Phase transformations in non-metallic inclusions under laser action

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Abstract. *It was found that in the process of pulsed laser action, various phase and structural transformations occur in non-metallic inclusions, which take place under nonequilibrium conditions. It is shown that the melting of inclusions under laser action is corresponded with change of their structure and phase composition. Also it is shown that the nature of these transformations depends on the type of nonmetallic inclusion. It was found that nonequilibrium phase transformations contribute to a change in the structure, phase composition, properties and sizes of nonmetallic inclusions, as well as the inclusion-matrix interphase boundaries of steel. It is shown that changes in the structure and properties of non-metallic inclusions affect their behavior and the formation of defects in the laser-strengthened layer of steel products.*

KEYWORDS: *NON-METALLIC INCLUSIONS, STEEL, PHASE TRANSFORMATIONS, LASER TREATMENT*

1. Introduction.

Steels contain non-metallic inclusions which influence on the character of strengthening during laser quenching. In the process of laser treatment non-metallic inclusions are fully or partly melted down or are remained hard, in reference [1-13]. In spite of short-term treatment the energy of laser radiation turns out sufficient for melting of the high-melting and low-melting inclusions, and also for the development of mass transfer processes which lead to enrichment of steel matrix with the elements of inclusions and also transfer of matrix elements to the surface zone of inclusions. Areas of steel matrix near non-metallic inclusions are the strongly oversaturated solid solution with different types of gradient and composite structures: gradiental zones with cascade and "spot" distribution of elements and nanohardness, dispersal zones with different types of microphases and nanophases, "tunnel" zones, and also zones with combine structure [1,14-20].

It is known that laser action affects the behavior of nonmetallic inclusions and the formation of defects during subsequent deformation [1, 21, 22], contributing to a change in the conditions for the formation of cracks. Therefore, it is of interest to study the nature of transformations occurring in nonmetallic inclusions under laser action. The goal of this investigation was to research phase and structural transformations in non-metallic inclusions under laser treatment of the steels.

2. Materials and Procedures

Specimens made of steels R7, 08Yu, 08T, 08Kp, 08Ch18N10T,ShCh15, NB-57, 12GS, E3, 60G were irradiated by laser in GOS-30M installation with an excitation voltage of 2,5kV and pulse energy of 10, 18, 25 and 30 J at heating rate of 10^5 $^oC/s$ and cooling rate of 10^6 $^oC/s$ with the action time of (1,0, 2,5, 3,6, 4,2 and 6,0)$\cdot 10^{-3}$ s. Non-metallic inclusions were identified by metallographic, X-ray micro spectral and petrographic methods [1]. Distribution of elements, microhardness and nanohardness of steel matrix near non-metallic inclusions were determined.

3. Results and discussion.

Phase transitions in nonmetallic inclusions occurring at the moment of laser action are their dissociation and melting (Fig. 1, a, b). This process is considered in works [1-9], where the features of crushing of non-metallic inclusions in the process of their partial dissolution and melting under pulsed laser exposure are investigated, which are associated with the following processes:

- disordering of their crystal lattice as a result of the occurrence of stresses caused by an increased density of defects and the penetration of atoms from the molten steel matrix by anomalous mass transfer;
- the formation of a micrometallurgical bath at the time of laser action, in which hydrodynamic flows arise, creating conditions for convective mass transfer of elements and the formation of heterophase complexes;
- the appearance in the structure of a microheterogeneous melt of dynamic heterophase complexes at the moment of melting of the initial inclusions, which are the centers of rapid crystallization of new "satellite" particles.

