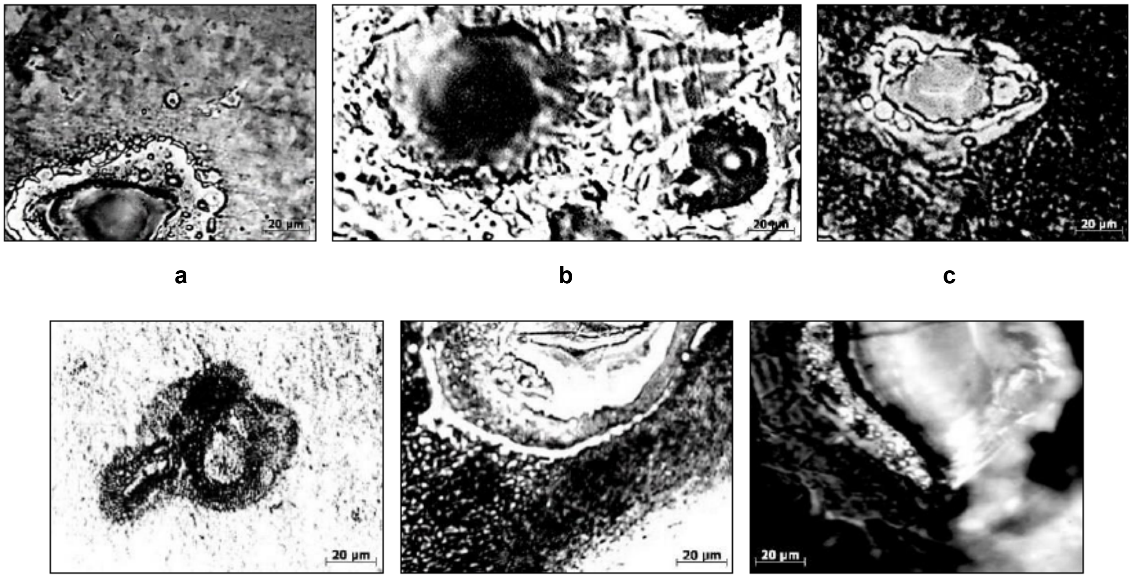
e f

Figure 2: Wave distribution of chemical elements in inclusions and steel matrix after laser treatment.

high-speed movement of the defects in the crystal structure that occur during thermal shock; the possibility of formation of a thermally nonequilibrium plasma; the appearance of convective and wave flows in the melt [16]; relaxation of thermoplastic stresses arising during irradiation; melting; electronic and electromagnetic interaction of inclusions and matrix [17]; formation in the surface areas of the inclusions of zones with an increased density of dislocations [7, 18].

Areas of saturation of the steel matrix with elements of non-metallic inclusions have a heterogeneous structure and may consist of one, two or three zones, which differ in the content of chemical elements (Figure **3**). The laser exposure mode affects the number of saturation zones of the steel matrix with chemical elements of non-metallic inclusions: the higher the pulse energy and the longer the exposure time, the stronger the tendency to the appearance of multilayer formations. At the same time, the influence of the type of inclusion and its state at the moment of laser exposure on the number of saturation zones was not found. This is due to the activation of the process of mass transfer of elements from the inclusions to steel matrix with an increase in the energy of the laser pulse and an increase in the possibility of its implementation with an increase in the duration of exposure. By that in non-metallic inclusions the surface zone saturated by the element of steel matrix may or may not be available.

An analysis of the distribution of chemical elements near non-metallic inclusions showed that in each zone a gradual decrease in the number of elements of a



a b c

d e f

Figure 3: Zones of interaction between non-metallic inclusions and steel matrix under laser treatment: **a** - SiO$_2$ steel E3; **b** - Al$_2$O$_3$, MnO·Al$_2$O$_3$, R7, **c** - TiCN, R7, **d** - (Fe,Mn)O, R7, **e** - FeS-(Fe,Mn)S, steel NB-57, **f** - Al$_2$O$_3$, 08Yu.

non-metallic inclusion was observed by removing them from the inclusion (Figure **2**, **a**, **b**). Moreover, the content of elements was maximum in the zone closest to the inclusion, and in the second and third zones it decreased, which led to the formation of a cascade of element concentrations near the inclusions (Figure **2c**).

