





materials letters

Materials Letters 59 (2005) 1619-1622

www.elsevier.com/locate/matlet

Modification of the growth-direction of the zinc coatings associated with element additions to the galvanizing bath

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Received 27 April 2004; accepted 30 August 2004 Available online 8 March 2005

Abstract

Steel sheets, which were galvanized in a laboratory electric furnace by hot dipping in a bath of molten Zn alloyed with Pb up to 1 wt.%, are characterized by a preferred crystallization of the majority of the grains. This was ascribed to the Pb particles, which enhance the growth of thermodynamically favored directions. The distribution of the Pb particles seems to play an important role to this phenomenon. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used in order to find the distribution map and to determine the phases that were formed.

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Keywords: Coatings; Recrystallization; SEM; XRD

1. Introduction

The surface of the galvanized coatings is commonly characterized by large grains called "spangles" [1]. Their formation is favored when Sb, Bi and especially Pb atoms are added to the zinc bath because all these metals lower the surface tension ahead of the growing dendrites and allow their growth velocity to increase, resulting in larger grains [2,3]. It was also found that grain size is influenced by the cooling conditions [2,3].

Hot dip galvanized coatings [4–8] resulted from an almost pure zinc bath, often show a strong (0001) basal plane texturing of the zinc crystals upon solidification. The same behavior was observed in the case of Al and Cu addition to the Zn bath. The crystal orientation is gradually changed when Pb atoms are added to the zinc bath. Pb additions finally lead to an inclination of the basal plane until the (2111) plane is aligned almost perfectly parallel to the sheet surface. This is because Pb atoms promote a rapid dentritic growth, which is characterized by secondary

dentritic arms. The secondary arms lie at 90° to the trunk from which they emanate [4]. Ni addition was also found to cause an inclination of the basal (0001) plane but in a degree less than that Pb additions do [9]. As far as we know, Ni additions rather result in a random distribution of the crystallites of the outer layer than cause a preferred orientation of them.

In this work, the role of the distribution of the Pb admixtures across the coating surface was examined in relation with the formation and the orientation of the grains. Also the influence of the cooling rate and of the surface tension on the growth of the outer layer was investigated. Scanning electron microscopy (SEM) was used to determine the distribution of the additions, while the phase identification and the texturing definition were carried out by XRD measurements.

2. Experimental

Hot-rolled thick sheets of steel containing 0.11% C, 0.55% S and 0.016% P have been galvanized in a laboratory electric furnace (Thermolyne 1400) inside a graphite crucible. The dipping time varied from a few

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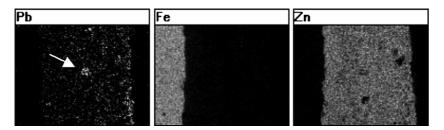


Fig. 1. Dot mapping of the coating formed of the zinc bath with 1% Pb. The arrow refers to a Pb inclusion.

seconds up to 1 min. The specimens, 40 mm long, 10 mm wide and 3 mm thick, were initially sandblasted and afterwards degreased in a non-ionic tenside containing $\rm H_3PO_4$, picked in an aqueous solution containing 16% HCl and fluxed in an aqueous solution containing 50% ZnCl_2 2NH_4Cl. The coating was casted through their immersion in the galvanizing bath at a temperature of about 450 $^{\circ}$ C. Different galvanizing baths including a melt of pure Zn and Zn melts alloyed with Pb were used.

Cross sections of the as galvanized specimen have been cut, mounted in bakelite, polished down and etched for microstructure observations. The phases of the coating were determined by X-ray diffraction (SEIFERT 3003 TT diffractometer with FeKa radiation), while the dispersion of the alloying elements was examined with a 20 kV JEOL 840A SEM equipped with an OXFORD ISIS 300 EDS analyzer.

3. Results and discussion

Pb atoms are uniformly distributed across the coatings (Fig. 1). A slight increment of the concentration of the Pb atoms is observed in the outer layer of the coatings. There are also some Pb inclusions as Fig. 1 and the diagram of Fig. 2 shows. The formation of the Pb inclusions is not clearly

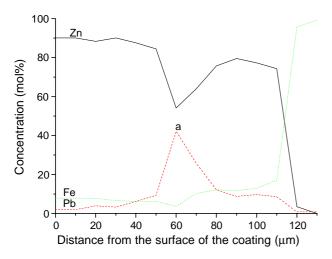


Fig. 2. Line scan of the cross-section of the coating. Peak (a) refers to the Pb inclusion.

explained. It is possible that some of the Pb particles are trapped inside the coating. However, they do not seem to affect the coating structure.

Fig. 3 shows that coatings resulted from a bath containing less than 0.2 wt.% of Pb particles exhibit a rather random distribution of the crystal grains. Consequently, it is likely that there is a critical concentration of Pb, below which the above-mentioned phenomenon is not observed.

This means that Pb additions at low concentration just destroy the (0001) basal plane texturing of the hot-dip galvanizing coatings [10].

By increasing the Pb-content up to about 1 wt.% and changing the cooling rate, new layers are produced with a rather strong texture in which the (101) planes are oriented parallel to the steel sheet.

In order to interpret the changes in the crystal orientation with respect to the Pb concentration, we made use of the solidification model for hot-dip galvanizing zinc coatings [4]. According to this, the preferred nucleation occurs in three steps as follows. The initial stage of crystallization of the outer layer involves growth of Zn basal plane (0001) parallel to the interface, whereas the surface remains liquid. The second stage involves slow thickening of the solid zinc with as light change in the orientation of the basal plane. The proportion of the basal plane orientation changes with variation of the coating grain size [10], which in turn varies with the solute additions to the galvanizing bath. In the case of Pb

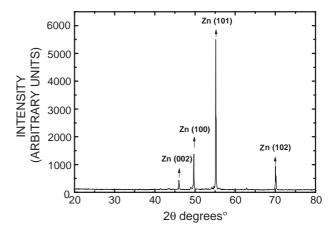


Fig. 3. X-ray diffraction of the coating formed by the Zn-0.2 wt.% Pb bath.

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