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Description of Seizure Process for Gas Dynamic Spray of Metal Powders from Non-Equilibrium Thermodynamics Standpoint

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Abstract: The seizure process has been considered from the non-equilibrium thermodynamics and self-organization theory standpoints. It has been testified that, for the intensification of powder mix particles seizing with the substrate during spraying, it is required that relatively light components of the powder mix should be preferably transferred into the friction zone. The theory inferences have been experimentally confirmed, as exemplified by the gas dynamic spray of copper-zinc powders mix.

Keywords: seizure; self-organization; spray of metal powders

1. Introduction

Some worn-out surfaces are not allowed to be heated during their renewal. For instance, when renewing locally-worn overhead contact wires for electric railroad transport, it is essential to avoid heating [1]. Overhead contact lines of high-speed railroads require the replacement of approximately 1.5 km (1500 kg) of overhead wires due to a local wear of 0.5 m [2].

In this regard, the renewal of locally-worn overhead contact wires, without dismantling, turns out to be a challenge.

The general requirements of renewal of worn overhead contact wire sections are as follows:

- Worn plane copper surface, 11 mm wide and up to 700 mm long, shall be subject to renewal, while thickness of renewed layer shall make up 1 to 2 mm;
- Rate of this layer spraying shall be a minimum of 2 m/h;
- Adhesion of sprayed layer and copper substrate shall be at least 15 MPa;
- Specific conductance of renewed layer shall be a minimum of 12 MS/m;
- Renewal process should not result in the contact wire annealing.

With due regard to the above requirements, gas dynamic cold spray could be suitable as a renewal technology [3]. During gas dynamic cold spray of copper-based powder, only carrier gas (normally air) will heat up to approximately 300 °C. Therefore, the sprayed surface will not heat up. This technology also allows for the spraying of layers having a thickness of a few millimeters at quite a high rate.

During the gas dynamic cold spray, the sprayed layer could seize with the substrate owing only to the seizure effect. In tribology, seizure may be perceived as the local engagement of two solid-state bodies due to the molecular force effect during friction [4].

The spray process proceeds as follows. The near-sound velocity air jet, with a metal powder, is sprayed onto the metal surface. A part of the powder particles bounces off the surface, while another part adheres to the surface owing to the seizure effect. When the air jet with powder is directed oblique to the surface at some angle, a tangential component will appear alongside with the normal velocity component. Therefore, the surface friction of powder particles occurs, followed by increased probability of seizure. This article will consider the seizure process from the non-equilibrium thermodynamics and self-organization theory standpoints, similar to [5].

There are a large number of articles on the use of non-equilibrium thermodynamics in friction processes. Detailed reviews are given, for example, in [6,7]. Interest in tribology to nonequilibrium thermodynamics stems from the fact that friction is a nonequilibrium and irreversible process that evolves and changes over time. Traditional thermodynamics does not deal with the description of the processes; it deals with the description of the initial and final states. There are reversible and equilibrium processes in traditional thermodynamics. Non-equilibrium thermodynamics deals with description of irreversible and nonequilibrium processes and their development over time [8]. The use of self-organization theory can explain the occurrence of spontaneous processes with negative entropy production prohibited in equilibrium thermodynamics [9]. However, there is a gap between the theory and real application of nonequilibrium thermodynamics in the practice of tribology. For more than 30 years, authors have been engaged in aspects of non-equilibrium thermodynamics, as applied to friction [10]. It has been shown that the passing of processes with negative entropy production reduces the wear rate. Therefore, the self-organization results in a reduction of wear rate. To reduce the wear rate, intensifying these processes and shifting the start of self-organization to mild friction conditions is necessary. For example, tribological material was alloyed by catalysts, resulting in lower wear rate [11]. Complex of the alloying of tribological materials, facilitating the passage of self-organization, results in lower wear rate [12,13]. Using the the stability of dissipative structures formula lubricating effect of electrical current was derived [14].

In the article, the methods of nonequilibrium thermodynamics were applied to the seizure process, based on the conditions of the passage of self-organization and the increase in seizure area.

2. Theory

According to the authors of [6], self-organization processes during friction will reduce the wear rate. In this case, it means a decrease in the portion of bounced particles.

