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Keywords

si, mg, al, coating, zn, quaternary, treated, laser, observed, phase

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A new quaternary phase observed in a laser treated Zn-Al-Mg-Si coating

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Abstract

The microstructure of laser resurfaced Zn-55Al-2Mg-1.5Si coating produced on a hot-dip simulator was characterised by transmission electron microscopy. A new quaternary phase was observed and its crystal structure was determined by electron diffraction.

Keywords: GALVALUME[®] steel coating; Coating materials; Laser treatment; Crystal structure; Zn-Al-Mg-Si system; Quaternary phase

1. Introduction

The GALVALUME[®] steel coating system (nominally Zn-55Al-1.5Si in wt.%), developed by Bethlehem Steel in the 1960s, exhibits a greater corrosion resistance than the conventional galvanised coating [1], but challenges remain in certain applications [2]. There is a need to develop a new coating which can demonstrate even better corrosion resistance. Recently, a second generation of GALVALUME[®] and ZINCALUME[®] steel coating with the composition of Zn-55Al-2Mg-1.5Si (in wt.%) was developed and patented by Bluescope Steel Limited. It is claimed that this coating has even better corrosion resistance than the original coating [3]. The addition of 2% Mg results in the formation of Mg₂Si and MgZn₂ phases predominantly in the interdendritic regions of the coating and the enhanced corrosion resistance depends on the specific phases present in the coating and their distribution. The enhanced performance of the Zn-55Al-2Mg-1.5Si coating is achieved by activating the α -Al dendritic phase and blocking the corrosion paths along the interdendritic channels [4]. Therefore, the amount and distribution of these Mg containing phases are important to the corrosion performance of the final coated product. Laser surface treatment provides a process to significantly refine the coating structure via extremely high cooling rates during solidification, improve the distribution of phase components and corrosion performance [5]. In this paper we report that a new quaternary phase was observed in a laser resurfaced Zn-55Al-2Mg-1.5Si coating and its crystal structure was characterised by TEM.

2. Experimental

In this investigation which is a part of a much larger research program on microstructure and phase equilibria of laser treated Zn-Al-Mg-Si coatings, a Zn-55Al-2Mg-1.5Si coating (wt.%) was produced on a hot-dip process simulator (HDPS) and then resurfaced with a diode laser operating at 5.5kW. The microstructure of the HDPS Zn-55Al-2Mg-1.5Si coating was studied on a JEOL JSM-6940 SEM at 15kV and the microstructure of the laser resurfaced coating were characterised in a JEOL 2011FX TEM at 200kV. TEM samples of 100nm thick were prepared by using a xT Nova NanoLab 200 Dualbeam focused ion beam miller at 30kV. An aging treatment of the laser treated coatings was carried out in air at 150°C for 24hrs. The microstructure of the aged treated sample was also studied by TEM.

3. Results and discussion

Figure 1a shows a backscattered electron image of a cross section of the HDPS Zn-55Al-2Mg-1.5Si coating and Figures 1b-e show the x-ray maps of Al K, Mg K, Zn K and Si K of the same area. Clearly Zn, Si and Mg are segregated in the interdendritic areas and Si can be present either as pure Si or as Mg₂Si (1c and 1e). The microstructure of the interdendritic area of the laser treated Zn-55Al-2Mg-1.5Si coating is too fine to be resolved in SEM and thus was studied mainly in TEM. Figure 2 shows the TEM microstructure of the overlay of the laser treated Zn-55Al-2Mg-1.5Si coating. It consists of dendritic α -Al matrix, large angular particles and eutectic features in the interdendritic areas. The nodular structures in the interdendritic regions were artefacts of the TEM sample preparation process. The cross section of the α dendrite is about 1 μ m which is significantly smaller than that of the untreated α dendrite (Figure 1a). TEM/EDS microanalysis was performed on these dendrites, the coarse angular particles and the eutectic Al and Zn plates in the interdendritic areas, and the results are given in Table 1. The beam size was about 50nm which is considerably smaller than the particle size so the matrix effect on the results should be negligible. The α dendrite has the average composition of 42Zn-55Al-1Mg-1Si (wt.%) which is close to the coating composition due to the extremely fast cooling rate, and the coarse angular particles (0.4-1 μ m) have the average composition of 51Zn-11Al-18Mg-20Si (wt.%). The eutectic Al and Zn plates have the composition of 18Zn-71Al-4Mg-5Si (wt.%) and 80Zn-17Al-2Mg-1Si (wt.%), respectively. The eutectic Al plates contained more Mg and Si than expected.

The crystal structure of the coarse interdendritic particles (new phase) was investigated systematically by electron diffraction and a portion of the Kikuchi map was established, as shown in Figure 3. The two major zone axes [0 0 1] and [1 1 0] of the phase are given in Figures 4a and 4b, respectively. The lattice parameters *a* and *b* were obtained from the [0 0 1] and *c* was obtained from the [1 1 0], giving *a*=0.790nm, *b*=0.695nm and *c*=0.414nm. Clearly the phase has a simple orthorhombic Bravais lattice. The obtained lattice parameters were then used to calculate the angles between the zone axes shown in Figure 3. The calculated angles are well matched with those experimentally measured; therefore the crystal structure of this new phase was confirmed to be an orthorhombic.

