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Research of surface activating influence on formation of adhesion between gas-thermal coating and steel substrate

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Abstract. Estimation of influence of physical and thermal activating on adhesion between steel substrates and thermal coatings has been performed. The substrates with surfaces obtained by and ultrasonic surface plastic deformation were used. To evaluate physical activating, pre-heating of the substrates to 600°C was performed. To evaluate the effect of thermal activating, the substrate surfaces after interfacial detachment were examined. Bonded areas on the substrate surfaces were measured by means of optical profilometry. The experiments have shown that surface physical activating is the main factor in formation of the adhesive bond between the coating and the substrate processed with the proposed methods.

1. Introduction

Deposition of particles on the substrate is based on impact force. Heated particles move to the substrate at a high velocity, so a high pressure occurs in the moment of particle impact. The pressure has two components: forward pressure and short pulse pressure produced by a hydraulic impact. A large magnitude of the pulse pressure contributes to cleaning the substrate surface in the zone of the impact and produces a physical contact between the particle and the substrate.

Chemical interaction between the particles and the substrate occurs under influence of forward pressure, which acts during the entire particle solidification and deformation. At the moment of collision, the particle undergoes deformation and its kinetic energy is converted into heat and deformation of the substrate.

Physical and chemical interactions between materials of the particles and the substrate occur as the result of heat transfer and plastic deformation of the surface micro relief at the moment of particle impact. The physical-chemical processes form adhesion i.e. interface bonding of the coating and the substrate [1].

Completeness of physical and chemical processes, proceeding in the contact zone, is defined by heat and kinetic energies of deposited particles and physical properties of contact materials [2]. The first two indicators are set by thermal spraying [1]. The third indicator is defined by the nature of contact materials and condition of the substrate surface. The simplest technique of adhesion control is the change of topography and stress condition of the deposited surface by its preconditioning [3-5].

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The preconditioning increases surface atom activity, which enhances their contact with atoms of the deposited material. There are a number of methods for surface activating: chemical activating - by clearing of absorbent substances from the surface; physical activating - by mechanical processing of the structure of the surface layer; thermal activating – by prior or concomitant heating of the substrate surface; that facilitates overcoming of the activation barrier [1, 3].

At physical activating, adhesion strength is defined by the actual contact area of the coating and the substrate, uniformity of surface topography and the degree of surface layer modification. At thermal activating, substrate heating is required up to a temperature ensuring chemical interaction between the coating material and the substrate. Substrate preheating increases the area of physical contact by means of better spreading or deformation of the particles on the substrate surface. Wherein, the adhesion in the area of physical contact increases due to increased local bonded areas. Activating is possible with increasing temperature, if there is no rapid oxidation. Oxide layers on low-heated metal surfaces do not limit contacts of the deposited metal particles. If there is a strong oxidation of the substrate, the layer on its surface may undergo interfacial detachment [2, 3].

The objective of this work was to evaluate influence of physical and thermal activating on adhesion experimentally. For this purpose preconditioning of substrate surfaces by rough cutting machining and ultrasonic surface plastic deformation was performed. To evaluate the effect of thermal activating, heating of the substrates to 600^{o}C was performed before spraying.

2. Materials and methods

For the research, flat samples of steel 45 were prepared. The sample surfaces were processed in two ways: rough cutting and ultrasonic finishing (USF). USF as a method of substrate processing is described in [6-8]. The preconditioning facilitated chemical and physical activating of the sample surfaces by removing oxide layer and producing hardening. The areas of effective contact between the substrate and the deposited particles vary due to various processes. Deposition of powdered nickel-based alloy was performed with a thermal spraying device using an argon-nitrogen plasma jet [9]. Deposition was performed in layers to form a coating with thickness of 300 microns. To evaluate the effect of thermal activating on adhesive bond formation, depositions were performed at a room temperature and at 600^{o}C.

Using MICRO MEASURE 3D station optical profilometer, surface conditions were examined before coating deposition and after its detachment. The device allowed examining three-dimensional image of the surface conditions and describing quantitatively content and morphology of the bonded areas [6].