Let us consider the friction and seizure process standpoint from the nonequilibrium thermodynamics and self-organization theory of Prigogine [7], similarly to that of [5]. The self-organization process will lead to the generation of dissipative structures [8,15]. According to the authors of [9], self-organization could break out in a system after a loss in thermodynamic stability. In this regard, let us examine the probability of loss in stability in the tribosystem.

When only one independent friction process is in progress in the tribosystem, entropy production will be expressed as follows:

$$\frac{ds_i}{dt} = X_h J_h = \frac{(kpv)^2}{\lambda T^2} \tag{1}$$

where J_h—heat flux, X_h— thermodynamic force inducing heat flux equaling to $gradT/T^2$, $J_h = -\lambda gradT$, along with this, $J_h = kpv$ (k—friction factor, p—pressure, v—sliding velocity), T—temperature, and λ—coefficient of thermal conductivity.

The source [9] illustrates that, in order to find conditions for the loss of stability in the thermodynamic system, the $\delta^2 s$ function could be used as a Lyapunov function. When the conditions of local equilibrium, being assumed to be stable, are met, it follows that:

$$\delta^2 s < 0 \tag{2}$$

where δ—fluctuation and s—specific entropy.

This value is defined as a negative definite function of increments of independent variables that are constituents of the Gibbs formula for the local state of the dissipative system. In this manner, system stability may be characterized on the basis of the $\delta^2 s$ function as a Lyapunov function. It follows that the local condition of stability would be an assumption [9]:

$$\frac{\partial}{\partial t}\left(\delta^2 s\right) \geq 0,\ at:\ \delta^2 s < 0 \tag{3}$$

where s—specific entropy of the system.

The time derivative of $\delta^2 s$ (3) is linked, as depicted in [9], with the entropy production induced by perturbations, i.e.,

$$\frac{1}{2}\frac{\partial}{\partial t}(\delta^2 s) = \sum\nolimits_n \delta X_n \delta J_n \ \geq 0 \tag{4}$$

The sum on the right-hand side is known as excess entropy production. Values δX_n and δJ_n are defined as deviations of relative fluxes and forces in a stationary state. If, starting from the perturbation, inequality (4) is observed, then this state is considered stable. However, under specific processes or the interaction of diverse processes, it is feasible to acquire a negative contribution to excess entropy production that increases as perturbation amplifies. In this case, the given state may turn out to be unstable (positive excess entropy generation being sufficient, but not required condition of stability).

Let us assume that friction is the only independent source of the energy dissipation in the system. In this case, excess entropy production, according to (3) and (4), would appear as follows:

$$\frac{1}{2}\frac{\partial}{\partial t}(\delta^2 s) = \delta X_h \delta J_h \tag{5}$$

Let us introduce a certain variable (φ) that characterizes the tribosystem deviation from equilibrium. In our situation, it may be a process variable, e.g., deviation of spray temperature from equilibrium spray temperature or flow rate.

When the system deviates from the stationary state, i.e., increase of the φ factor, excess entropy production, with allowance for (1), will equal to (considering that only k and λ depend on φ):

$$\frac{1}{2}\frac{\partial}{\partial t}(\delta^2 s) = \delta\,(kpv)\,\delta\left(\frac{kpv}{\lambda\,T^2}\right) = \frac{(pv)^2}{T^2}\left(\frac{1}{\lambda}\left(\frac{\partial k}{\partial \varphi}\right)^2 - \frac{k}{\lambda^2}\frac{\partial k}{\partial \varphi}\frac{\partial \lambda}{\partial \varphi}\right)\delta\varphi^2 \tag{6}$$

The right-hand side of expression (6) may become a negative one due to the sign of the second multiplicand. In order for (6) to become negative, it is required that it meet the following assumption:

$$\frac{\partial k}{\partial \varphi}\frac{\partial \lambda}{\partial \varphi} \ > 0 \tag{7}$$

Assumption (7) is met when the friction factor and thermal conductivity, simultaneously, decrease or increase as φ variable increments.