It is known that under shock compression pressure, the normal stresses in steel exceed the yield point, while shear stresses become higher than the critical value and the material flows [19]. As a result, dislocations multiply, dislocation reactions occur, which contributes to the appearance of vacancies and an increase in the dislocation density in the laser impact zone up to $10^9...10^{12}$ cm^{-2} [20]. New mobile dislocations appear, their movement is associated with the relaxation of thermoplastic stresses arising during irradiation, which contributes to the implementation of anomalous mass transfer [21-23].

Stress relaxation in the zone of laser action is carried out by plastic shears and rotations, as well as by twinning [20]. Microplastic processes of stress relaxation are localized near non-metallic inclusions, where zones of shear-rotational deformation are observed. Laser exposure is essentially thermal shock. During abrupt heating to high temperatures, the high pressures develop in shock waves, which create a concentration of thermal and deformation stresses near the inclusions. For the relaxation of these stresses there is an extremely short time of shock compression. The described conditions provoke an avalanche relaxation of stresses near the inclusions (Figure **4**, **a**, **b**), where complexly deformed zones appear (Figure **4**, **c**), indicating high-speed shear-turn plastic deformation processes with elements of a wave nature. In some areas of these zones, there are signs of recovery and recrystallization high-speed processes (Figure **4**, **d**, **e**). And yet, despite the rather significant heating temperature, the main mechanism of stress relaxation is high-speed plastic deformation.

It is known that a pulsed laser action is a thermal shock that generates significant stresses and their wave relaxation [24]. Obviously, wave stress relaxation accompanies the anomalous mass transfer of the inclusion components into the steel matrix (Figure **4f**). In this case, the stress relaxation waves are superimposed on one another, which gives rise to the wave nature of the mass transfer of chemical elements from non-metallic inclusions into the steel matrix.

A detailed analysis of the curves of the gradient cascade distribution of elements near the inclusions (on the example of R7 wheel steel) made it possible to reveal some of their features. They are related to the fact that, along with clear drops in the radiation intensity of elements in the presence of two or three saturation zones, there are cases of mismatch of these drops for different elements near one inclusion (Figure **2**, **d**, **e**). The boundaries of the first, second and third saturation zones were determined by the most active

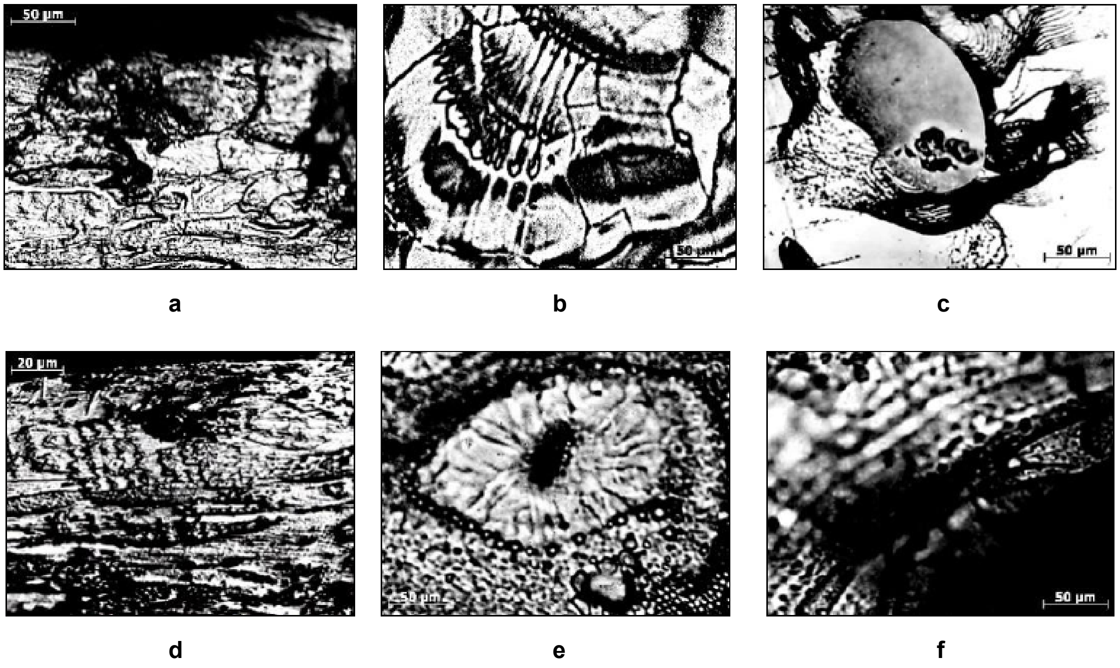


Figure 4: Plastic stress relaxation near inclusions under laser action.

chemical element that penetrated to the maximum distance from the initial inclusion. Within the indicated saturation zones, Mn atoms penetrate to the greatest distance from the initial inclusion, then Si atoms, and finally S atoms. At the same time, Ca atoms, as a rule, penetrate a short distance from the initial inclusion, and in the presence of two or three saturated zones, only in the one that is adjacent to it. These data indicate the different rates of migration of atoms of various elements in molten steel in the laser melting zone.

