

Identification of surface precipitates found on the surface of steel annealed for timplating

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Tin plate products are widely used in the packaging industry. The quality of the surface tin coating is paramount as it protects the material from corrosion. Grain boundary precipitates may form on the surface of low carbon steels during annealing prior to tin plating. These precipitates affect the quality of the tin coating when they are greater than 250nm in diameter as they act to de-wett the coating disrupting the tin coating process not only leaving the coating uneven which appears as a region of low reflectivity in affected areas but can also reduce the corrosion resistance of the tin plate product in the affected areas [1].

These surface defects caused by the surface grain boundary precipitates were mainly observed in steel sheet batch annealed in 4% H₂ + 96% N₂ gas environment which is reducing for iron. It is important to characterise these surface precipitates in order to understand the formation mechanics and minimise or eliminate the surface defect occurring in the batch annealing cycle. In order to reproduce the surface precipitates a steel sample with a composition shown in Table 1 was annealed under various pressures (from 0.1 Torr to 1x10⁻⁵ Torr) at 700°C. The surface precipitates were successfully reproduced in the pressure range 0.1 Torr to 1x10⁻⁴ Torr. Chromium is added to the steel to minimise surface graphitisation.

Figure 1 shows a TEM image of the grain boundary precipitates. It is also observed that finer particles are also present on the surface of the grains. Both the reproduced grain boundary precipitates and the industry precipitates were characterised by SEM and TEM. They were identified to be the spinel oxide MnCr₂O₄ by a combination of convergent beam electron diffraction and energy dispersive spectroscopy (EDS). Figure 2 shows an indexed nano diffraction pattern of the 011 zone axis. Figure 3 shows a convergent beam diffraction pattern of the 011 zone axis displaying a symmetry of 2mm. The indexed diffraction patterns showed that the precipitates have an FCC crystal structure with the symmetry of the diffraction patterns indicating a m3m point group. The lattice parameter of the precipitates were measured to be 0.83 nm, which is close to 0.845 nm reported in the literature for the MnCr₂O₄ spinel [2]. The finer particles observed on the grain are also believed to be MnCr₂O₄ spinel because they have a similar elemental ratio to that of the grain boundary precipitates. Figure 4 shows a typical EDS spectrum of the spinel precipitates. The chromium to manganese ratio is reasonably constant across many particles with chromium having approximately twice the amount of manganese.

This MnCr₂O₄ spinel is commonly observed on the surface of high chromium steels (stainless) when exposed to oxidising atmospheres [2], however this is the first time this spinel has been observed on the surface of low carbon, low alloy steel. It is thermodynamically predicted that chromium and manganese in the steel will selectively oxidise to form Cr₂O₃ and MnO respectively in atmospheres that are reducing for iron. It is proposed that these two oxide products combine to form the MnCr₂O₄

spinel by a solid state reaction at the annealing temperature. The greater size of the particles at the grain boundary compared with the particles on the grain surface results from the fact that grain boundaries act as fast diffusion paths for the chromium and manganese.

Table 1: Composition of steel

Element	C	Cr	Mn	P	S	Ni	Al	Si	Cu	V	N
Wt %	0.065	0.059	0.24	0.014	0.013	0.028	0.033	0.005	0.009	<0.003	0.0015

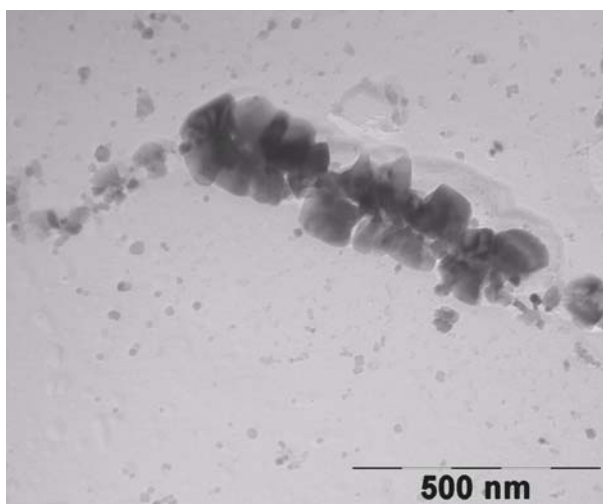


Figure 1: TEM image of precipitates.