Outcomes of experiments [10,16] imply that, friction without seizure generation of the second structures leads to a decrease in the thermal conductivity of surface layers, and a decrease in the friction factor. In the course of seizure, the friction factor and thermal conductivity will build up. Therefore, it has been experimentally proven that, as φ variable increments, assumption (7) is met. As the negative contribution exceeds the positive one, as to the absolute value in (6), assumption (3) may be violated, and the system may become unstable. In this case, probability, rather than optionality of loss in stability, is preconditioned by the fact that assumptions (2) and (3) are defined as the requisite, but not sufficient, conditions of stability.

There are two simultaneous processes on a sprayed surface during friction. The first process is defined as powder particles seizing with treated material, while the second one is defined as normal friction. These processes are running simultaneously and, therefore, they could be substituted into a single equation for entropy production.

We are interested in the enhancement of the seizure process; therefore, let us consider the conditions for loss in thermodynamic stability of the system, along with concurrent enlargement of the seizure area.

We will adopt the following notations:

Friction factor in locations without seizure, k
Total contact area, G (non-variable)
No-seizing contact area portion, n
Seizing contact area portion, $1 - n$
Mechanical stress under extension of seizure bridges, σ
Sliding velocity, v
Clamping force, p
Transferred material density, ρ
Rate of mass transfer, w
Rate of mass transfer within normal friction zone, w_T
Rate of mass transfer within seizure zone, w_S
Transferred material density within normal friction zone, ρ_T
Transferred material density within seizure zone, ρ_S
Thermodynamic force causing the mass transfer, X_m
Thermodynamic force causing the mass transfer within normal friction zone, X_T
Thermodynamic force causing the mass transfer within seizure zone, X_S
Thermodynamic flux of the mass transfer, J_m
Temperature, T
Coefficient of thermal conductivity, λ
Non-equilibrium factor, φ

The entropy production equation will have three terms that characterize general friction, seizure, and mass transfer. The entropy production of general friction is determined by (1).

Mass transfer mechanisms in friction are not studied enough, so for the entropy production for the mass transfer ($\frac{ds_{im}}{dt}$), we write, in general terms:

$$\frac{ds_{im}}{dt} = X_m J_m \tag{8}$$

According to the authors of [7], flux of mass transfer can be represented as the multiplication of the density of the material transferred, the rate of mass transfer and contact area:

$$\frac{ds_{im}}{dt} = \frac{X_m \rho w G}{T} \tag{9}$$

Mass transfer within the general friction zone and seizure zone will apparently proceed in different ways. Therefore, let us break up the Equation (9) term that characterizes mass transfer into two summands:

$$\frac{ds_{im}}{dt} = \frac{X_m \rho w G}{T} = \frac{X_s \rho_s w_s \left(1-n\right) G}{T} + \frac{X_T \rho_T w_T n G}{T} \tag{10}$$

We assume that there is no sliding within the zones of seizure. That is why the velocity parameter can be represented by the speed of deformation of welded asperity junctions between the rubbing bodies. We can consider seizure as just a given spontaneous process with no energy (activation) required to start. Therefore, the entropy production for seizure ($\frac{ds_{is}}{dt}$) is determined by the deformation of welded asperity junctions:

$$\frac{ds_{is}}{dt} = \frac{\sigma v G \left(1-n\right)}{T} \tag{11}$$

In Equation (11), the thermodynamic force-mechanical stress under extension of seizure bridges, σG, thermodynamic flux—a rate of deformation equal to sliding velocity, v.

Thus, the equation of entropy production is the following:

$$\frac{ds_i}{dt} = \frac{(kpv)^2}{\lambda TnG} + \frac{\sigma v\,(1-n)\,G}{T} + \frac{X_s \rho_s w_s\,(1-n)\,G}{T} + \frac{X_T \rho_T w_T nG}{T} \tag{12}$$

Self-organization may commence after the tribosystem has lost thermodynamic stability. A nonequilibrium factor, φ, will be used as a systematic equilibrium deviation factor.