In the moment of laser action process of dissolution or melting of non-metallic inclusion happens owing to disordered transitions of atoms of inclusion over boundary with molten steel matrix. Mechanism of super-speed dissolution and melting of inclusions connects with mutual mass transfer of atoms (inclusion ↔ matrix) across interface boundaries which are melted also. Abnormal mass transfer across inclusion-matrix boundaries are accompanied by means of electrons exchange between inclusions (donors) and steel matrix (acceptor) [1]. Electromagnetic field inducing in the time of laser radiation influence on the conditions of mass transfer. Definite forces action on the components of alloy under this field and direction of these forces depends on magnetic properties of components of alloy. Action of forces causing with electromagnetic field promotes of mass transfer of components of inclusions and steel matrix which possess of different magnetic properties (magnetic moments). Thus electron interaction between inclusion and steel matrix is got complicated owing to electromagnetic interaction between atoms of contacting phases. Mass transfer of components from steel matrix to the surface layer of inclusion can to accelerate the process of dissolution or melting of inclusion if solubility of these elements in inclusion is sufficiently great. Variation of chemical composition on the surface of inclusion and advance of solubility limit of matrix elements realizes the conditions for transition of surface layer of inclusion into liquid state with minimum energy expense on the break of interatomic bonds. Evidently that perhaps connected with distortion of inclusion lattice with the atoms of steel matrix and also with appearing of high-density of crystalline defects and considerable stresses in surface layer of inclusion. Thus in hyper-nonequilibrium conditions of laser action the zone with high-density of vacancies and dislocations in surface layer of inclusion contacting with melted steel matrix is formed. According to dislocation theory of melting, for example [1-9], regions of this zone imagining heavy distortion areas with practically disordering lattice perhaps the nucleuses of liquid phase. Atoms with the most breaching electron configurations present in heavy distortion area on the surface of inclusion (nucleus of liquid phase).

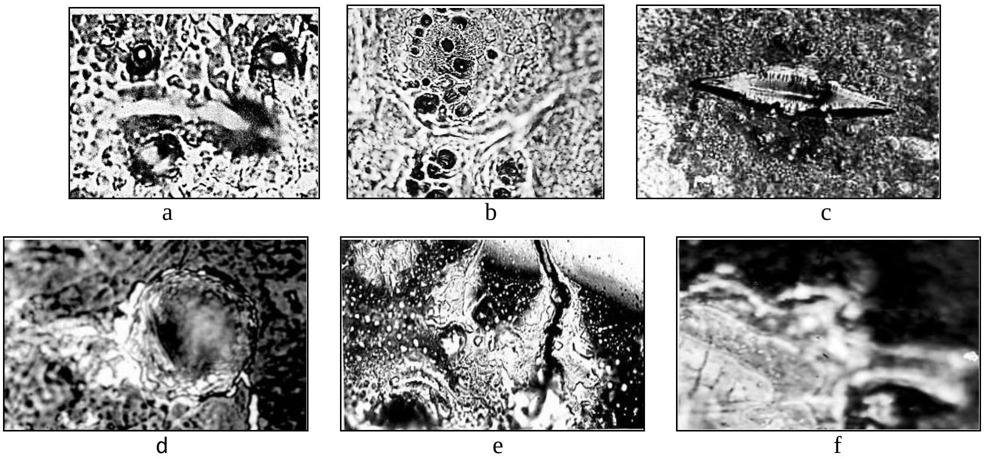

Figure 1. Dissolution and melting of non-metallic inclusions under laser action (a, b), bands of rapid crystallization in non-metallic inclusions (c, d) and Phase decay of non-metallic inclusions under laser crystallization (e, f); x500x6

After laser quenching from liquid state the areas of laser crystallization in surface layer or in all volume of inclusion are formed. Ultrasmall grainess, columner shape of grains, zones of shear are characteristics of these areas (Fig. 1, c, d). In the time of laser melting the high degree of nonequilibrium of liquid phase, bifurcation of melt and also transition from laminar to turbulent flow of liquid are appeared that ensure gradient of oscillation pressure on the inclusion-matrix boundary (liquid if inclusion and steel matrix were melted, or semi-liquid if steel matrix was hard) controlling convective and abnormal flows of mass transfer. Considerable stresses appearing in thin surface layer of inclusion and steel matrix in the result of local heat flashes of laser radiation [1], together with action of reactive forces of recoil owing to ejection from zone of treatment of liquid allows to high-temperature deformation of liquid interlayers continuing under crystallization during cooling. In some non-metallic inclusions being homophase before laser action phase decay in process of nonequilibrium crystallization was happened. That connects with mixing of liquid under action of hydrodynamics forces and temperature gradients. In inclusions disperse particles of second phase (Fig. 1, e) or interlayers of different chemical compositions (Fig. 1, f) were appeared. The size of these new phases do not depends on energy of impulse practically but it is increased with increase of the time of laser action.

