Effect of Phase Transformation on the Properties of Metallic Coatings

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Introduction

Coating of steels with a layer containing Al or Al_mFe_n intermetallic phase or phases results in several advantages of which the most important one is increase of corrosion resistance. That is why this coating has been subject of numerous papers with concordant but also with contradictory statements (1).

In our opinion, observations virtually contradicting to each other originate from the different test conditions, on one hand. Furthermore, structures found in most of these investigations often contain one or several metastable phases, and a variety of their appearance, quantity and relations with the test conditions may be possible (2).

Tests and Measurement Results

In the following we report on tests with hot-dip aluminized coating of a low-carbon steel (0.09 wt.%). Investigations were carried out in order to get information concerning influence of phase transformations pearlite→austenite and ferrite→austenite on layer thickness, phases contained in the layer and subcoating regions of the steel.

The test equipment was described in a former paper (3). An Al-bath of technical purity was used as Al melt, with test temperatures of 700 and 900 °C, as well as immersion time of 1 to 120 sec chosen with the aim to implement observations in practical use. After immersion, specimens were water and air cooled.

Test results are contained in diagrams (Fig. 1. to 4.) and in metallographic pictures (Fig.5. and 6.). Thickness of intermetallic layer versus immersion time is depicted in Fig. 1. Test results agree with expectations that thickness of intermetallic layer s changes with time according to the function of

$$s=kt^n$$

Obviously, thickness of the intermetallic layer practically does not depend on cooling, the slight difference is explained by the little longer immersion time due to slow cooling. Thickness of the compound layer in function of time factor t^n is demonstrated in Fig. 2. This coincides with usual observations in measuring diffusion layer thickness. However, we have to note that the exponent's value shows a strong difference. Value of n at the temperature of 700 °C hardly differs from the value of 0.5 considered in the literature to be right for these processes, but we measured n=0.420. However, at the higher temperature of 900 °C we got only n=0.278. The value found at lower temperatures may be regarded as measurement uncertainty, but the latter one can be accepted by no means as measurement uncertainty. This statement is supported by the observations from earlier measurement series (3) results of which are depicted together with latest results in the same figure (Fig.3.) showing values of *n* in function of temperature. We will come back to the values of time exponent when evaluating results.

Fig. 4 demonstrates the narrow range of coating where no change in hardness was found after immersion at 900 °C. This increase of hardness was not observed in measurement series at 700 °C.

Discussion of Test Results

Our evaluation comprises, first of all, effect of phase transformation during immersion on coating formation. The lowest temperature has been chosen because at that temperature there is no phase transformation in steels. Dissolving of tertiary cementite in ferrite is neglected because in our opinion this does not perceptibly affect formation of coating. The most remarkable measurement result is the continuous decrease of exponent *n* in function of temperature, as shown in Fig. 3. We attribute it to the phase transformations occurring in steel and coating.

In steel there is no phase transformation in measurement series at 700 °C. At the surface, in contact with the Al melt, a solid solution Fe-Al and a liquid phase layer Al-Fe should form. No impede for formation of the solid solution Fe-Al appears as both metallic components are crystalline at the given temperature and Al has a high solubility in ferrite. A lower C-solubility of the solid solution Fe-Al than that of ferrite might serve as an impede, however, the available phase diagrams do not imply this. Pearlite groups at the surface and close to the surface do impedeformation of solid solution Fe-Al in the whole coating. That is why increase of intermetallic layer's thickness may be expected under conditions specified for diffusion only at the surface decreased by the quantity of pearlite, and at ferrite-ferrite crystallite boundaries slightly faster. At these boundaries not only the solid solution but also the high-Fe melt progress quickly, which may explain the presence of a structure in which steel crystallites deeply penetrate into the compound layer. As even Fe dissolves in Al melt only rather limitedly, these phases containing C survive in liquid layer. Fig. 5. shows a coated layer proceeding on 700 °C after 120 sec.