The requisite system stability condition will be determined by the sign of excess entropy production. In this case, excess entropy production will equal as follows (considering that only k depends on φ):

$$\sum_i \delta J_i \delta X_i = \delta\,(kpv)\,\delta\frac{kpv}{\lambda TGn} + \frac{\delta\sigma\delta\,(v\,(1-n)\,G)}{T} + \frac{\delta X_s \delta\,(\rho_s w_s\,(1-n)\,G)}{T} + \frac{\delta X_T \delta\,(\rho_T w_T nG)}{T}$$

$$\begin{aligned}\sum_i \delta J_i \delta X_i = {} & \tfrac{pv^2}{\lambda TGn}\left(\left(\tfrac{\partial k}{\partial \varphi}\right)^2 - \tfrac{k}{n}\tfrac{\partial n}{\partial \varphi}\right)(\delta\varphi)^2 - \tfrac{vG}{T}\left(\tfrac{\partial \sigma}{\partial \varphi}\tfrac{\partial n}{\partial \varphi}\right)(\delta\varphi)^2 + \tfrac{G}{T}\tfrac{\partial X_s}{\partial \varphi}\left(\tfrac{\partial \rho_s}{\partial \varphi} w_s(1-n)\right. \\ & \left. + \tfrac{\partial w_s}{\partial \varphi}\rho_s(1-n) - \tfrac{\partial n}{\partial \varphi}\rho_s w_s\right)(\delta\varphi)^2 + \tfrac{G}{T}\tfrac{\partial X_T}{\partial \varphi}\left(\tfrac{\partial \rho_T}{\partial \varphi} w_T n + \tfrac{\partial w_T}{\partial \varphi}\rho_T n + \tfrac{\partial n}{\partial \varphi}\rho_T w_T\right)(\delta\varphi)^2\end{aligned} \tag{13}$$

The right-hand side of Equation (13) features four addends. It is likely that, in order for excess entropy production to be less than zero, each addend should preferably be less than zero. At a deviation from equilibrium thermodynamic forces are increased, *i.e.*, $\frac{\partial X_s}{\partial \varphi} > 0$, $\frac{\partial X_T}{\partial \varphi} > 0$.

As previously mentioned, during seizure, the following occurs:

$$\frac{\partial k}{\partial \varphi} > 0;\ \frac{\partial n}{\partial \varphi} < 0 \tag{14}$$

In this regard, the first addend on the right-hand side of Equation (13) will be positive.

The second addend enters the sum having a "negative" sign; hence, for enhancing the probability of loss in stability, this should be positive. Taking (14) into account, the second addend may be positive at:

$$\frac{\partial \sigma}{\partial \varphi} < 0 \tag{15}$$

Taking (14) into account, in order for the third addend to become negative, it would need to meet the following assumptions:

$$\frac{\partial \rho_s}{\partial \varphi} < 0;\ \frac{\partial w_s}{\partial \varphi} < 0 \tag{16}$$

Taking (14) into account, in order for the fourth addend to become negative, it would need to meet the following assumptions:

$$\frac{\partial \rho_T}{\partial \varphi} < 0;\ \frac{\partial w_T}{\partial \varphi} < 0 \tag{17}$$

Whereas (14) is strictly observed, maximum probability of loss in stability of the tribosystem will suit assumptions (14)–(17).

Assumptions (16) and (17) mean that, for self-organization, along with simultaneous enhancement of seizure, relatively light components of the powder mix should be transferred into the seizure zone. The introduction of heavy elements should lead to a decrease in the seizure area. Alloying of coating for cutting tools using a heavy element (tungsten) led to a significant reduction in seizure [17,18].

3. Experiment

This section will demonstrate the outcomes of the examination of friction seizure. Gas dynamic spray will be used as an example.

Gas dynamic spray is defined as gas jet spraying of metal powder, or a mix of several metal powders, onto a surface. The gas stream flows at a near-sound velocity. The gas stream entrains the metal powder and delivers it to the surface. The powder particles hitting the metal surface are exposed to intensive plastic flow deformation. A part of the metal powder bounces off the metal surface, while the other part adheres to the surface owing to the seizure effect.

The gas dynamic spray process was carried out over the flat surface of cold-worked copper. Copper powder and a mix of copper and 20% zinc were used as the powders. Air was used as a carrier gas. The air stream was heated up to 300 °C. The air stream velocity was about 90% of the speed of sound.

With a SEM microprobe (AMETEK, Inc—CAMECA SAS, Gennevilliers, France), the surface of the substrate and sprayed layer were investigated. The study surface was perpendicular to the surface of the substrate.

