

Possibility of Zinc Embrittlement in Fire

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ABSTRACT

Zinc embrittlement is known as a kind of liquid metal embrittlement, a phenomenon where austenitic stainless steel and nickel alloy becomes brittle and/or cracks when it comes in contact with molten zinc. Zinc embrittlement can occur due to poor design and/or construction, but this study is focusing on the fire case.

In the fire case, galvanized steel is heated by flame, and when molten zinc drops on austenitic stainless steel, some plant owners believe the zinc embrittlement will occur. In order to prevent zinc embrittlement, some plant owners request shields to protect austenitic stainless steel piping and equipment that are located in close proximity to and, in particular, beneath galvanized steel structures, piping or equipment. However, it is not proven that a molten zinc drop can cause zinc embrittlement without the direct contact between galvanized steel and austenitic stainless steel.

In this study, laboratory tests and a pool fire simulation test were carried out to confirm whether zinc embrittlement occurs by fire without the direct contact between galvanized steel and austenitic stainless steel. As a result, it turned out that the risk of zinc embrittlement in fire case was very low without the direct contact of galvanized steel materials to austenitic stainless steel materials.

Key words: zinc embrittlement, liquid metal embrittlement, fire case

BACKGROUND

In the Flixborough Disaster, a chemical plant explosion in 1974 in the UK killed 28 people. The primary cause was inadequate repair work, and as a secondary cause, zinc embrittlement was observed at austenitic stainless steel piping.

As a lesson learned from this incident, some plant owners request to provide “Zinc Attack Protection” (ZAP) i.e., metal shield for stainless steel piping (examples are shown in Figure 1 and Figure 2), under galvanized steel piping or structures such as stairways/walkways to protect from molten zinc droplets in case of a fire. However, the source of zinc was not clear in Flixborough Disaster. Galvanized stairways/walkways or galvanized steel wire, which was used to secure the lagging box, were assumed

to be the source, but the source has not been clearly identified.¹ Galvanized steel wire might contact directly with the austenitic stainless steel piping or molten zinc might drop from melted galvanized stairways/walkways.²

INTRODUCTION

Zinc embrittlement is a phenomenon where austenitic stainless steel becomes brittle and/or cracks when it comes in contact with molten zinc.³ It is a kind of liquid metal embrittlement, where metal brittles when in contact with specific liquid metal. S. Sadigh showed that crack by zinc embrittlement occurs when all of the following conditions are met,^{4, 5}

- Molten zinc comes in contact with austenitic stainless steel.
- Austenitic stainless steel is subjected to tension stress.
- Austenitic stainless steel temperature is above 750°C.

It is well known that zinc embrittlement occurs in welding, e.g. direct welding between austenitic stainless steel and galvanized steel,⁶ or zinc-rich painted steel. Zinc embrittlement by the direct welding can be prevented by proper design study, specification and construction procedure. Therefore, this cause of the zinc embrittlement will not be discussed in this study.

In addition, some plant owners believe that zinc embrittlement occurs in a fire case where austenitic stainless steel is in direct contact with galvanized steel, and molten zinc from the galvanized steel may come in contact with the austenitic stainless steel. Additionally, if austenitic stainless steel is located under galvanized steel, a molten zinc droplet from the melted galvanized steel may drop onto austenitic stainless steel and cause the zinc embrittlement to occur.

In this paper, the possibility of zinc embrittlement in a fire case, especially by molten zinc drop, i.e. without direct contact, is discussed with some experimental data.

EXPERIMENTAL PROCEDURE

Two types of experiments as below were conducted.

a) Heating Test of Galvanized Steel Plates

In order to observe whether zinc embrittlement can occur by a molten zinc drop or not, galvanized steel plates (100 mm × 100 mm × 6 mm, zinc thickness 300 μm) were heated by electrical heaters for experiment No.1, 2, and 3. In order to simulate an actual fire with direct exposure to flame, a gas burner was used to heat the galvanized steel plate as experiment No.4. For all of the experiments, austenitic stainless steel plates (UNS S30400, no paint, 100 mm × 100 mm × 5 mm) with electrical heaters attached were placed beneath the galvanized steel plates. Figure 3 shows the experimental apparatus.

For experiment No.1, 2, and 3, electrical heaters were attached to the top side of galvanized steel plates and the temperature was set to 800°C, because the zinc vaporizing point is 907°C and austenitic stainless steel embrittlement vigorously occurs at 750°C. The surface temperature of the heated galvanized steel plates was measured by thermocouples.