Retardation of diffusion caused by pearlite groups is expressed in the fact that value of *n* is smaller than 0.5 to be obtained when solving the Fick's differential equation. A similar retardation can be observed at temperatures above the eutectic one. Here the quantity of austenite at the boundary where the coating with Al-content is in contact with regions which may be regarded as steel increases with raising the temperature. The layer separating the outside coating from the former steel regions increasingly moves toward the inside of the steel because Fe-content of the coating originating from the steel mass increases its quality and sizes.
The solid solution Fe-Al is a body-centered cubic lattice, the austenite with face-centered lattice must disappear. At the same time, C-solubility of the Al-Fe coating (irrespective of whether it is a solid solution or any Al_mFe_n intermetallic compound) is very low. Although literature contains some relevant data, each of them is smaller than the average C-content of steels. This means that growth of coating containing Al is hampered by C-content of the steel because any C-content below 0.09% may be dissolved at temperatures above the eutectoid one only in

austenite, and austenite must be present in a quantity containing this amount of C. Maximum solubility of austenite at any T_i temperature is given by the intersection of the SE curve and temperature line. Thus, before the continuously thickening outside layer an austenite layer forms with the given C-content but the integrated quantity of dissolved carbon increases with growth of the intermetallic layer. Presence of this layer, its C-content and width growing with time are proved by Fig. 4. with the hardness depending on the distance from the phase boundary.

Hardness of specimens hardened in water and cooled by air shows that border of steel with originally unhardenably low C-content can be hardened martensitic which is indicated by the Vicker microhardness of 1000 or above. Also the higher hardness of air-cooled specimens suggest the higher C-content.

Fig. 6 demonstrates the degree of C-content growth in the subcoating region. The border layer of the steel became practically fully pearlitic in comparison to the base material containing little pearlite before. Transformation of this layer into martensite in the water-hardened specimens causes the high hardness depicted in Fig.4.

At steel surfaces with ferrite crystallites the solid solution Fe-Al can form simply by Al diffusion into ferrite. This is a relatively simple process disregarding the forced C-diffusion mentioned above. The higher the temperature, the less the quantity of ferrite at the moment of immersion is. If amount of ferrite is large enough, temperature slightly surpasses the eutectoid one, then, lateral growth of ferrite ensures ferite formation at the whole surface.

With temperature increase quantity of ferrite falls, and Al-solubility and amount of ferrite can only limitedly ensure continuous Fe-Al formation at the surface, that is why there is a growing need for appearance of the phase Fe-Al at the steel surface even through a nucleation process. This impedes coating formation even more. With increasing temperature, role of Al-diffusion decreases due to other phase transformations and its forced growth. We think that this is the reason for increasing difference of time's exponent *n* from the theoretical value of 0.5 for pure diffusion processes.

Conclusions

Tests outlined above show that the exponent *n* in the function $s = kt^n$ differs from the theoretical value of 0.5 more and more with appearance of phase transformation processes at the immersion temperature which take place in steel due to temperature, due to appearance of the strange phase and due to their minimum C-solubility.

References

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Thickness of intermetallic layer

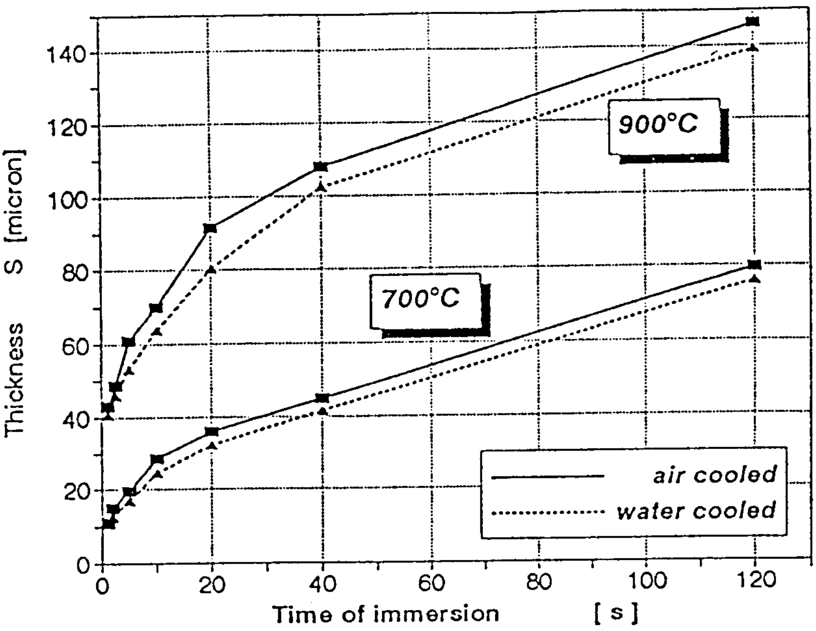

Fig. 1.