4. Results and Discussions

When spraying the copper powder, lamination occurred, while bonding strength only reached 3 MPa to 5 MPa. When spraying a mix of copper and zinc powders, bonding strength reached 10 MPa to 12 MPa.

Distributions of chemical elements in the sprayed layer near the surface of the substrate are shown in Figures 1–4. Investigations were carried out with a SEM X-ray microprobe.

Micrographic investigations of sections on the boundary between the substrate and sprayed layer using a SEM X-ray microprobe testified that, when enriching the near-surface area (area adjacent to the substrate) sprayed by the powder mix with zinc, the spray strength was quite high, and lamination was not observed (Figures 1 and 2).

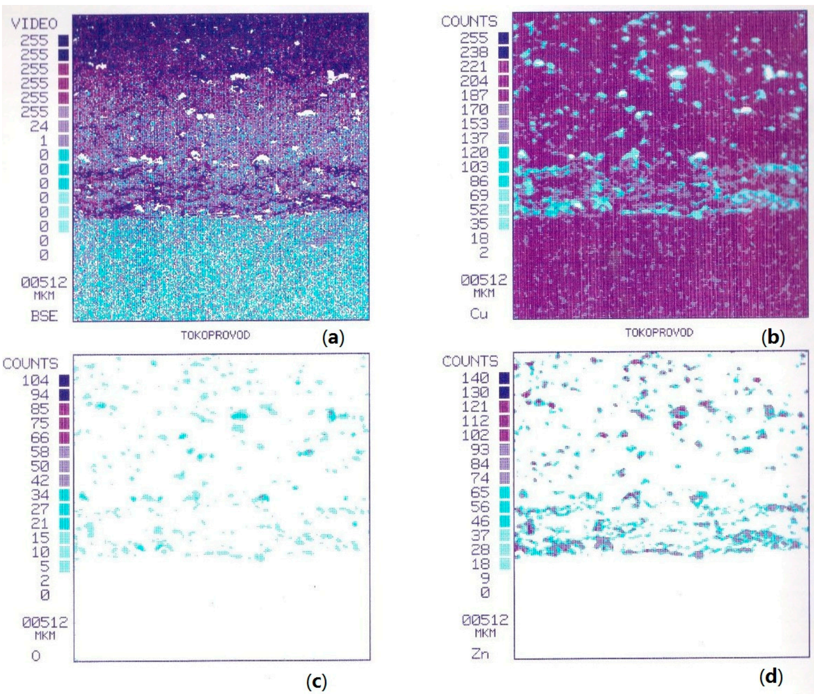

Figure 1. Image of boundary between sprayed layer and substrate (sprayed layer is on top of all images) with near-surface area enriched with zinc. Squares sizes 512 × 512 µm. Images were produced in: secondary electrons (**a**); in characteristic radiation of copper (**b**); in characteristic radiation of oxygen (**c**); and in characteristic radiation of zinc (**d**).