The relative coarse size of the orthorhombic phase suggests that the phase was formed at temperatures higher than that of the eutectic reaction of $L \rightarrow Zn + Al$. It is likely that the solidification of the laser resurfaced coating started with the α -Al dendrite, followed by the formation of the quaternary phase and lastly the eutectic reaction. The hot-dip simulated coating without laser treatment was also studied and pure Si and Mg₂Si were observed in the interdendritic areas. It is proposed that upon the laser heating the Si and Mg₂Si were melted rapidly, without extended diffusion due to the nature of the rapid heating in the laser treatment. The new orthorhombic phase was formed in the regions with highly concentrated Mg and Si, and grew rapidly. The formation of this phase led to the composition of the remaining liquid approaching the eutectic composition of binary Al-Zn, and finally the fine eutectic Al and Zn were formed. The relative fine plates of the Al and Zn indicate that the eutectic reaction occurred at relative low temperatures.

In view of the fact that the new orthorhombic phase was not observed in the untreated coating, it is possible that the phase is a metastable phase introduced by the laser treatment process because of the superfast cooling rate. A subsequent aging treatment of the laser treated sample was conducted at 150°C for 24 hrs in air to test stability. TEM microstructure of the

aged coating is shown in Figure 5. It can be seen that the orthorhombic phase is surrounded by Zn-rich particles which were precipitated during the aging treatment. In addition, Mg_2Si particles were also observed in the interdendritic area. The compositions of the α matrix, orthorhombic phase, Mg_2Si and Zn-rich particles are given in table 2. Clearly the composition of the orthorhombic phase was not altered by the aging treatment. The composition of the α matrix, as expected, has changed a lot after the aging treatment due to mainly the precipitation of Zn particles. The absence of Mg_2Si particles in the laser treated samples and significantly finer size of the Mg_2Si particles in the aged sample may suggest that the Mg_2Si was formed during the aging treatment at 150°C . The observation of the new orthorhombic phase in the aging treated coatings suggests that it may not be a metastable phase induced by the extremely fast cooling rate of the laser resurfacing treatment. This is further supported by the observation of the quaternary phase in other laser treated coatings namely 55Al-Zn-3Mg-1.5Si and 55Al-Zn-5Mg-4Si where the quaternary phase was observed in the naturally aged (6 month at room temperature) and aged samples (the same aging treatment) but not observed in the fresh laser treated samples.

This new phase may be a genuine quaternary phase because it contains four different elements and three of them are in similar amount and the fourth one is only slightly less than the rest (in at.%) and its composition or crystal structure does not match any known phases reported in Al-Zn-Mg [6] or Al-Zn-Si [7] or Al-Zn-Mg-Si [8,9] or Mg-Zn-Si [10], or Al-Mg-Si [11] systems. The new phase may be important to the corrosion properties of rapidly solidified '55%Al'-Zn-Mg-Si coatings. Since it replaces the interdendritic Mg_2Si and MgZn_2 observed in the interdendritic regions of untreated Zn-55Al-2Mg-1.5Si coating the corrosion behaviour of the laser treated Zn-55Al-2Mg-1.5Si coating would expected to be significantly different from that of the untreated Zn-55Al-2Mg-1.5Si coating. Clearly the laser resurfacing does not only refine the microstructure of the coating but also change the phases in the interdendritic areas.

4. Conclusions

A new quaternary phase was observed in the interdendritic area of a laser treated Zn-Al-Mg-Si coating and its crystal structure was determined by electron diffraction to be simple orthorhombic with the lattice parameters of $a=0.790\text{nm}$, $b=0.695\text{nm}$ and $c=0.414\text{nm}$.

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References

- [1] H. E. Townsend, Continuous Hot Dip Coatings, ASM Handbook, Vol. 5 (1994), 339-348.
- [2] Q. Liu, 2008 China Forum on Development of Continuous Galvanized Steel Sheet, Beijing, China, Oct (2008).
- [3] Bluescope Steel Ltd, (2009), International Patent Application, WO2009111842A1.
- [4] Bluescope Steel Ltd, (2010), International Patent Application, WO2010102343A1.
- [5] Bluescope Steel Ltd, (2007), International Patent Application, WO2007134400A1.
- [6] P. Liang, T. Tarfa, J.A. Robinson, S. Wagner, P. Ochin, M.G. Harmelin, H.J. Seifert, H.L. Lukas, F. Aldinger, *Thermochimica Acta*, 314 (1998) 87-110.
- [7] V Raghavan, *J phase Equilibria and Diffusion*, Vol. 28, No 2 (2007) 197.

- [8] Q. Li, Y.-Z. Zhao, Q. Luo, S.-L. Chen, J.-Y. Zhang, K.-C. Chou, *Journal of Alloys and Compounds*, 501 (2010) 282-290.
- [9] V Raghavan, *J phase Equilibria and Diffusion*, Vol. 32, No 1 (2011) 72-74.
- [10] S. De Negri, M. Skrobańska, S. Delfino, A. Saccone, *Intermetallics*, 18 (2010) 1722-1728.
- [11] H Feufel, T Godecke, H L Lukas and F Sommer, *Journal of Alloys and Compounds*, 247 (1997) 31-42.

Figure 1. X-ray mapping of the Zn-55Al-2Mg-1.5Si coating.

Figure 2. Overlay microstructure of laser treated Zn-55Al-2Mg-1.5Si coating.

Figure 3. Experimental Kikuchi map of the new orthorhombic phase.

Figure 4. Electron diffraction patterns of (a) $[0\ 0\ 1]$ and (b) $[1\ 1\ 0]$ of the new orthorhombic phase.

Figure 5. Overlay microstructure of aged Zn-55Al-2Mg-1.5Si coating.