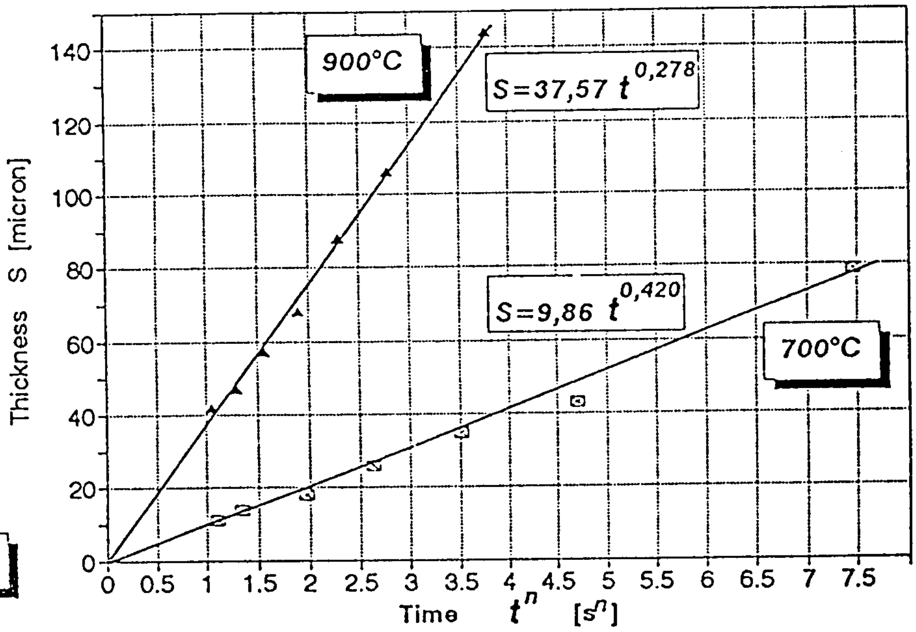

Fig. 2.

Values of the exponent n in condition of the temperature.

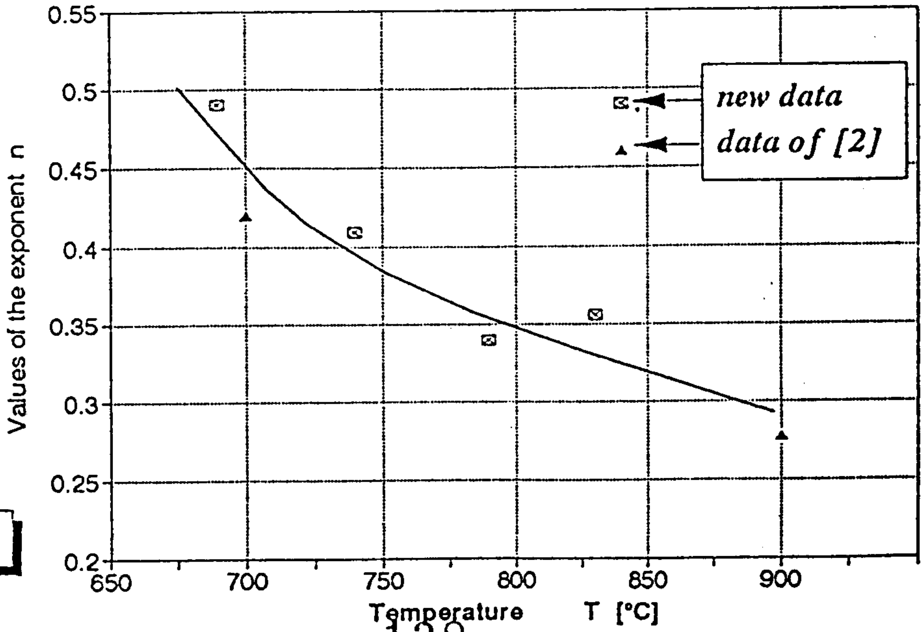

Fig. 3.