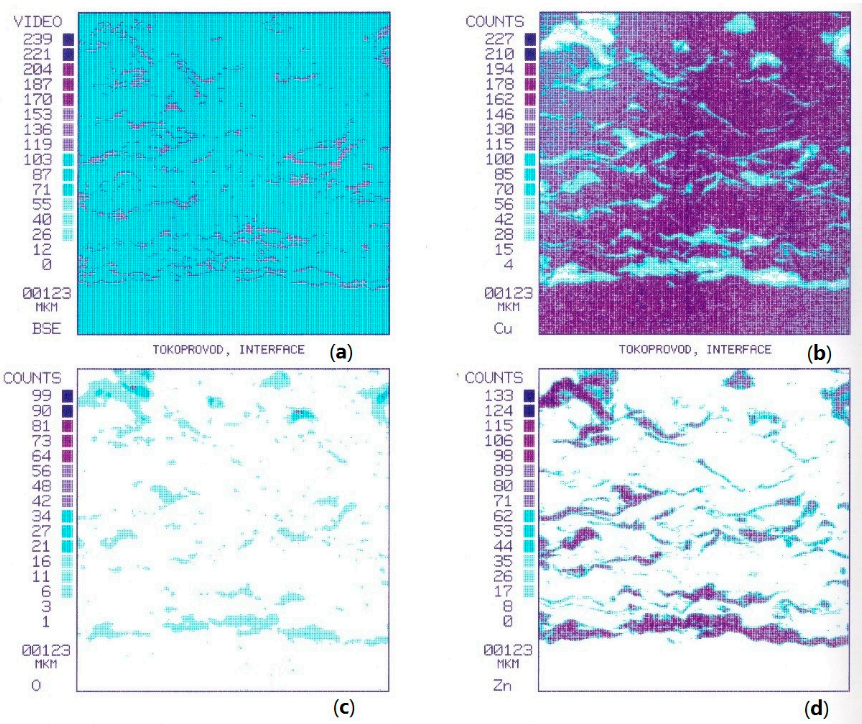

Figure 2. Images of the structure of the near-surface area enriched with zinc (sprayed layer is on top of all images). Square sizes 123 × 123 μm. Images were produced: in secondary electrons (**a**); in characteristic radiation of copper (**b**); in characteristic radiation of oxygen (**c**); and in characteristic radiation of zinc (**d**).

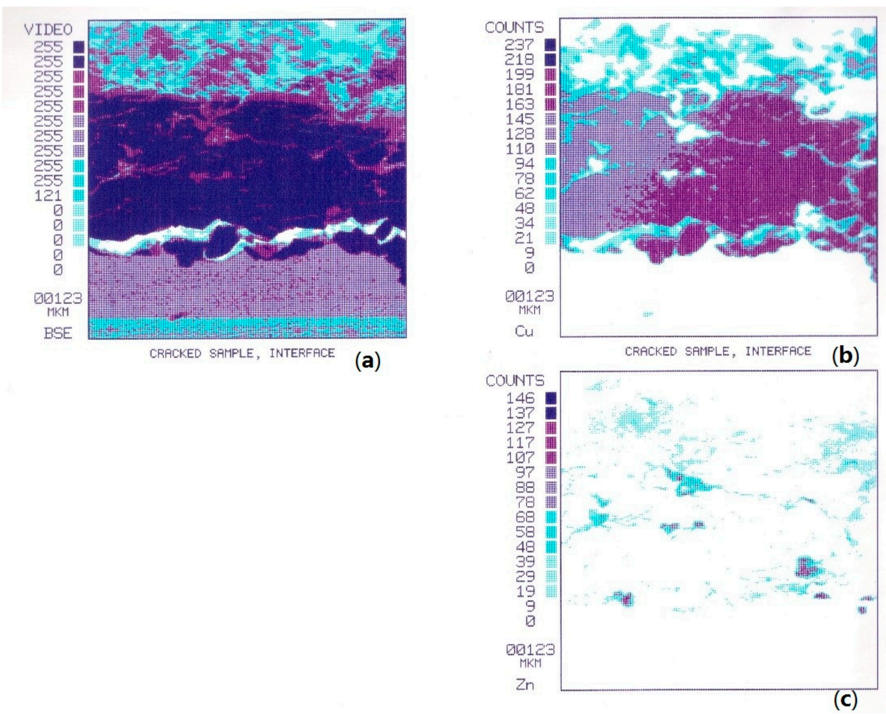

Figure 3. Images of boundary with a crack between sprayed layer and substrate (sprayed layer is on top of all images) with substrate enriched with copper. Square sizes 123 × 123 μm. Images were produced: in secondary electrons (**a**); in characteristic radiation of copper (**b**); and in characteristic radiation of zinc (**c**).

