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DSC STUDY OF THE DEPOSITION REACTIONS OF ZINC PACK COATINGS UP TO 550°C

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Zn pack coating formation takes place in three steps as differential scanning calorimetry shows. The initial step (at 193.9°C) is endothermic and involves the transformation of α-NH_4Cl to β-NH_4Cl and the NH_4Cl decomposition to NH_3 and HCl. During the second step (at 248.6°C), which is exothermic, Zn^{2+} salts are formed and most probably $ZnCl_2$. Finally at 264.1°C (endothermic reaction) it seems that $ZnCl_2$ is decomposed to form Zn that is deposited on the ferrous substrate. The as-cast Zn diffuses in the iron substrate forming the gamma and delta phase of the Fe–Zn phase diagram. Al_2O_3 is not involved in the above-mentioned mechanism and acts only as filler.

Keywords: *chemical vapor deposition, DSC characterization, metallic coatings, pack cementation*

Introduction

Zinc has a number of characteristics that make it very well-suited for use as a protective coating for ferrous substrates against atmospheric corrosion [1–3]. Their performance results from their ability to react with the atmospheric compounds (O_2, CO_2 and H_2O) which form over the coating surface dense, adherent films whose rate of corrosion is considerably below that of ferrous materials (barrier protection). Additionally, zinc is anodic to iron and steel and consequently offers cathodic protection.

A number of different methods of casting zinc coatings are commercially available. The most widely used is hot-dip galvanizing [1–3]. In this case the ferrous substrate is immersed in a bath of molten zinc and as a result it is covered by a layer of zinc with an average thickness of a few tens of micrometers. The effectiveness of this method is undisputable [1–3]. However its high environmental impact [4] imposes the investigation of alternative coating techniques friendlier to the environment. A promising technique that could be used instead of hot-dip galvanizing is chemical vapor deposition (CVD) by pack cementation [5]. In this case a zinc diffusion coating is formed by heating the substrate up to 400°C covered with a mixture of powders containing zinc and a halide activator. Pack cementation offers high integrity coatings which are composed by two layers referring to the gamma (Γ) and the delta (δ) phase of the Fe–Zn phase diagram. Their corrosion resistance is similar to that of the hot-dip galvanized coatings [6].

The present work examines the formation mechanism of zinc coatings deposited with pack cementation. For this purpose it is necessary to determine the chemical reactions and physicochemical transformations that take place between the powders of the mixture. The most reliable method to distinguish the different phenomena that occur during this process is the determination of the enthalpy changes that every phenomenon causes. These changes could be detected using differential scanning calorimetry (DSC) [7–9]. DSC offers also the temperature at which every transformation accomplishes. However, DSC measurements give only an energetic overview of the total phenomenon. So, for the determination of the pack mechanism with more details, it is necessary to determine also the intermediate products of every reaction or transformation. For this purpose the vapors evolved during powder heating were analyzed with quantitative methods of classical analytical chemistry.

This investigation is of great importance because it offers important data for the optimization of pack cementation which, scaling up, can be used for industrial applications. The determination of the intermediate products could assist in the selection of cheaper reactants and in the design of more convenient processes so as to avoid exposure of the personnel to hazardous materials. However the most important is that through data of that kind, the best reaction temperatures could be defined and energy loss could be avoided.

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Experimental

The powder mixtures used in the DSC experiment are reported in Table 1. Concerning the mixtures 1 and 3 a small piece of commercial, hot-rolled, low carbon steel sheet SAE 1010 was immersed in the powder in every experiment. The mixture 2 was used only to determine the thermal behaviour of pure NH_4Cl under these conditions.

Table 1 Powder mixtures examined with DSC

Mixture no.	Compound/mass%		
	Zn	NH_4Cl	Al_2O_3
1	70	5	25
2		100	
3	93	7	

The thermal behaviour of these mixtures was investigated using a Setaram DSC 141 differential scanning calorimeter. Temperature and energy calibrations of the instrument were performed using the well-known melting temperatures and enthalpies of high purity zinc and indium. The samples weighing about 15 mg were crimped in sealed stainless steel crucibles to avoid any gas leakage and an empty stainless steel crucible was used as reference. This study was non-isothermally performed by heating the specimens from room temperature up to 550°C with a heating rate of 10 K min^{-1}. N_2 was used as a carrier gas.

In order to determine the intermediate products, powder with the composition of mixture 1 was heated up to 400°C in an open crucible which was connected with a vessel containing Nessler reactant (alkaline solution of $K_2(HgI_4)$) [10]. This solution reacts exclusively with NH_4^+, producing red-brown precipitate and it is very sensitive to this ion. Consequently, it is suitable to determine whether ammonia is formed during pack cementation. Furthermore, a similar method was used to determine whether the gaseous products contain Zn^{2+}. The gaseous stream produced by heating the powder mixture 1 was dissolved in a solution of $K_3[Fe(CN)_6]$ [10]. This compound reacts with Zn^{2+} by forming a yellowish precipitate.