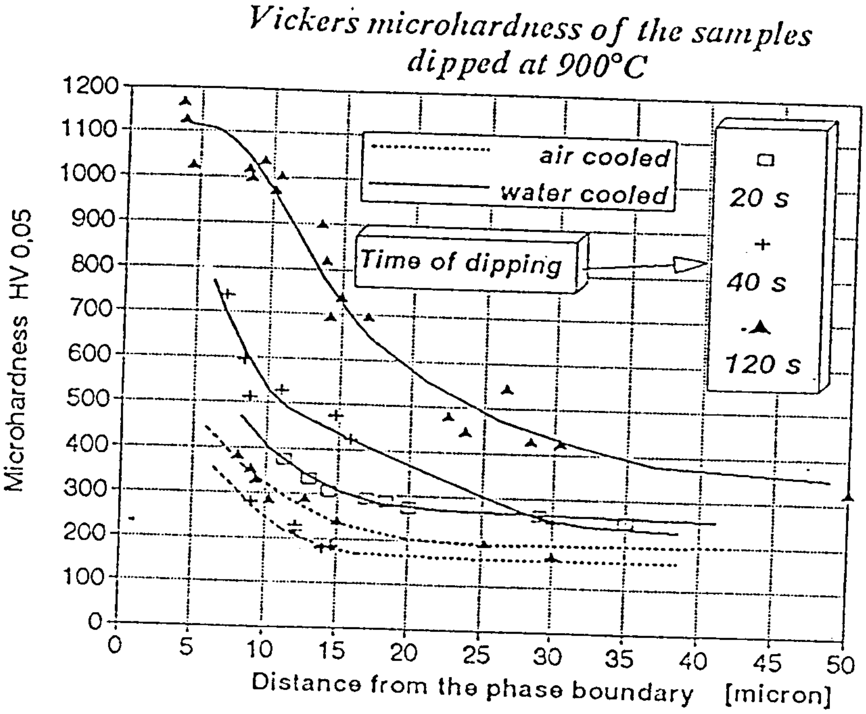

Fig. 4.

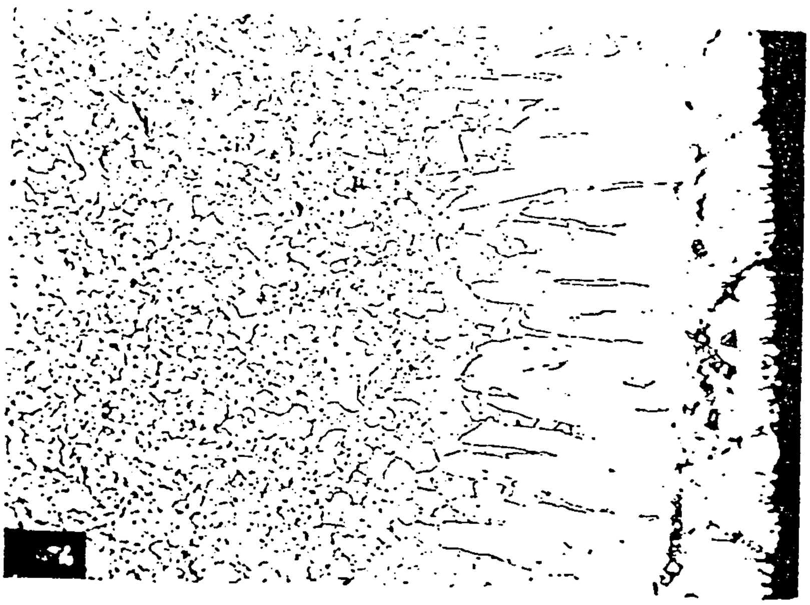

Fig. 5. 400x

Fig. 6. 400x