3. Results and discussion

As it is known, the actual bonding between the particle and the substrate does not occur in the entire area of chemical contact, but in local bonded areas. The bonded areas are sites on the contact surface, which form stable metal bonds between the material particles and the substrate material. Local interaction between contacting materials is due to localization of chemical interaction in areas with the highest reserve energy. Reserve energy occurs due to presence of structural defects. Active centers on the substrate surface may be impurity atoms, vacancies, dislocation steps [1, 2]. At detachment, bonds between the coating and the substrate exceed cohesive forces in bonded areas. Failures occurred in the coating volume itself, and some fragments of material remained bonded to the substrate surface (Fig. 1).

Thus, the bonded areas form the actual content of contact between the coating and the substrate. Expansion of the bonded areas throughout contact surface demonstrates gradation of physical and chemical process development at the interface "coating - substrate". As shown in [4], a stable bond of particles with the substrate occurs if bonded areas occupy 40 - 70% of the contact surface.

Let us examine how different methods of substrate surface precondition influence formation of bonds between the coatings and the substrate. To improve the adhesion it is advisable to apply coating with a higher surface roughness. A rough surface has better thermo-physical conditions for activating behavior, which increases the adhesion of deposited particles. On tops of projections temperature will be higher than in grooves, and period of heat action on the micro-projections will be longer as well [3].

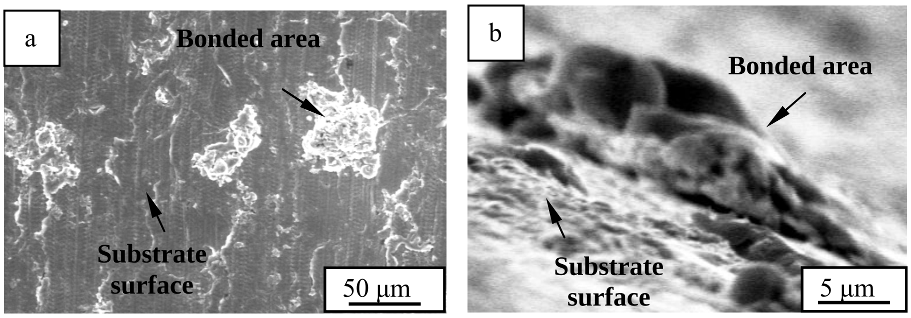

Figure 1. SEM image of bonded areas on surface of steel substrate after coating detachment

To perform the rough surface, rough machining was first chosen for preconditioning of the substrate surface. Exterior surface is shown in Figure 2 a.

The substrate surface roughness is formed by cutting tool advance. When advancing, the cutting edge removes chips spirally layer by layer and forms a microprofile. Cross section of the microprofile is specified by the cutting tool geometry. To obtain a ragged surface, the cut tip is displaced below the part axis; this displacement increases cutter vibration, thereby the projections on the substrate surface are crushed. As shown in Figure 2b, surface topography is formed of circulated lines of surface projections. The projections have a height of about 10 micron and a pitch of 200 micron. Tops of projections are partially smoothed, partially cut. Grooves have sharp forms. Line anisotropy of surface topography is strong.

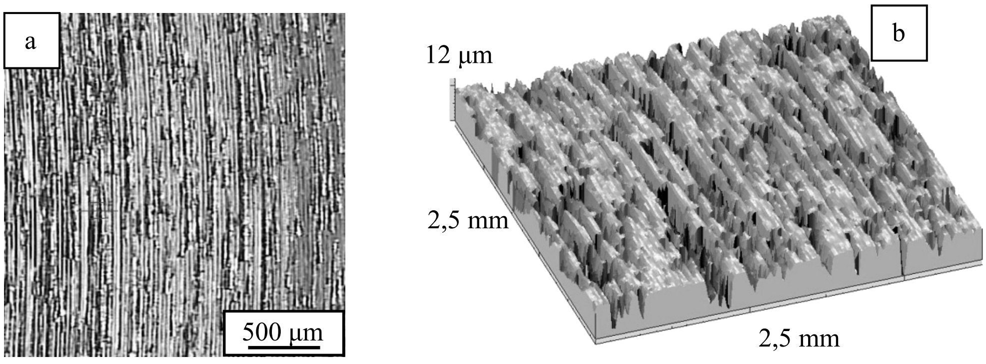

Figure 2. Image of substrate surface after rough cutting

It is believed, that surface microrelief in the form of closely spaced wells with profile radii greater than radii of sprayed particles is the most appropriate for formation of stable adhesion. Such a surface is formed by ultrasonic finishing (USF) [6].