Furthermore, the as-formed coatings were examined with scanning electron microscopy by using a 20 kV Jeol 840A SEM equipped with an Oxford ISIS 300 EDS analyzer and the necessary software to perform line scan and chemical mapping of the samples. The examination with SEM took place in order to investigate the Zn diffusion which also involves in the coating formation.

Results and discussion

A typical scanning electron micrograph of the pack coating formed using a powder with the composition of mixture 1 is presented in Fig. 1. Two layers are observed which refer to the gamma (Γ) and the delta (δ) phase of the Fe–Zn phase diagram as the line scan of Fig. 2 shows. These observations imply that inward diffusion (e.g. diffusion of Zn in the substrate) takes place, because no Al_2O_3 or other powder inclusions are observed in the coating [5].

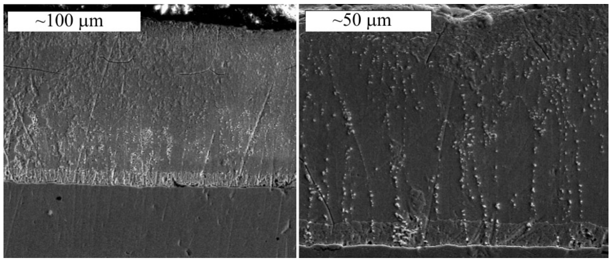

Fig. 1 SEM micrographs of coatings formed with the mixture 1 at 400°C and heating time 2 h

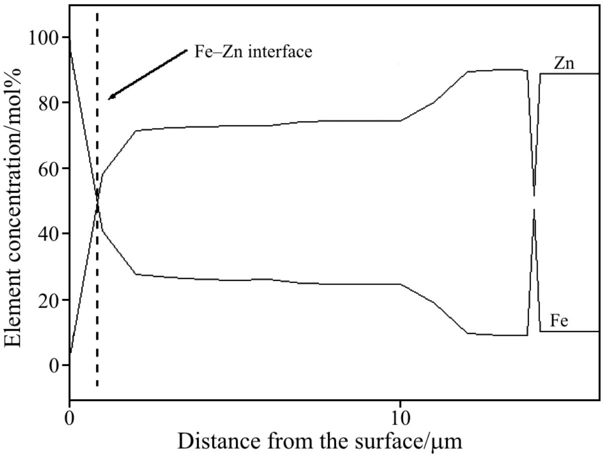

Fig. 2 Line-scan of the cross-section of the coating formed with the mixture 1 at 400°C and heating time 2 h

The DSC plot acquired during heating the mixture 1 up to 550°C is presented in Fig. 3 (plot a), where three transformations are observed. The first one at 193.9°C (referring to the peak A in Fig. 3) is endothermic and the energy absorbed is low. The next at 248.6°C (referring to the peak B in Fig. 3) is exothermic and comparatively wide, which means that the phenomenon takes place at a long temperature range. Therefore it is likely to be composed by several elementary reactions which are accomplished at very close temperature intervals. The final at 264.1°C (referring to the peak C in Fig. 3) is endothermic and very steep, while at 419°C zinc melting was also recorded. Zinc melting does not participate in the coat-

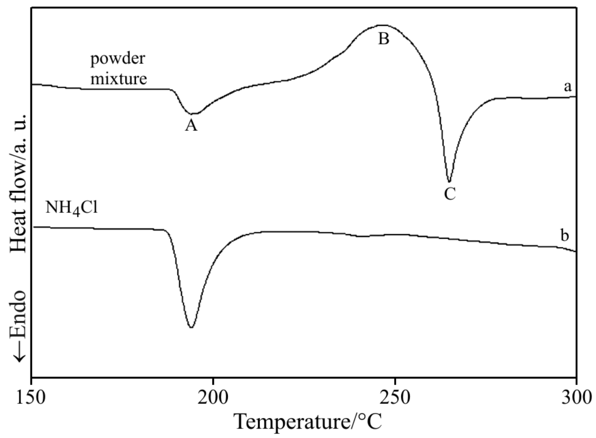

Fig. 3 a – DSC plot of mixture 1 composed by 70 mass% Zn, 5 mass% NH_4Cl and 25 mass% Al_2O_3 and b – DSC plot of pure NH_4Cl

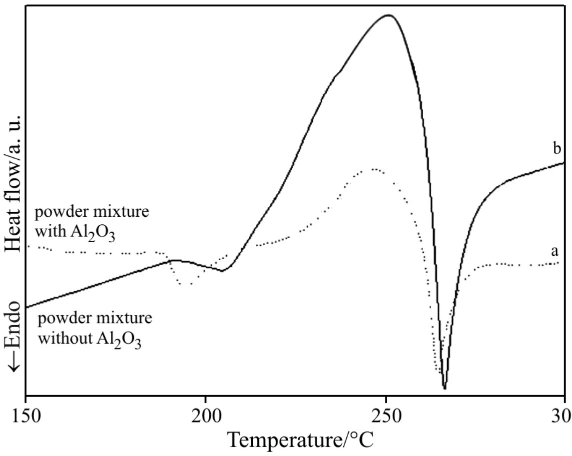

Fig. 4 a – DSC plot of mixture 1 composed by 70 mass% Zn, 5 mass% NH_4Cl and 25 mass% Al_2O_3 and b – DSC plot of mixture 3 composed by 93 mass% Zn, 7 mass% NH_4Cl

ing formation because the deposition temperature is limited at 400°C, as it has been already mentioned and as a result it is not presented in Fig. 3.