Obviously, there is some relationship between these results and the difference in the diffusion coefficients of various alloying elements in liquid iron [25]. Undoubtedly, the conditions under which the indicated diffusion coefficients were determined are far from those that are realized at the moment of pulsed laser action, when abnormal mass transfer occurs, rather than diffusion processes. The authors of [25] showed that alloying elements diffuse in liquid iron at rates that differ significantly from each other, which is associated with their different solubility in clusters and the disordered zone of the melt. In this work, alloying elements are divided into three groups according to the degree of solubility in liquid iron. Elements of the first group (Mn, Ni, Co, Pd, Pt) easily dissolve in clusters, their diffusion coefficient D is close to the self-diffusion coefficient of the iron atoms, they dissolve indefinitely in liquid and solid iron. Elements of the second group (Cr, N, C, Zn, Cu, Mo, V, Nb, Al, Cd, W, Ti, Zr, O, S) have an increased solubility in the disordered zone. They are infinitely soluble in liquid iron and sparingly soluble in solid iron. Their diffusion coefficients fluctuate over a wide range relative to D of the iron atoms. Elements of the third group (Na, Mg, Ca, H) are sparingly soluble in both liquid and solid iron, their diffusion coefficients depend on the atomic radius.

As for the conditions of pulsed laser exposure, the sharp heating of the melt in a thin surface layer obviously violates its equilibrium structure and also causes cluster polymorphism [25], which should significantly and differently affect the nature of the abnormal mass transfer of the atoms of various chemical elements. At the same time, there is a relationship between the rates of diffusion of impurities in liquid iron with the rates of their abnormal mass transfer in the melt under laser exposure. The wave nature of stress relaxation, as well as high-speed mass transfer during laser action, is realized in an inhomogeneous field of temperatures and stresses, which is typical for pulsed laser exposure [1-5], therefore, fluctuations in the ratios of element concentrations in the saturation zones of the steel matrix in the range of 1.2 ... 1 ,8.

It should be noted that along with the cascade distribution of chemical elements near non-metallic

Table 1: Values of Nanohardness H_n^i and Coefficient K_i (Indicated in Brackets) of Steel Matrix Near Non-metallic Inclusions and far from them H_n

Inclusion, steel	Condition in the time of laser action		H_n, x 10, MPa	H_n^i, x 10, MPa, (K_i) in zones		
	Inclusion	Steel Matrix		1	2	3
TiN, TiCN, 08H18N10T	hard, meltdown	liquid	275	470(1,71)	390(1,42)	-
MnO·Al_2O_3, Al_2O_3, R7	hard / meltdown	hard liquid	620	899(1,45) 1079(1,74)	769(1,24) 936(1,51)	694(1,12) -
FeS-(Fe,Mn)S, 08kp	liquid	liquid	260	405(1,56) 411(1,58)	367(1,41) -	286(1,1) -
MnO·SiO_2 2MnO·SiO_2, 08kp	liquid	liquid	260	421(1,62) 452(1,74)	361(1,39) 340(1,31)	- 294(1,13)
SiO_2, R7	hard	liquid hard	620	1080(1,74) 960(1,55)	858(1,38) -	- -
CaO·MnO·SiO_2, R7	liquid	liquid	620	1156(1,84)	1027(1,63)	-
FeO-TiO_2, 08T	meltdown	hard	280	460(1,64)	385(1,38)	-
Cr_2O_3, FeO·Cr_2O_3 MnO·Cr_2O_3,08H	meltdown	liquid	256	460(1,80) 445(1,74)	368(1,44) 380(1,48)	- 320(1,25)

inclusions, a “spot” distribution of inclusion elements over sections of the steel matrix was found (Figure **2**, **f**). The nature of such a distribution of chemical elements is not related to wave stress relaxation [9, 10].

