

Influence of the addition of aluminium into molten zinc bath on the kinetics of formation of intermetallic phases in the system Fe—Zn

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Kinetics of formation of intermetallic phases in the systems Fe—Zn and Fe—Zn(1% Al) were investigated at temperature 735 K. Thicknesses of the intermetallic layers were determined by means of a metallographic microscope and an X-ray microanalyzer and the observed differences were explained. It was found that an addition of aluminium influences mainly formation of zinc-rich phases and it has almost no influence on the growth of other intermetallic phases. The mean interdiffusion coefficient in phases Γ_1 (77.5—78.5% Zn) and Γ (67—68% Zn) was found to be $D = 3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ ($T = 735 \text{ K}$). Growth of phases $\delta_1 + \zeta$ in the system Fe—Zn can be described in time interval 0—8 min by a parabolic relationship: $d/\mu\text{m} = 20.5\sqrt{\tau/\text{min}}$. When 1% of aluminium is added into zinc bath the growth of the phases δ_1 (FeZn₇) + ζ (FeZn₁₃) depends on pretreatment of steel base. If the surface is treated before hot-dip process in HCl solution then the growth of the phases $\delta_1 + \zeta$ can be described by the relation $d/\mu\text{m} = 15.2\sqrt{\tau/\text{min}}$. When the surface is treated in solution $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ we obtain $d/\mu\text{m} = 19.1\sqrt{\tau/\text{min}}$.

Была изучена кинетика образования интерметаллических фаз в системе Fe—Zn и Fe—Zn(1% Al) при температуре 735 К. Были сравнены толщины слоев при определении металлографическим микроскопом и рентгеновским микроанализатором и объяснены наблюдаемые различия. Было найдено, что добавка алюминия оказывает влияние в основном на образование фаз богатых цинком и имеет только незначительное влияние на образование остальных интерметаллических фаз. Был определен средний коэффициент взаимной диффузии в фазах Γ_1 (77,5—78,5% Zn) и Γ (67—68% Zn), который при температуре 735 К $D = 3 \times 10^{-10} \text{ см}^2 \text{ с}^{-1}$. Рост фазы $\delta_1 + \zeta$ в интервале времени 0—8 мин в системе Fe—Zn можно описывать параболическим соотношением $d/\mu\text{км} = 20,5\sqrt{\tau/\text{мин}}$. Толщина фазы $\delta_1 + \zeta$, образующейся в системе

Fe—Zn(1% Al) обусловлена способом обработки поверхности подложки Fe. Если эта поверхность обработана в растворе HCl, рост этой фазы в интервале 0—8 мин можно описать уравнением $d/\text{мкм} = 15,2\sqrt{\tau/\text{мин}}$ и при обработке с раствором $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ $d/\text{мкм} = 19,1\sqrt{\tau/\text{мин}}$.

Zinc coatings are widely used for protection of mild steels against corrosion [1]. If we use hot-dip galvanizing, it means when steel is immersed into molten zinc bath, the base reacts with molten zinc with formation of intermetallic compounds, which influences mechanical and anticorrosive properties of zinc coatings. Aluminium is a common addition to zinc. It is added in amounts of 0.1—0.3 mass % with the aim to retard the formation of intermetallic phases. This effect has been studied by many researchers. Review of papers dealing with this problem can be found in monograph [2] (pp. 94—101). It follows that there are different opinions on the mechanism of influence of aluminium addition. Most of authors claim that there is an “induction period” during which the intermetallic phases do not grow [2]. It has been found [3—5] that the “induction period” increases at constant temperature with the increase of aluminium content in zinc bath. On the other hand, the increase of temperature decreases this induction period. Quantitative data on the induction period published in literature are rather different. *E.g.* according to [3] the induction period at 450°C caused by 0.5 mass % Al is 8 min while according to [4, 5] it is about 45 min. There is also no generally accepted opinion on the mechanism of the retardation effect of aluminium. *Bablik* [6] explains it by formation of a thin layer of aluminium oxide on the surface of iron in the moment of its immersion into molten zinc. However, most of authors prefer hypothesis according to which a thin layer of FeAl_3 or Fe_2Al_5 is formed at the iron surface. They assume that this layer hinders reaction between iron and zinc [4, 7—13]. The existence of these layers has not been proved experimentally.