Melting of inclusions under laser action is corresponded with change of their structure and phase composition. Mass transfer of components from steel matrix to the surface layer of inclusion can to cause various transformations.

The components of steel matrix penetrate into surface areas of non-metallic inclusions that promotes formation of solid solutions (Fig. 2, 3, a). For example surface area of inclusion Al_2O_3 in the steel 08Yu corresponds to $(Fe,Mn)O \cdot Al_2O_3$. The width of saturated zones in inclusions is about 5…10 mcm. Carbon has to penetrate into surface areas of inclusions too and carbide phases can to form.

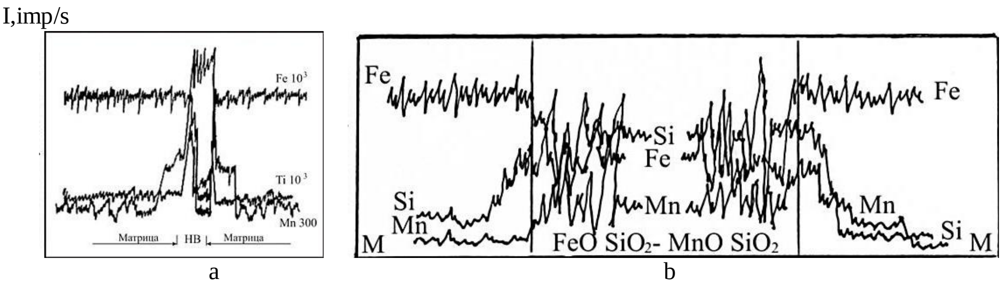

Figure 2. Distribution of elements in contact zones inclusion-matrix steel: $MnO \cdot TiO_2$ (a), $FeO \cdot SiO_2$-$MnO \cdot SiO_2$ (b)

One of the results of interaction between non-metallic inclusions and steel matrix is the formation of new bounding phases around inclusions (Fig. 3, b). The width of these phases is about 5…7 mcm. They represent the two-dimensional interlayers hardly connecting with both inclusion and steel matrix. Formation of bounding phase at a little time of laser action bears witness about collective character of this process owing to activation of group of different atoms in the conditions of high temperature and pressure. In the results on the boundary inclusion-steel matrix the complicated system is realized owing to thickening of some quantity of components:

$$N_i = n_i^i \cdot V_i + n_i^m \cdot V_m + G_i \cdot F_{i\text{-}ph} \qquad (1)$$

where N_i – quantity of redistriduting atoms; n_i^i and n_i^m – atoms densities of Mn, S, Fe, Al etc;
V_i and V_m – atoms volumes of inclusion and steel matrix; G_i – adsorbtion on the interphase boundary having area $F_{i\text{-}ph}$.

Formation of bounding phases in the moment of laser action happens when non-metallic inclusion, steel matrix and interphase boundary inclusion-matrix are melted. Owing to interaction between inclusion and steel matrix the bounding phase having the chemical composition and structure differed from initial inclusion and steel matrix is formed.