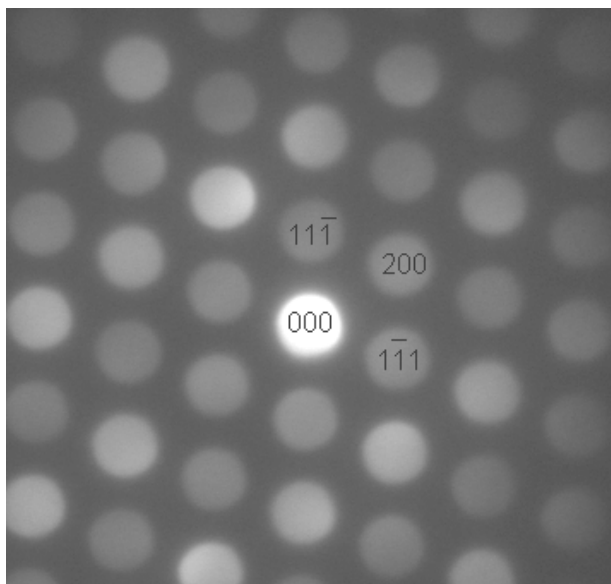


Figure 2: Indexed nano diffraction pattern of the 011 ZA.

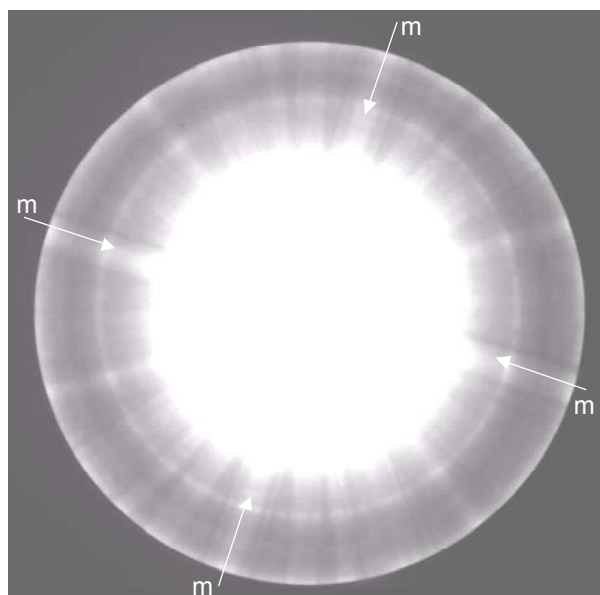


Figure 3: Convergent beam diffraction pattern of 011 ZA showing a symmetry of 2mm.

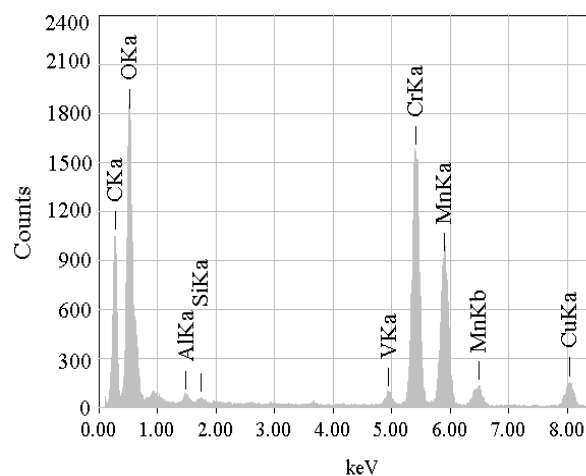


Figure 4: EDS spectrum of precipitate.

References

- [1] Killmore C. 2nd National Steel Conference, IMEA, 2003.
- [2] Saeki S, Saito T, Furichi R, Konno H, Nakamura T, Mabuchi, K, Itoh M. Corrosion Science; 1998;40:1295.