

Formation of coatings from a liquid phase on the surface of iron-base alloys

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Abstract

The study discloses the present state of the art regarding the technology and investigations of the phenomena that take place during the formation and growth of aluminum and zinc coatings hot-dip formed on iron products. In its cognitive aspect, the study offers an in-depth analysis of the partial processes that proceed in metal bath at the solid body – liquid metal interface. It is expected that the present study will help in a more detailed description of the respective phenomena and in full explanation of the mechanism of the coating growth, taking as an example the growth of aluminum coatings. The obtained results can serve as a background for some general conclusions regarding the thickness evolution process in other hot-dip coatings.

Keywords: Hot dip aluminizing, Coating from a liquid phase, Mechanism of growth

1. Introduction

Iron content in the Earth's crust amounts to about 5.6 wt.% which makes this metal the second most abundant after aluminum (about 7.4 wt.%). Owing to numerous deposits of magnetite, hematite, limonite, siderite and pyrite, iron is the cheapest of all metals and its production has totally dominated the market of metallic structural materials. Iron-base alloys are mainly those of carbon steel ($C < 2$ at.%) and cast iron ($C > 2$ at.%). A drawback of carbon steels and cast irons is their low corrosion resistance in humid air and in the aqueous environment. In sixties and seventies of the past century, when losses due to corrosion suffered by the high-industrialized countries reached 10% of the annual gross domestic product, numerous programs for fighting corrosion were developed and put into operation. Among many technologies that are supposed to protect the steel and cast iron from electrochemical corrosion, hot-dip galvanizing, that is, the technique of producing coatings from liquid phase, is generally considered the most effective and, at the same time, cheapest

method for protecting the surface of the above mentioned alloys. By this technique are produced, among others, the coatings of zinc, tin, lead, and aluminum [5,14,22].

Hot-dip galvanizing is also the most popular technology for protection of iron-base products from the atmospheric corrosion. In foreign and domestic technical literature, the results of numerous studies on zinc and aluminum coatings produced by hot-dip process are published, but there are many controversial ideas in this respect. Particularly controversial and disputable is the problem of the mechanism that governs the growth of zinc coatings.

The results of the experiments collected by the authors from the long-lasting research indicate that the process of hot-dip coating formation should rather be regarded as a sort of "controlled corrosion process". Adopting this idea as a point of departure for further investigations, attention has been focused on the phenomena and processes that occur at the liquid-solid interface. Detailed analysis of the data available in literature indicates that most of the authors [5,6,14,22] examine the kinetics and mechanism of the formation of hot-dip coatings, neglecting

the effects that take place in metal bath and focusing their attention only on the processes of diffusion that occur in solid phase. The few authors who do pay attention to the surface phenomena, like dissolving of iron in the metallization bath, permanently disregard the effect that this process may have on the coating formation [1,6,22].

Experience acquired during research teaches us that, despite some differences that quite naturally must result from the fact that different metals are used for a metallization bath, the mechanism of coating formation from a liquid metal phase is always the same. This phenomenon can be best explained on the example of an aluminum coating deposited on iron.

2. The technology of hot-dip coating fabrication

Zinc coatings are the most popular anti-corrosive coatings, applied in prevailing part on sheets, strips and wires. Coatings on these products are made by continuous methods. Recently, the technology and automatization have been improved so much that they guarantee the highest possible profitability of the manufacturing process, mainly due to a very low level of the zinc losses during coating fabrication and production output incomparably higher than that obtained when individual batches of parts [1-4,7,11-22] are immersed in bath. Zinc coating by dipping each batch separately continues being used in fabrication of protective coatings on rolled products of the closed profile (e.g. pipes), on some castings and on the ready-for-use structural elements of complex geometry.

Zinc coatings are not the only coatings fabricated on industrial scale on products made from iron-base alloys. Tin and lead coatings are also used, but in most cases they are customized and produced to protect the steel from corrosion in some specific corrosive media. Tin coatings have been widely used by food industry. Lead coatings, on the other hand, have proved suitable for applications in the sulphur-containing atmospheres. Nowadays, a decrease in demand for tin and lead coatings fabricated by immersion is observed [2,4,8].