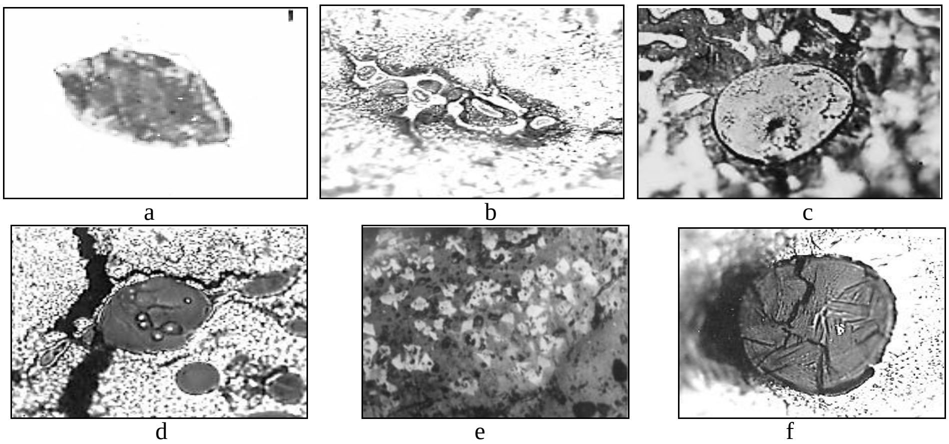

Figure 3. Non-metallic inclusions after laser action: x500

In the liquid state this layer perhaps close to the local state with coordination of atoms corresponding to the structure of metastable phases for temperatures and pressures in given region. If in the moment of laser melting the interaction of components on the interphase boundary is not carried out one can leads to formation of heterophase fluctuations close to the structure of any stable or metastable phases. Diffusion of any components in inclusion and steel matrix is described according to equations of Fick with different coefficients of diffusion so one can carries out the withdrawal of that component from the interphase boundary into inclusion or steel matrix. Also on the interphase boundary the layer with new chemical composition and structure one can to form. The chemical composition of bounding layer or bounding phase depends on temperature, pressure, concentration of elements in inclusion and steel matrix and also on the character of thickening of these parameters on interphase boundary in the moment of laser action. Bounding phase can to have transitional state from the inclusion to steel matrix or represents solid solution on the base of components of both inclusion and steel matrix or also represents the intermediate phases. State of the bounding phase perhaps is stable but more often it is metastable.

Formation of new phase owing to mass transfer across interphase boundary inclusion-steel matrix perhaps is accompanying with displacement of initial position of that boundary (Kirkendall effect). Energy of activation of bounding phase formation is:

$$W_{ph} = N_{at} \cdot \lambda_{ph} \qquad (2)$$

where λ_{ph} – heat of the transition to new state; N_{at} – quantity of atoms in the bounding phase.

Change of free energy ΔW_{ph} determining probability of the formation of bounding phase under laser action is:

$$\Delta W_{ph} = \Delta W_{chem} + \Delta W_{sur} + \Delta W_{elas} + \Delta W_{def} \qquad (3)$$

where ΔW_{chem} – change of the chemical energy; ΔW_{sur} - change of the surface energy in consequence of the formation of new interphase boundary; ΔW_{elas} - change of the elastic energy determining with defference of atom volumes of inclusion, steel matrix and bounding phase; ΔW_{def} - change of the energy connecting with interphase defects.

The research of bounding phases was shown that they may be different not only with chemical composition but also with structure. Bounding phases with crystalline, nanocrystalline and also amorphous structure were discovered.

In some non-metallic inclusions being on the surface of steel specimens which has homophase structure before laser action the new phases in thin surface layer were discovered. The analysis was shown that their nature is not the same. In the inclusions of some simple oxides (MeO, Me_2O_3, MeO_2) and of the some complicated oxides ($MeO \cdot Me_2O_3$, $nMeO \cdot MeO_2$) the dispersed particles of more lower oxides (Fig. 3, c) or of the pure metal were discovered (Fig. 3, d). The products of dissociation of oxides are shown in Table 1.

Evidently in the simple oxides the reduction of metal happened partly or fully and some products of reduction, for example Al_2O, CrO, SiO, are typical for the high-temperature state and at low temperatures they are not stable [1]. Reduction of the complicated oxides happened without decomposition on the simple oxides. Metal of the compound lower oxide was fully restored, metal of compound higher oxide was partly restored. Dissociation of oxide happens owing to laser action when ions of oxygen are removed from the lattice of initial oxide. These ions are moved to surface and removed to environment but in the places of oxide lattice the distortions are arisen. Growth of local distortions leads to reconstruction of lattice of the higher oxide to lattice of the lower oxide or metal which is strongly distorted owing to high concentration of oxygen vacancies.

Process of reduction of oxides is begun on a few reaction nucleous – the crystalline defects. It passes with high speed in the conditions of generation of the new crystalline defects. The depth of penetration of reduction process is about 10…15 mcm. On the surface of each inclusion the areas with different stage of reduction are been. That bears witness about inhomogeneity of laser radiation and of the defect structure of oxides and also about high speed of reduction process. This process happened more easy in the lower oxides MeO than in the higher oxides both independent and being in the composition of spinels and silicates.