Inclinations of the sides of surface projections are important for deformation and spreading of the sprayed particles. The cuts between the projections should be wide, with sloping lateral surfaces; which enable the particle to be deformed to a larger size. Projections contribute to improvement of thermal conditions for contact between the spray particles and the substrate [3]. Figure 3 shows the USF-processed surface

Surface topography after USF is a trace, shaped by two movements of the tool. The first movement is superposition of grooves left on the workpiece with the deforming tool (Fig. 3a). The second movement is the plastic flow of metal from each individual impact of the tool (Fig. 3b). A tool indenter has a spherical shape. As a result, the surface is formed, which comprises cuts and projections flowing into each other, with height up to 1 micron and pitch of roughness in transverse direction - approximately 100 microns, longitudinally - about 10 microns. Line anisotropy is flattened by plastic metal flow caused by individual tool strokes [6]. USF is also characterized by surface deformation, which gives access of structural defects such as dislocations and grain boundaries to the surface [7].

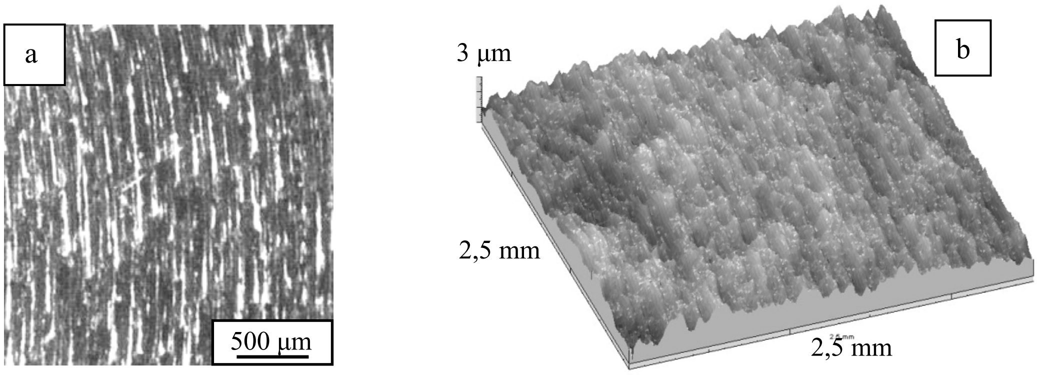

Figure 3. Image of substrate surface after USF

Thus, before deposition, substrates with different surface conditions were obtained. They differed from each other in roughness, surface topography, the effective area of contact between the sprayed particles and the substrate. Then surface conditions after interfacial detachment of the coating were analyzed.

The state of the substrate surface processed by rough machining after detachment of the coating was examined.

Figure 4a shows the surface after detachment of the coating deposited to the substrate at room temperature.

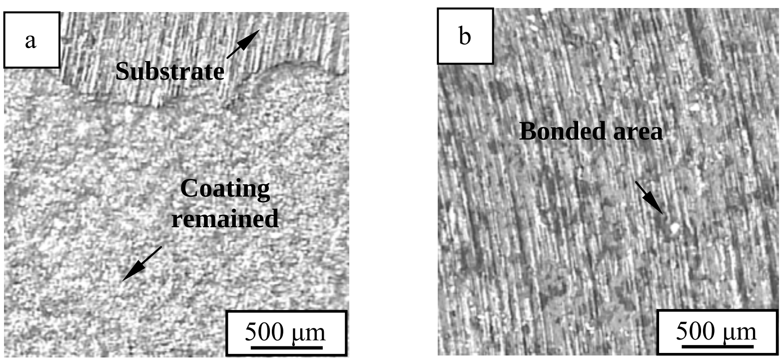

Figure 4. Surface processed by rough machining after detachment of coating deposited to substrate: a) at room temperature, b) preheated to 600^{o}C