Aluminum coatings form a separate group of hot-dip coatings, and they are characterized by corrosion resistance superior to that of the conventional zinc coatings. Two basic types of the bath are used in this case, viz. Al+11%Si alloy (type 1) and „pure” aluminum (type 2) [9]. The coatings differ in their properties. Coatings of type 1 offer good plastic properties but lower corrosion resistance and appearance inferior to that of coatings of type 2, which – in turn – have metallic lustre and better corrosion resistance on the cost of lower plastic properties. Aluminum coatings of both types are characterized by the resistance to electrochemical effects 4 to 8 times higher than the zinc coatings. The additional advantage of aluminum coatings is their resistance to corrosion at high temperatures. The improved high temperature corrosion resistance results from the formation of an alumina Al_2O_3 layer on the surface of the galvanized products. The technology of galvanizing has several variants, which differ in the technique of the preliminary surface treatment before the main process of the formation of a metallic protective layer begins

[1-6,11-16]. The surface treatment can be done by the following methods:

- heat treatment in gas atmosphere by Sendzimir’s process,
- chemical treatment combined with application of fluxes in the form of aqueous solutions or molten salts,
- combined treatment,
- chemical degreasing, oxidizing and reduction in gas atmosphere,
- degreasing by annealing and etching in acid solutions.

In continuous methods, the sheet surface is usually treated in gas atmosphere. In the batch technique of coating fabrication, combined techniques are applied, i.e. the surface treatment by chemical processing and the use of fluxes, which are aqueous solutions or molten salts.

After the preliminary surface treatment of products, they are immersed in metal bath and let stay in this bath for a time long enough to make the coatings start growing on their surface. The temperatures used most commonly in a bath for the metallising treatment are given in Table 1.

Table 1.
The most commonly used temperatures of the galvanizing bath

Bath composition	Bath temperature [°C]
Zn	440-460
Zn high-temperature	530-560
Zn+5%Al	400-420
Zn+55%Al	590-640
Al	690-750
Al+11%Si	590-660

As a result of the galvanizing process, coatings of a characteristic structure are obtained. Selected structures of the hot-dip coatings are shown in Figure 1.

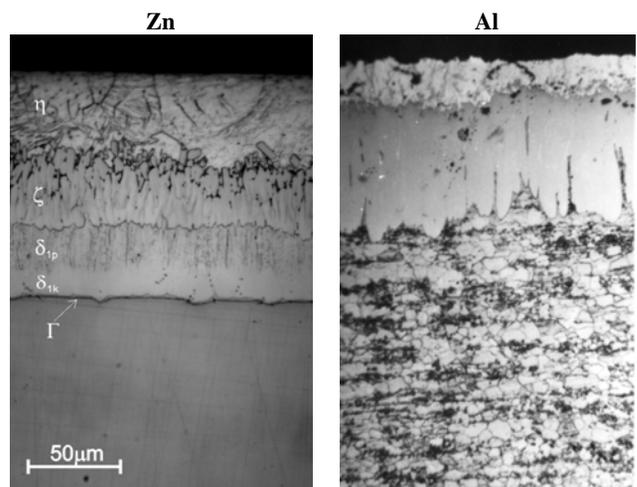


Fig. 1. The structure of aluminum and zinc coatings

The structure of the coating shown in Figure 1 is schematically presented in Figure 2. Aluminum coating on Armco iron consists of two layers. The layer closer to the substrate is composed of Al_3Fe_2 phase. It has a well-developed interface of

a shape that is usually referred to as „tongues”. Each tongue-like crystallite is a monocrystal and its axis is concurrent with the c axis of an elementary cell. The Al_3Fe_2 crystallites are observed to grow at a maximum rate in direction of the c axis, and this is due to a specific nature of the Al_3Fe_2 lattice. This means that the growth factor will reach its maximum value when an angle between the c axis and the plane of interfacial reaction is equal to 90° .