Table 1. Products of dissociation of oxides

Initial inclusion	New phases	Initial inclusion	New phases
Simple oxides		Complicated oxides	
Al_2O_3	Al_2O, Al	$FeO \cdot TiO_2$	Fe, TiO
Cr_2O_3	CrO, Cr	$MnO \cdot Al_2O_3$	Mn, Al_2O
FeO	Fe	$MgO \cdot Al_2O_3$	Mg
TiO_2	TiO, Ti	$MgO \cdot Cr_2O_3$	Mg, CrO
MnO	Mn	$FeO \cdot Cr_2O_3$	Fe, CrO
MoO_2	MoO	$FeO \cdot SiO_2$	Fe, SiO, Si
V_2O_5	VO_2	$MnO \cdot SiO_2$	Mn, SiO, Si

In the inclusions of endogenic or exogeneous complicated silicates having multicomponent composition and representing in initial state the oversaturated solid solutions the dispersed particles were observed after laser action. These inclusions are low-melting and they are melted under laser action forming liquid solutions. In the result of the new liquid phases are formed which are crystallized as the hard phases under following very rapid cooling (Fig. 3, e). Chemical composition of these phases depends on the composition of initial inclusion and character of liquation phenomenon.

Laser treatment allows to fix some high-temperature phases of inclusions and also the whole inclusions. For example, SiO, CrO, Al_2O, Cr_2O, Cr_2O_3, Mn_3O_4, Cr_3O_4. These inclusions were discovered in the areas of melting and intensive evaporation of steel under laser action. The compared analysis of microhardness of inclusions showed that it is increased after laser action (Table 2).

The two groups of the non-metallic inclusions are shown. Microhardness of the inclusions of the first one is risen in 1,1…1,2 time. Microhardness of the inclusions of the second one is risen in 1,5…1,8 time. This is connects with presence or absence of polymorphic transformations in inclusions. In non-polymorphic inclusions microhardness rises in 1,1…1,2 time owing to increase of density of crystalline defects and also of the thermal stresses. In inclusions Al_2O_3, SiO_2 ets polymorphic transformations happen with high speed over to shear mechanism. That may to lead to the brittle fracture of inclusion (Fig. 3, f).

Table 2. Microhardness of non-metallic inclusions before (1) and after laser action (2)

steel	inclusion	H_{μ} , · 10, MPa	
NB-57, 08kp	MnO	275	360
08kp	FeO	428	548
08kp	Fe_2O_3	1250	1900
08YU	Al_2O_3	1984	3028
08H18N10T,	Cr_2O_3	1568	2575
E3	SiO_2	1581	2856
08T	TiO_2	624	1083
08H18N10T	$FeO\text{-}TiO_2$	556	912
SHH15	MgO	1262	1499
08кkp	$FeO\cdot Fe_2O_3$	605	955
ШХ15	$MgO\cdot Al_2O_3$	1724	1920
08GCYuTF	$MgO\cdot Fe_2O_3$	1518	1702
08XH	$FeO\cdot Cr_2O_3$	564	638
08Yu	$MnO\cdot Al_2O_3$	1600	1730
08T	Ti_2O_3	1525	2229
E3	$2FeO\cdot SiO_2$	860	980
NB-57, R6M5	$2MnO\cdot SiO_2$	916	1140

Phase stresses in the lattice arising under shear polymorphic transformations promote increase of microhardness of inclusions in 1,5…1,8 time. Microhardnes of some complicated silicates increased in 2,0…2,7 time after laser action. Evidently this connects with amorphization of these inclusions.

*4. **Conclusions.*** Laser action causes various phase and structural transformations in non-metallic inclusions, which take place under nonequilibrium conditions. The nature of these transformations depends on the type of non-metallic inclusion. Nonequilibrium phase transformations contribute to a change in the structure, phase composition, properties and sizes of nonmetallic inclusions, as well as the inclusion-matrix steel interphase boundaries. These changes affect the behavior of non-metallic inclusions and the formation of defects in the laser-strengthened layer during the subsequent operation of steel products.

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