When detaching of the coating, destruction occurred at the interface fractionally. In this case adhesive and cohesive forces correlated in the coating. In the substrate areas, where detachment occurred at the interface, some bonded areas can be observed. Their content is about 4%. It can be noted, that the bonded areas consist of deposited particles, attached to the grooves of the substrate, rather than to the projections. Consequently, contact between the particles and the substrate occurs due to sticking of the sprayed material into the grooves of the substrate surface. Flat surface projections do not form adhesion bonds with the deposited particles because of unfavorable topography of the roughness peaks. It is known that the surface with roughness peaks, isolated from each other, is characterized by maximum temperature gradient and cooling rate of the sprayed material [3]. Then, temperature increase on the substrate peaks leads to formation of chemical bonds and bonded areas.

However, despite absence of physical and chemical bonds at the "coating - substrate" interface, the coating has high adhesion. This is conditioned by mechanical engagement between the sprayed material and the effective substrate surface. One can not exclude formation of residual stresses favorable for interface adhesion, which arise due to heterogeneity of coating and substrate properties and temperature gradient [1]. Because of residual stresses, the spraying material is attached into the grooves of the substrate surface.

Substrate preheating to 600^{o}C changes conditions of adhesion bond formation significantly. When heating, a continuous surface oxide layer occurs on the surface which can be classified as a scale diffusion layer. Such oxide layers on iron and carbon steels are characterized by low heat resistance and tendency to flaking. Therefore, when sprayed particles impact the substrate surface, local clearance of iron oxides and its activation can occur [2].

The coating deposited on the pre-heated rough cut surface is detached *completely* over the interface (Fig. 4b). After coating detachment the bonded area content is only about 1%. Destruction of base oxides occurs only on certain peaks of the surface microrelief, and single bonded areas are formed there. Then, low surface activating is conditioned by complex anisotropic topography of the rough cuts and high surface roughness. Process of oxide layer destruction under hydraulic impact of the liquid drop is hindered. Mechanical engagement of the deposited material with the substrate also does not occur because of change of surface condition at oxidation. The surface loosens, its roughness decreases. Furthermore, the heating partly relieves residual stresses which reduce attaching of the deposited particles into the grooves of the substrate surface. As a result of all the factors, surface activating does not occur during spraying, and coating does not form adhesion bonds with the substrate.

The coating deposited on the pre-USF surface is detached *partially* over the interface (Fig. 5a). The resulting coatings, as well as the coating sprayed onto the rough cut substrate, have a high adhesion to the substrate. However, mechanisms of adhesive bond formation differ. This is proved by the topography of interfacial detachment "coating - substrate" (Fig. 5 a). On the substrate surface a large number of bonded areas are observable. Sizes of the bonded areas vary from 15 to 40 microns, which are smaller than those of the sprayed particles. Distances between bonded areas coincide with the distances between the surface projections i.e. about 100 microns. Content of bonded areas formed from separate deposited particles is about 10%.

In some surface regions, sprayed particle agglomerates are observable, which are held by complexes of closely spaced bonded areas. The total content of both the bonded areas and the agglomerates is about 40%.

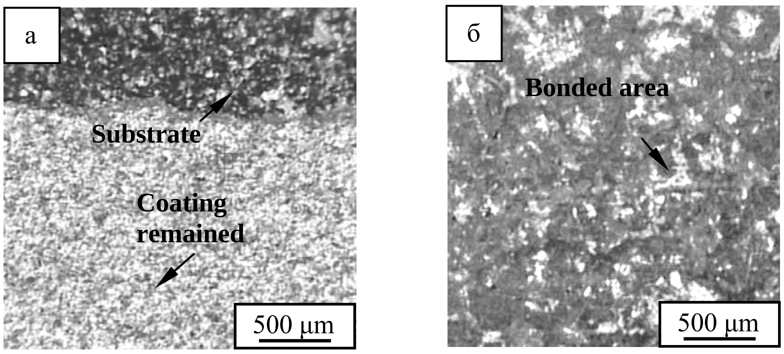

Figure 5 Image of pre-USF substrate surface after interfacial detachment of coating deposited: a) at room temperature; b) preheated to 600°C