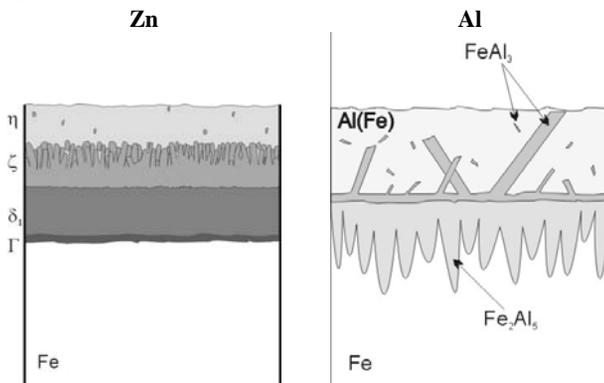


Fig. 2. The structure of aluminum and zinc coatings

If the growth does not occur at an angle of 90° to the surface plane, the neighbouring crystallites can act as inhibitors limiting each other's growth (a competitive growth). At the initial stage of growth, there are numerous nuclei of random orientation. If the neighbouring crystallites are not nucleating at the same time, or if their growth does not assume a parallel course, they can mutually obstruct their own growth. This reduces locally the thickness of the layer below its maximum value. On the surface of a layer of the η phase there is a thin film of the Al_3Fe phase. Its thickness remains constant and practically independent of the galvanizing time in a bath of constant temperature. From this layer to the external layer, the columnar crystallites of Al_3Fe phase are growing. They are growing on the surface of the Al_3Fe phase, which forms a part of the intermediate layer; they are also present as loose items in the external layer. Deep etching of the coating has proved that these crystallites are „growing out” from the intermediate layer (see Figure 3).

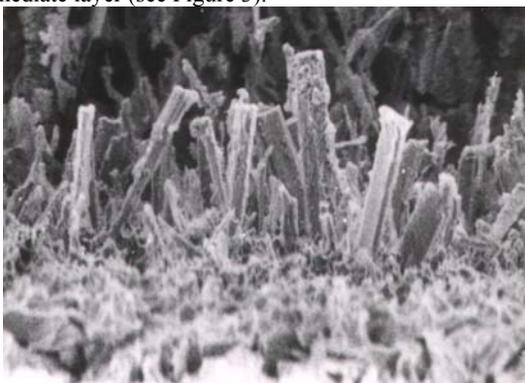


Fig. 3. A view of the surface of diffusion layer in hot-dip aluminum coating deposited on white cast iron at the temperature of 1023K during the time of 300s; deep etching [14]

The inclusions of Al_3Fe phase present in the external layer are formed as a result of the secondary crystallization of Al_3Fe phase from a solution that forms the external layer in an iron-saturated coating (the Nernst diffusion layer). When aluminum coating is formed on some materials (cast iron, for example), the Al_3Fe phase acts as a skeleton on which the external layer of the aluminum coating is built up. The number, shape and dimensions of the crystallites of the Al_3Fe phase depend on the galvanizing time and temperature, and also on the type of the substrate material. The stronger is the substrate tendency to the dissolution and the more of iron is dissolved in aluminum bath, the larger and coarser are the crystallites of Al_3Fe phase in the external layer. In this layer of coating, the matrix is a solid solution of iron in aluminum, containing about 0,34%Fe.

As results from the examinations of the coating structure, the phase formed on the boundary with metal bath has a different morphology. So, a thesis has been put forward that the difference may be due to a different mechanism of growth. To prove this thesis it has been necessary to determine:

- the kinetics of the process of the coating growth on the substrate of commercially pure iron in aluminum bath with a standard addition of iron,
- the mass transport velocity in a liquid phase of the iron-aluminum bath system using a capillary to avoid the effect of a „mechanical” compensation of the iron concentration in aluminum bath,
- the iron transport velocity at the solid-liquid interface under the conditions of convection stirring of the bath,
- the iron dissolution process rate under the kinetic conditions of a spinning disk used for stirring of the bath, when the dissolution rate is independent of the spinning velocity.

The results of these investigations are presented in [22]. Their analysis allows a description of the mechanism of the hot-dip coating formation to be made.

3. Mechanism of aluminum coating growth

The reaction going on between the iron/iron-base alloy and aluminum bath can be divided into a number of time steps during which partial processes of the growth of a diffusion layer take place.

The individual time steps of the growth of a hot-dip coating on an iron product in aluminum bath are shown in Figure. 4.

During time step τ_0 , when the „cold” iron gets in contact with liquid aluminum, the bath temperature drops locally (occasionally the bath may even solidify) while heating the immersed charge. The heat transfer process is going on until iron reaches the temperature necessary to initiate a reaction in which both solid metal (iron) and the liquid aluminum bath will take part. Until this time, a high-rate heat transfer process is observed to take place between the cold iron surface and hot liquid metal. Within the lapse of this time numerous other processes occur as well. Proceeding at a very high rate, they are difficult to investigate. During this initial period, very important are the surface phenomena and strongly exothermic reaction going on between iron and aluminum. Current knowledge of this subject enables

judging that the process of “spreading” of liquid aluminum on the surface of iron takes place simultaneously with the reaction of the formation of iron-aluminum phases. Fed with the energy of reaction, the surface process is very intense. Examining the mechanism by which the coating growth starts, one can observe that the conditions are favorable when the solid – liquid interface has no gas adsorbed in it. This state can be achieved when a layer of flux is deposited on the surface of the treated product. It is difficult to establish which of the phases in an Fe-Al system (η

Al_3Fe or Al_5Fe_2) is formed first on the surface of an iron product. In literature [5,6,14,22] the opinion is prevailing that it is the η - Al_3Fe phase. Yet, it seems that for a description of the mechanism of the coating growth, knowing at this stage of the process which of the intermetallic phases from an iron–aluminum equilibrium diagram shall emerge first is quite unnecessary. The first step is completed when the surface of iron gets coated with the products of reaction.