This work is a contribution to solution of this problem. We confirmed that an addition of aluminium hinders formation of intermetallic phases. However, no “induction period” during which the layers do not grow was observed. We found that aluminium influences mainly the growth of zinc-rich phases δ_1 , ζ . Further we found that the retardation effect of aluminium depends substantially on the treatment of surface of material before the hot-dip process is carried out. This conclusion explains great differences among data published in literature.

Experimental

Samples for investigation of growth of intermetallic phases were prepared by immersing steel plates (ČSN 11 370) into molten zinc or in a bath containing 99 mass % Zn + 1 mass % Al. The samples were heated for 1, 3, 5, 8 or 120 min at 735 ± 1 K. Temperature was measured by PtRh10—Pt thermocouple protected by a closed corundum tube. Polished

samples were investigated by means of a metallographic microscope Epityp II. These samples were etched by 3% solution of nitric acid in ethanol. Some of the samples were investigated also by means of an X-ray microprobe JXA-5A. On the basis of these data the distribution of concentration of iron and zinc was determined and the interdiffusion coefficients were calculated using the Boltzmann—Matano method [14].

Before dipping into molten metal bath the samples were degreased and treated in the following mordants (composition given in mass %):

- diluted HCl 1 : 1,
- diluted HCl and subsequently in solution containing 20% $ZnCl_2$ + 10% NaCl + 10% KCl,
- diluted HCl and then in solution containing 15% NH_4Cl + 2.5% $ZnCl_2$.

The last series of samples was covered electrolytically by 1 μm zinc layer before the hot-dip process was carried out. Composition of electrolyte was the same as in the former case. Cathodic current density 10 mA cm^{-2} was used.

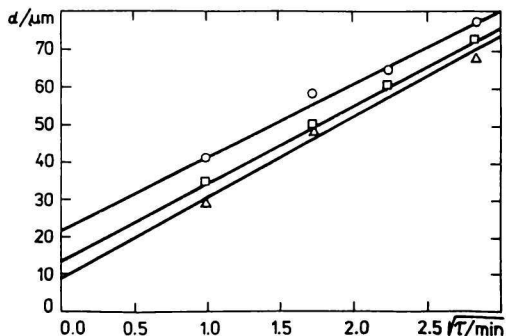
Results and discussion

Five samples for all experimental conditions were prepared. Growth of intermetallic layers was studied by means of a microscope on several places of each sample. A set of approx. 30 data was obtained for all experimental conditions. The obtained data were treated using methods of statistical mathematics.

At the hot-dip zinc process the following intermetallic phases are formed: Γ_1 (Fe_5Zn_{21}), Γ (Fe_3Zn_{10}), δ_1 ($FeZn_7$), ζ ($FeZn_{13}$). Mean thicknesses of the intermetallic layers as they were observed in the optical metallographic microscope are presented as function of time in Figs. 1 and 2.

In Fig. 1 the growth of intermetallic phases in samples immersed in pure molten zinc is plotted as function of time. It follows that growth of the intermetallic layers is governed by a parabolic law even if the extrapolated value to zero time does not equal zero, which is in disagreement with physical reality. Regression lines fitted to experimental data have the following parameters (r is the correlation coefficient):

Fig. 1. Thickness of intermetallic phases formed in the system Fe—Zn as it was observed in a metallographic microscope plotted as a function of time. Temperature 735 K. Each line corresponds to different method of pretreatment of sample before the hot-dip zinc process. Δ Sample treated in HCl solution; \square sample treated in solution NH_4Cl + $ZnCl_2$; \circ sample covered electrolytically by 1 μm zinc layer.



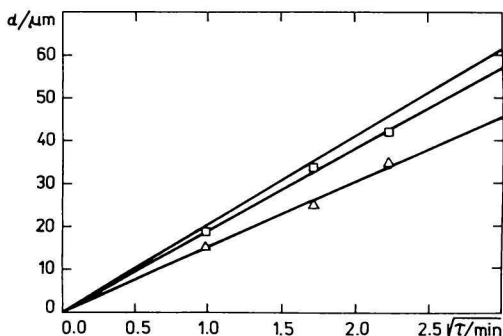


Fig. 2. Thickness of intermetallic phases formed in the system Fe—(99% Zn + 1% Al) as it was observed in a metallographic microscope plotted as a function of time. Temperature 735 K.