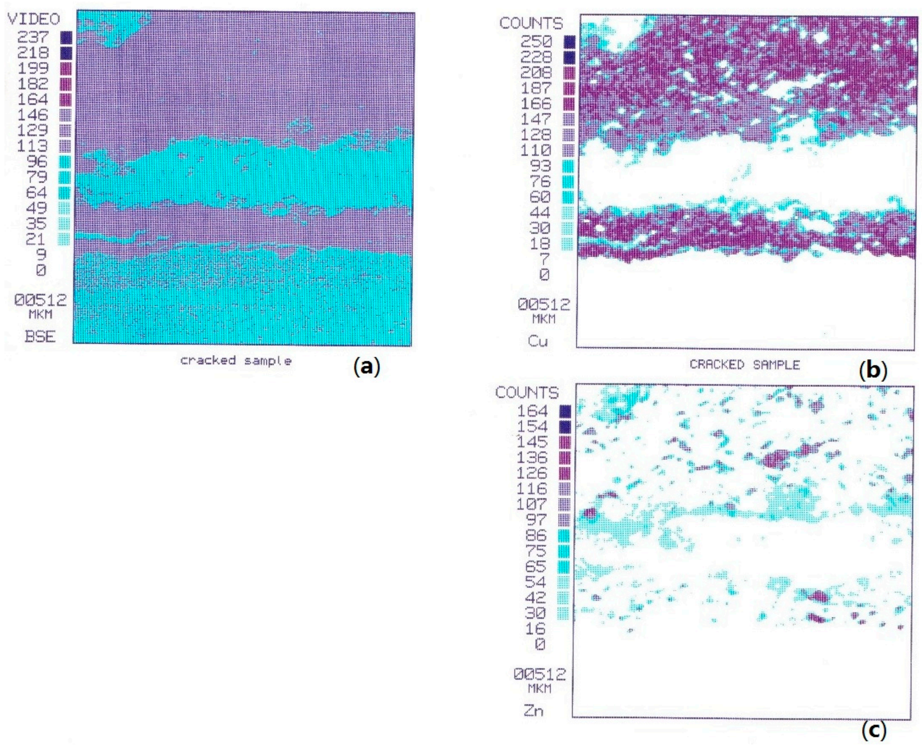

Figure 4. Structure of the near-surface area enriched with copper in the vicinity of crack. Square sizes 123 × 123 μm. Images were produced: in secondary electrons (**a**); in characteristic radiation of copper (**b**); and in characteristic radiation of zinc (**c**).

Lamination was observed when the sprayed layer maintained evenly distributed particles of the copper/zinc powders mix, i.e., the near-surface area enriched with zinc never occurred (Figure 3), or the near-surface area enriched with copper occurred (Figure 4).

Figures 3 and 4 depict the crack originating from the lamination of the sprayed layer off the near-surface area enriched with copper.

Therefore, during spontaneous formation of the near-surface area enriched with zinc, the sprayed layer will feature a quite-high substrate bonding strength. Laminations are not observed.

During spontaneous formation of the near-surface area enriched with copper, the sprayed layer will feature a quite-low substrate bonding strength. Laminations are observed.

Hence, during spontaneous predominant mass transfer of the relatively light component (zinc) into the seizure zone, the seizing area increases.

During spontaneous predominant mass transfer of the relatively heavy component (copper) into the seizure zone, the seizing area shrinks.

This draws conclusions from the previous section demonstrated that the seizing area decreases under predominant mass transfer of the relatively heavy component.

During spraying, we found that there are two possible outcomes (Figures 1 and 2) under the same conditions. The first is the separation of the powder mixture, which leads to an increase in adhesion to the substrate. The second is a lack of separation of the powder mixture, which leads to a decrease in adhesion to the substrate. This is similar to bifurcation. To increase the probability of a result, the composition of the surface region, rich in zinc, was determined. It contains 50%–54% Zn. The initial mixture contained only 20% Zn. According to the authors of [9], a system that cannot come to an equilibrium tends to reduce entropy production of the process. When seizure occurs, the friction stops and entropy production decreases. Friction is an artificial process; the system response to friction is a natural process. To ensure the necessary passage of a natural process (seizure), the powder mixture must contain 50%–54% of Zn. Increasing zinc content leads to an undesirable decrease in electrical conductivity of the sprayed layer. When zinc content in the mixture was 20% and 30%, the adhesion was 10.4 MPa and 12.3 MPa, respectively. In approximately 1/3 of the experiments, cracking was observed in the absence of a zinc-rich layer. When the zinc content in the mixture is 50%, adhesion was 19.6 MPa. Cracking was not observed.

5. Conclusions

Application of nonequilibrium thermodynamic methods and self-organization theory demonstrated that, during spraying a mix of powders for enhancing powder particles seizing with the substrate, it is required that the seizure zone be enriched with relatively light components of the powder mix.

This inference has been experimentally confirmed, as exemplified by a spray of copper/zinc powder mix.

The optimum composition of the deposited mixture of Cu-Zn, in terms of its adhesion to the substrate, is Cu-(50%–54%) Zn.

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