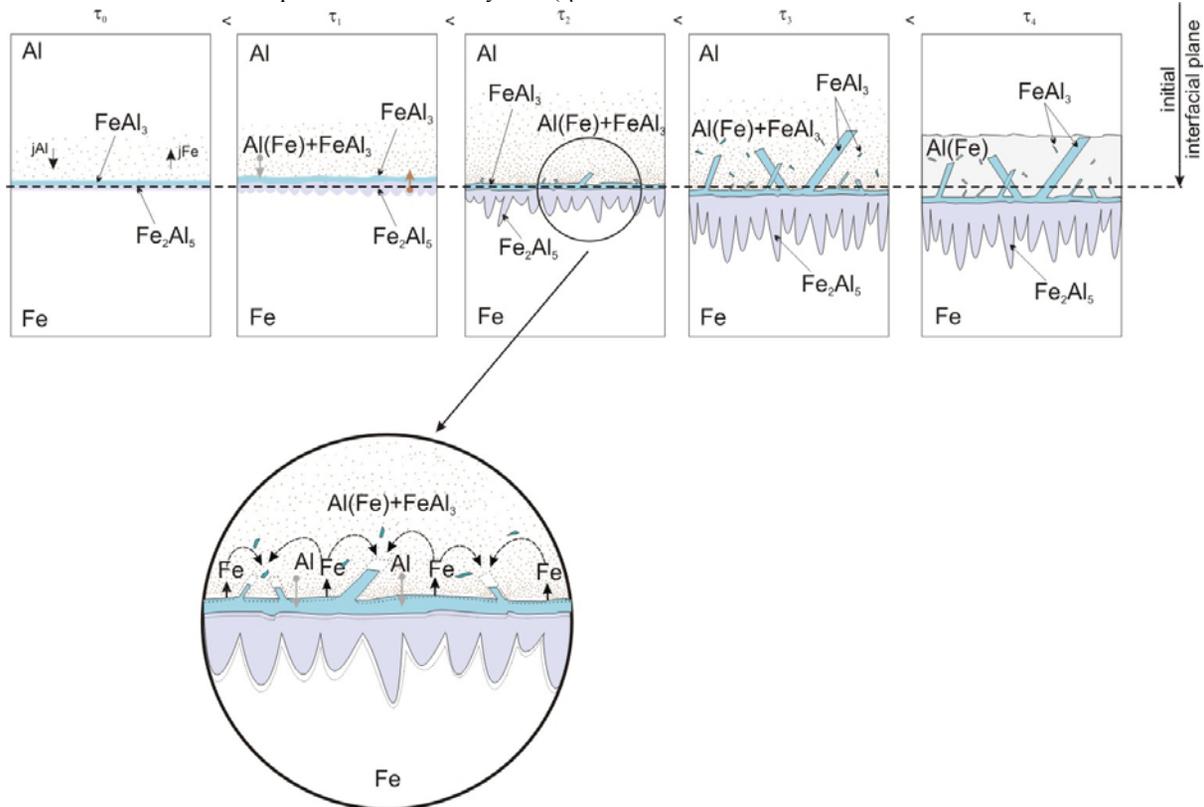


Fig. 4. Mechanism of aluminum coating growth

During time step τ_1 , as a result of the two-directional diffusion (known as a reaction diffusion), the phases of the crystallographic lattices different than the lattices of the diffusing metals are formed. A characteristic feature of the process of reaction diffusion is that its rate frequently depends not only on the diffusivity of individual elements present in the phases but also on the kinetics of interfacial reactions. The formation of new phases during reaction diffusion implies some discontinuities in the concentration of the diffusing constituents. The lack of one compact phase layer is observed. So, these are the heterogenous reactions in a non-homogeneous medium.

The process includes the following stages:

- diffusion of substrate (Fe and Al) to the phase boundary area,
- effect of the Fe and Al atoms transport through the phase boundary caused by breaking of some, already existing, bonds and the formation of new ones,

- diffusion of elements through a layer of the new intermetallic phases.