The cascade nature of the distribution of nanohardness values in the zones of saturation of the steel matrix with elements of non-metallic inclusions of the cascade type was found [Table **1**]. The values of nanohardness depend on the chemical composition of the steel and the type of non-metallic inclusion, however, near the inclusions (or in the first saturation zone) they are 1.45…1.8 times greater than in the steel matrix far from the inclusion. In the second and third supersaturation zones, the values of nanohardness exceed the values of n away from non-metallic inclusions by 1.25…1.64 and 1.1…1.3 times, respectively. Value of nanohardness of steel matrix in all oversaturated zones near non-metallic inclusions and value of coefficient K_i depends from the condition of non-metallic inclusion and steel matrix in the moment of laser action. This distribution of nanohardness indicates the inhomogeneous nature of the strengthening of the steel matrix near nonmetallic inclusions. Coefficient K_i is determined by the ratio of the nanohardness of the steel matrix in the saturation zone to the nanohardness of the steel matrix away from the non-metallic inclusion [9, 10]. These results are closed to the results of determining the microhardness near inclusions after laser exposure obtaining in [9, 10].

The values of the nanohardness of the first (or the only) saturation zone of the steel matrix near non-metallic inclusions depend on the laser exposure mode [Table **2**], and it is possible to choose the laser beam energy values corresponding to the maximum hardening of the steel matrix.

Main factor of laser strengthening of local areas of steel matrix is its microalloying from inner sources - non-metallic inclusions. The appearance of cascade saturation zones during the formation of liquation strengthened areas contributes to formation of micro composite layers near non-metallic inclusions. Structure of these zones maybe single-phase (oversaturated solid solutions) but often dispersal microphases and nanophases – “satellite” particles are observed (Figure **3**, **a**, **f**). The initial inclusion and composition of steel matrix determine the chemical composition of “satellite” particles [9, 10].

Non-metallic inclusions as internal sources of microalloying of the steel matrix contribute to the formation of microcomposite zones of the cascade type, which are segregation formations with a non-uniform distribution of chemical elements. Dispersed microphases and nanophases, “satellite” particles, are often observed in these zones (Figure **3**, **a**, **f**). They are formed in places of supersaturation of the steel matrix with elements of the original non-metallic inclusions. Appearance of “satellite” particles promotes formation of dispersal microcomposite layers or layers with combine structure near non-metallic inclusions. Obviously the variation of regime of laser action will allows to regulate structure of these composite systems.

It should be noted that the mass transfer of chemical elements into the steel matrix contributes to the partial dissolution of the initial non-metallic inclusions, which causes a decrease in their average size and a decrease in the level of steel contamination with inclusions in the strengthened surface layer [6]. In addition, shock waves contribute to the fracture of high-melting and low-melting inclusions, which at the time of laser exposure are, respectively, in a solid (meltdown) or liquid state [6].

In addition, the mutual mass transfer of chemical elements affects the structure and properties of inclusion-matrix boundaries [8]. The influence of laser action on the structure of interphase boundaries inclusion-matrix, as well as on the processes of crack formation near non-metallic inclusions during subsequent deformation is established [6, 26]. Laser exposure contributes to a change in the mechanism

Table 2: Nanohardness of Steel Matrix Near Inclusion $FeO \cdot Cr_2O_3$ in Steel 08H under Different Time of Action

τ_{pulse}, 10^{-3}, s	Laser beam energy W_{pulse}, J			
	10	18	25	30
1,0	333	457	448	375
3,6	350	486	460	389

and parameters of crack formation under various conditions of plastic deformation.

CONCLUSIONS

The transformation of non-metallic inclusions as sources of internal alloying contributes to the formation of gradient and microcomposite saturation zones of the steel matrix under conditions of anomalous mass transfer during laser processing. Gradient saturation zones with a cascade and " spot" distribution of elements and nanohardness, dispersed zones and zones with a combined structure were formed. Saturation zones of the steel matrix near inclusions are the segregated strengthened areas with different levels of alloying with elements of non-metallic inclusions.

The formation of a cascade distribution of chemical elements in the saturation zones is due to the wave nature of the relaxation of thermo-deformation stresses near non-metallic inclusions at the time of laser exposure. Signs of different rates of anomalous mass transfer of chemical elements of non-metallic inclusions into the steel matrix during laser melting are revealed, which is associated with different solubility and mobility of the atoms of alloying elements in liquid iron.

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