In the case under study a high adhesion between the coating and the substrate is ensured by several factors, including formation of favorable substrate topography. Surface microrelief in the form of closely spaced wells with profile radii commensurable with radii of sprayed particles is the most appropriate for formation of stable adhesion. Inclinations of the sides of surface projections are important for deformation and spreading of the sprayed particles. Grooves between projections should be wide, with sloping lateral surfaces, which enable particles to be deformed to larger sizes. Projections should be separated from each other. Such a surface is formed by ultrasonic finishing (USF). Roughness peaks, during depositing of molten particles, are heated and actually welded with crystallizing particles to form bonded areas. This can be seen in the photograph of interfacial detachment of the coating (Fig. 5a). Arrangement of the bonded areas corresponds to the distance between roughness peaks.

One more factor ensures intensive chemical interaction between spray particles and the pre-USF substrate material. A large amount of surface crystal structure defects ensure formation of stable chemical bonds between the sprayed material and the substrate material. Evidence of chemical activating mechanism is proved by "coating-substrate" interface uncontrasty.

As it is described in our previous work, metallographic analysis of coating cross-sections does not reveal the interface in a non-etched micro-section [10]. After chemical etching a stable interface of materials and single micro-pores become observable. Coating detachment occurs by growth of cracking in the coating solid body, just above the "coating - substrate" interface. A thin layer of sprayed material remains on the substrate surface; which is commensurate with the height of two or three malformed particles [10]. Such areas of stable particles have the appearance of agglomerates on the detachment surface.

Preheating of the pre-USF substrate to 600^{o}C increases a contact temperature and reduces an energy barrier of chemical interaction of materials. However, an oxide layer in the contact area interferes the depositing; so it should be removed. As it is proved by the above experiment, when using the rough cut surface, coating failed. Using pre-USF substrate, the task was completed.

Figure 5b shows "coating - substrate" interfacial detachment. On the coating surface the bonded areas are observable. Their size varies from 10 to 100 microns. Some bonded areas take the form of some deposited particles. Most of the bonded areas are represented as agglomerates of the deposited particles. A total content of the bonded areas is about 45%; therefore about half of the surface is activated despite of the oxide layer.

Surface topography obtained by USF ensures activating. Destruction of the oxide layer occurs on the peaks of micro-roughness at collision with sprayed particles. Impact and deformation of liquid particles perform local clearance of the substrate surface from iron oxides and surfece activating. Time of particle action onto the substrate is sufficient for forming of chemical bonds between the contacting materials [11-13].

Increased contact temperature also provides relaxation of residual stresses. Then, during formation of the chemical bond between the sprayed material and the substrate material, maximum of inter-atomic bonds are kept as a result of activated diffusion processes, which flow rates are set by on-process temperature.

Conclusion

When applying plasma coatings to the substrate preconditioned by rough cutting, the main mechanism of adhesive bond formation is sticking of spray particles in the grooves of the surface. If the substrate is preheated, the oxide layer interferes with sticking of the spraying material to the substrate surface. Adhesion does not occur between the substrate heated to 600^{o}C and the coating.

Surface physical activating followed by chemical activating are basic mechanisms of formation of adhesion between coatings and pre-USF substrates primarily at the roughness peaks. The coating, sprayed on the substrate at a room temperature, has an enforced adhesive bond. This occurs because the additional energy of 600^{o}C substrate heating partially compensates for the loss of energy required for passing the potential barrier caused by the oxide layer interference.

For the above-described methods of substrate preconditioning, physical activating of the surface is the main factor that ensures formation of the adhesive bond at the interface "coating - substrate". Thermal activating of the substrate surface is relevant if, during spraying, system reserve energy exceeds the potential barrier, which is to be passed for oxide layer removal.

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