At the initial stage, this period should be regarded as a sequence of transient states characterized by an interchangeable aluminum-to-iron (substrate) and iron-to-aluminum (bath) diffusion. Due to this effect, in a relatively short time, the phases anticipated by a binary iron–aluminum system are formed. From the phase equilibrium diagram for Fe-Al system, at a temperature typical of the aluminizing process, the structure of aluminum coating should comprise a solid solution of aluminum in iron and intermetallic phases with increasing aluminum content (AlFe_3 , AlFe , ζ - Al_2Fe , η - Al_3Fe , Fe_2 , and θ - Al_3Fe). At this stage of the process, the solid phase dissolution in metallic liquid is also initiated. Stage τ_1 ends the initial period of the coating growth.

During time step τ_2 , after the initial period described above, further growth in the thickness of the already formed intermetallic compounds of the coating in the zone of the intermetallic Fe-Al phases is observed as well as a dissolution of the phase in

contact with aluminum bath. Observations of the growth of hot-dip aluminum coatings indicate that these reactions are proceeding at a very high rate, while the growth of individual layers is controlled by a process much slower, i.e. by diffusion. Hence it follows that for a description of the diffusion layer growth under the conditions of the hot-dip galvanizing process, the processes of diffusion should be examined as well. Only two intermetallic phases in the structure of coatings have the thickness sufficient to make the examinations possible. These are the phases of η - Al_5Fe_2 and θ - Al_3Fe [5,6,9,14-22]. One can assume that other phases present in the Al-Fe equilibrium system are characterized by the diffusion coefficients so low that the formation of layers of a sufficient thickness is not possible.

Possible course of reactions on various phase boundaries is shown in Figure 5.

To determine the direction of displacement of the individual phase boundaries and the main process responsible for the mass transport it is necessary to determine the respective ratios between the fluxes of the diffusing reactants. As a result of the carried out experiment of witnessing the diffusion process in coating, from the position of markers (Fig. 6) it has been concluded that the growth of coating is possible because it is the aluminum flux diffusion to a substrate that plays the leading role here. So, consequently, all further studies were based on the assumption that the growth of a layer depends on the aluminum flux and its diffusion to the substrate.

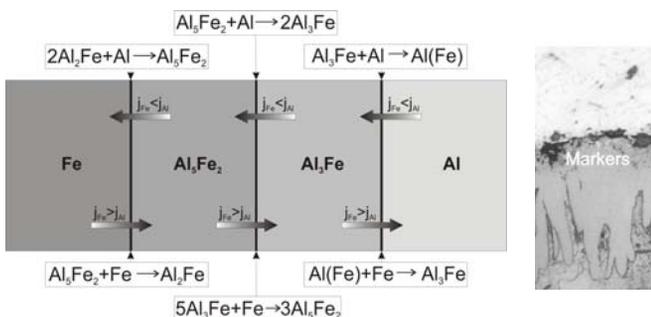


Fig. 5. Model of reaction on the interface borders during hot dip aluminizing and position of markers

The intermetallic Al_3Fe phase is contacting aluminum bath, where the composition of a thin outer layer is changing in function of the degree of saturation with Al. This, in turn, changes the concentration of aluminum across the thickness of the intermediate layer of Al_3Fe . The outcome is diffusion of aluminum atoms through the individual layers to iron. On the phase boundaries, aluminum enters in reaction with the intermetallic compounds already present there.

The growth of η Al_5Fe_2 phase is possible owing to the reaction:



This phase is not visible on an image of the coating microstructure, but we know that it is present under the layer of η Al_5Fe_2 phase, and it is only its thickness that makes the observations impossible.

The growth of thickness of the diffusion layer of η Al_5Fe_2 is not accompanied by the growth of ζ Al_2Fe phase. The dynamic growth of phase η is progressing due to the path of easy diffusion made by the vacancies in aluminum sublattice and in a rhombic lattice of this phase [5,14,22].

On the Al_3Fe and Al_5Fe_2 phase interface, a reaction is going on promoting the θ Al_3Fe phase growth:



This makes the diffusion path “longer” and the aluminum flux diffusing in this phase “shorter”. With a relatively large diffusion flux of aluminum in the liquid, this must result in supersaturation of the examined intermetallic phase in contact with the bath, followed by its dissolving. This may occur due to the formation of $\text{Al}+\text{Al}_3\text{Fe}$ eutectic. Then, owing to a low temperature of the eutectic, melting of the supersaturated phase will take place. The outcome will be the reduced thickness of Al_3Fe phase and, as a consequence, intensification of the growth of a diffusion flux.