Consequently, it is possible to deduce that the coating formation takes place in three steps. However the endothermic transformation at 193.9°C is due to the transformation of α-NH_4Cl to β-NH_4Cl [11], as plot b in Fig. 3 shows, which refers to pure NH_4Cl. Thus it could be deduced that this phenomenon is not related to the coating formation. However, above 200°C, the substance sublimes and after sublimation it dissociates completely in the gaseous phase into ammonia and hydrochloric acid. Consequently under these conditions the reaction system, as far as it concerns NH_4Cl, should contain solid NH_4Cl, gaseous NH_4Cl, NH_3 and HCl. As the temperature raises the fraction of the gaseous phase increases while the solid phase is depleted.

Regarding the exothermic transformation at 248.6°C, it could be ascribed to a large number of composition reactions between the powder compounds, such as reactions between Zn and HCl or NH_3 formed during the decomposition of NH_4Cl. These reactions are exothermic and take place in several steps, as XRD study verified [12]. Consequently the larger width of the peak is justified.

Concerning the final peak at 264.1°C which is endothermic, this is likely to be connected to decomposition reactions of the compounds formed at lower temperature. These reactions are usually endothermic.

Al_2O_3 seems to be rather inert with regard to Zn and NH_4Cl as the comparison of the two plots (a and b) in Fig. 4 shows. In this case, although no Al_2O_3 was added to the DSC crucible, no essential change was observed at the DSC plot. The limited retardation in the first endothermic peak, as well as the small one, which is developed during the exothermic reaction, are of course changes in the initial thermograph due to the absence of the Al_2O_3. But, as it is also seen, these variations do not alter the morphology of the diagram, which describes the coating process. Hence the coating formation is accomplished through reactions where, as far as regarding the powder, only Zn and NH_4Cl participate. Al_2O_3 seem that affects this process slightly and acts mainly as filler.

To sum up the conclusions drawn by DSC plots, it could be stated that the coating formation takes place in minimum three steps. The first one includes NH_4Cl transformation. The second could refer to a sum of composition reactions, while the third one refers probably to a sum of decomposition reactions. Al_2O_3 does not take part in any of these reactions.

To establish however a mechanism, it is necessary to determine the intermediate products of the reactions that take place during the heating period of the powder. For that purpose an open crucible with mixture 1 was initially heated up to 400°C. The surface of the crucible was connected with a polyethylene tube to the bottom of a vessel containing Nessler reactant. As soon as the temperature in the crucible rose up to about 200°C, the Nessler reactant was coloured yellow–red. This observation proves that ammonia (NH_3) was evolved from mixture 1 which was dissolved in the Nessler reactant leading to its coloration. The same experimental set up was used to determine whether Zn^{2+} ions are formed. As the temperature of the crucible reached about 260°C, the $K_3[Fe(CN)_6]$ solution was colored yellowish.

Hence, it could be deduced that the formation of pack coatings begins with the transformation of α-NH_4Cl to β-NH_4Cl. After the transformation the salt sublimes and dissociates in the gaseous phase into ammonia and hydrochloric acid. It is likely that the HCl and NH_3 vapors evolved from NH_4Cl decomposition react with Zn forming $ZnCl_2$. $ZnCl_2$ easily forms coordination compounds with NH_3 and NH_4Cl, so by taking into account the large excess of Zn in the reaction system, probably compounds of that kind are also formed although they were not detected. Finally the as-formed Zn compounds are likely to be decomposed at the surface of the ferrous substrate producing metallic Zn which diffuses in the ferrous substrate.

Conclusions

From the above analysis it is obvious that the coating formation of Zn pack coatings takes place in three steps. The initial (at 193.9°C) is endothermic and involves the transformation of NH_4Cl and the NH_4Cl decomposition. During the second step (248.6°C), which is exothermic, probably $ZnCl_2$ is formed. Finally at 264.1°C (endothermic reaction) $ZnCl_2$ is seemingly decomposed to form Zn that is deposited. Al_2O_3 is involved only slightly in the above-mentioned mechanism and acts only as filler. This first 'calorimetric' description of the Zn pack coating gave at the moment qualitative only results. Besides these the quantification of the described coating process is also important, something which is in progress, together with the comparative study of the effectiveness of the method, concerning its use as on alternative protective coating.

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