△ Sample treated in HCl solution; □ sample treated in solution $\text{NH}_4\text{Cl} + \text{ZnCl}_2$; — reduced thickness of intermetallic layer in the system Fe—Zn.

a) $d/\mu\text{m} = 9.063 + 21.478\sqrt{\tau/\text{min}}$ ($r^2 = 0.979$); treated in HCl.

b) $d/\mu\text{m} = 13.385 + 20.709\sqrt{\tau/\text{min}}$ ($r^2 = 0.999$); treated in solution containing $\text{NH}_4\text{Cl} + \text{ZnCl}_2$.

c) $d/\mu\text{m} = 22.084 + 19.40\sqrt{\tau/\text{min}}$ ($r^2 = 0.990$); 1 μm zinc layer was deposited electrolytically before the hot-dip process.

It is obvious that the slopes of all three lines are in limits of error the same. Investigation of samples by means of an X-ray microprobe revealed why the “zero time thickness” differs from zero when samples are studied by an optical microscope. The real situation is namely as follows. The samples are studied at ambient temperature. At this condition we found on the side of zinc an uncompact phase containing 0–5 mass % Fe. After etching the sample in 3% solution of HNO_3 in ethanol the structure of this phase is different from the phase of pure zinc. But in an optical microscope we cannot distinguish it from the compact intermetallic layer. It was found further that this phase was not present when aluminium had been added into zinc bath. This is demonstrated in Fig. 2 where the time dependence of the thickness of intermetallic phases as they were observed in the system Fe—Zn(1% Al) is plotted. The results obtained in the system Fe—Zn(1% Al) are compared with the time dependence of “reduced thicknesses”. The “reduced thickness” is calculated by subtracting zero time thickness from total thickness of the intermetallic layer formed in the system Fe—Zn as it was observed in an optical microscope. From Fig. 2 it is obvious that at 735 K the intermetallic layers grow more slowly in the system Fe—Zn(1% Al) than in the bath of pure zinc. It can be also seen that kinetics of growth depend on a pretreatment of the surface of steel base. Regression line for reduced thickness in the system Fe—Zn can be described by the equation

$$d/\mu\text{m} = 20.52\sqrt{\tau/\text{min}} \quad (r^2 = 0.993)$$

Regression lines for the dependence of thickness of intermetallic layer on time in the system Fe—Zn(1% Al) are as follows:

$$d/\mu\text{m} = 15.24\sqrt{\tau/\text{min}} \quad (r^2 = 0.997); \text{ treated in HCl.}$$

$$d/\mu\text{m} = 19.08\sqrt{\tau/\text{min}} \quad (r^2 = 0.999); \text{ treated in solution containing NH}_4\text{Cl} + \text{ZnCl}_2.$$

Explanation of the influence of treatment in different solutions on the growth of intermetallic layers is as follows. When the steel samples are immersed in solution containing NH_4Cl and ZnCl_2 a thin zinc layer is deposited on the sample due to an exchange chemical reaction. (The deposited zinc layer can be observed by means of an X-ray microprobe.) In this case iron oxides are not present on the surface of sample. We can assume that these iron oxides react with aluminium under formation of aluminium oxide or a compound containing iron and aluminium oxides. The formed oxide layer is bound strongly to the steel base and it hinders transport of zinc atoms into the bulk of steel. Simultaneously it hinders dissolution of zinc-rich phases δ_1 and ζ in molten zinc. This assumption is in agreement with all the observed facts. It is also in agreement with that we did not observe any selective adsorption of aluminium at the surface of samples covered by zinc coating.

The above discussion was oriented towards conditions which are typical for hot-dip process. When the samples were heated for 2 h it was possible to identify individual phases more precisely and also to determine distribution of concentrations in these phases. Using Boltzmann—Matano method we determined a mean interdiffusion coefficient in the phases Γ_1 and Γ ; $D = 3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. This value is in good agreement with the data presented in [15]. It should be remarked that in [15] the diffusion has been studied in the diffusion pair Fe—phase δ_1 . The good agreement between the two sets of data which were obtained in different conditions allows to conclude that different boundary conditions had no substantial influence on the growth of Γ phases.

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