Due to this phenomenon, the θ Al_3Fe phase will be growing in thickness first, to remain at the same level throughout the rest of the galvanizing process.

The atoms of iron or, which is much more probable, the clusters of Al_3Fe phase [5,14,22] are passing to the bath and form around the phase boundary a supersaturated solution of iron in aluminum. Owing to the process of diffusion and movement taking place in the liquid, iron is transported inside the bath. This creates the conditions favourable for saturation with iron of other regions present in the bath. Because of a low rate of iron transport inside the bath and limited solubility of iron in aluminum, favourable conditions are also created for the crystallization and growth of columnar crystallites of Al_3Fe phase. Their growth takes place on the surface of a layer of the intermetallic phase, at the crystallographically preferred sites. Since there is a local drop of iron concentration around the sites of the secondary crystallization, proper conditions are created for the aluminum bath to enrich its iron content through dissolution. In literature it is discussed when exactly, i.e. at which time step of the process, the columnar crystallites start growing. Eggeler [7] and co-authors assert that these crystallites are formed by crystallization when the coated element is emerging from the galvanizing bath. In the opinion of these authors, the crystallization may be due to the presence of iron dissolved in aluminum bath and “caught” in a bath volume when drawn out together with the treated product.

In [5,14,22] it has been proved that the columnar crystallites of Al_3Fe phase are formed in liquid bath by the secondary crystallization from liquid aluminum supersaturated with dissolved iron surrounding the galvanized product. To better prove this thesis, an experiment was carried out. It was thought to replace liquid aluminum in the external layer of the coating with lead. To achieve this purpose, a two-layer bath was prepared. In the upper zone of immersion chamber it was composed of aluminum, while in the lower zone of immersion chamber and in the zone where product emerges from the bath it contained lead. Tests were made on specimens of hypoeutectic white cast iron. Having prepared the surface of the specimen, it was immersed in the upper zone of the bath containing aluminum at a temperature of 963K. After the lapse of 180 seconds, the specimen was transferred to the lower zone of the bath, this time containing lead. The temperature of the lead bath was slightly lower than the temperature of the aluminum bath. After holding the specimen for

300 seconds, it was removed from the bath, and while being drawn out it was passing through the zone containing lead. The structure of thus produced coating was composed of two-layers. Similar as in the case of aluminum coatings, the intermediate layer was composed of an Al_3Fe_2 phase. On the other hand, the external layer of the coating was composed of the crystallites of the Al_3Fe phase growing out from the substrate and from the mixture rich in lead (95,2-98,5%Pb) that was filling the spaces between the crystallites. The thickness of the lead coating depends on the height of the crystallites of Al_3Fe phase. The above discussed partial processes of the coating growth are running simultaneously and are characterized by some degree of interaction. During the growth of aluminum coating, a state of the dynamic equilibrium is created; its origin lies in the physico-chemical properties of the elements and intermetallic phases, and in the kinetics of the actually running processes.

During time step τ_3 , the processes are still going on. The thickness of the η phase layer is growing in an almost parabolic way in function of the immersion time. The surface separating the intermediate layer from the coating is shifting from the plane of the initial phase boundary to the substrate interior. The content of iron dissolved in the bath is increasing. Within the zone of diffusion, a dynamic state of equilibrium is forming. It depends on the size of the aluminum flux diffusing in different intermetallic phases and on the rate of iron transport in bath, and hence on the thickness of the Nernst diffusion layer.

Time step τ_4 starts after the product has emerged from the bath. Due to the heat exchange with environment, a drop of temperature on the surface of the treated element is observed. On the surface of iron at the time instant τ_4 there is a well-formed layer of intermetallic phases in which the zone of the η Al_3Fe_2 phase is predominant and adhering to the surface. On its surface there is a thin layer of θ FeAl_3 phase with columnar crystallites growing out of it. They are surrounded by a thin film of iron-containing liquid aluminum taken out from the bath. The volume of the liquid is probably a function of the bath viscosity, the latter one being in turn dependent on the dissolved iron content.

4. Conclusion

The above described model of a mechanism of the sequential growth of the coating layers on iron is of a general character, and as such can be adapted and used effectively in description of the mechanism of formation of any arbitrary coating where the processes of dissolution and secondary crystallization take place.

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