The heating test condition is shown in Table 1. The oxygen (O₂) gas concentration was reduced to 5 mol% and 0.15 mol% by nitrogen (N₂) gas purging in order to simulate actual fire situation where the O₂ gas concentration at the surface of flame is at approximately 2 mol%, decreases as it approaches the inside, and becomes nearly 0 mol% at the center.⁷

For experiment No.1, 2, and 3, the duration of the heating was 30 minutes, and after reaching the maximum temperature, the temperature was preserved. Meanwhile for experiment No.4, the duration of

the heating was 10 minutes. After heating, the electrical heaters were turned off and the plates were naturally cooled down. Subsequently, cross-sectional microscopic observation of the galvanized plates was conducted.

b) Pool Fire Simulation Test

In order to simulate an actual pool fire situation, an oil pan filled with 100 L of kerosene was placed at the lower level of a 2200 mm high, 1500mm wide frame as shown in Figure 4, and pool fire simulation test was conducted. Galvanized steel plate was placed at the upper level of the frame, and austenitic stainless steel plate specimens (UNS S30400) were placed at the middle level of the frame.

The test specimens were prepared by welding two long plates (100 mm × 1500 mm × 3 mm) longitudinally (by SMAW), and the surfaces were in the as-welded condition. The plates were welded to provide residual stress because cracking by zinc embrittlement does not occur without stress. It is well known that residual stress levels in and near to the weld can be very high, up to material yield strength.⁸

For comparison purpose, galvanized steel plates were directly placed on top, at the edge part of the austenitic stainless plates. The temperature during the fire simulation test was checked by thermography.

After the fire simulation test, the presence of zinc on the austenitic stainless steel plate surfaces was inspected by using Dithizone reagent. The original color of the reagent is green, and it will turn to purple when zinc is presence and orange when zinc is absence. Dye Penetrant Testing (DPT) was conducted to confirm if cracking occurred or not, and cross-sectional Scanning Electron Microscopy (SEM) was conducted to observe whether grain boundary penetration by zinc happened or not.

RESULTS

a) Heating Test of Galvanized Steel Plates

Figure 5 shows the graph of temperature, time, and O₂ gas concentration for experiment No.3. For galvanized steel plates that were heated by electrical heaters (experiment No.1, 2, 3), approximately after 5 minutes the heating began, the temperature reached zinc melting point (approximately 420°C) and reached the maximum temperature within 10 minutes. The galvanized steel plates and austenitic stainless plates temperature was 100°C lower than the electrical heaters setting temperature. Meanwhile, Figure 6 shows the graph of temperature and time for experiment No.4, where the heating was done by using gas burner. The temperature reached zinc melting point in approximately 5 minutes after the heating began.

The surface condition of the galvanized steel plates after the heating test are shown in Figure 7, and the cross-sectional microstructure of the plates are shown in Figure 8. As for the surface condition, for experiment No.1, 2, 3, the galvanized layer melted, and oxide scale formed on the surface. However, there was no molten zinc drop observed in any experiments. Likely, this is due to the surface oxidation and surface tension of the melted zinc. Blisters were observed on the heated galvanized surface, where the color turned brown and oxidized. The galvanized layer was oxidized. The microstructure of galvanized layer was changed to porous structure after solidification.

Similarly, there was no molten zinc droplet observed for experiment No.4. In addition, the cross-sectional microstructure of plate shows that the galvanized layer condition was similar to result from experiment No.1, 2, and 3. However, for experiment No.4, it can be seen that the even the zinc layer melted, but the iron-zinc layer below it did not melt.

b) Pool Fire Simulation Test

Figure 9 shows the appearance of a pool fire simulation test. The fire was extinguished after burning for 35 minutes. Based on the thermography result shown in Figure 10, the temperature at the center of burning point was 1000°C, and the surrounding temperature was 500°C.

After the experiment, the austenitic stainless steel plate color turned to brown, and high temperature oxidation scale was observed.

At other than the edge of the austenitic stainless steel plate surface (Figure 11), there were few traces of very pale purple portions detected by Dithizone method, indicating that contamination by zinc did occur. However, there was no crack observed by DPT results or microscopic observations.

Meanwhile at the edge part of the austenitic stainless steel plate where the galvanized steel plate was placed directly on top of it, zinc was detected as purple indication near the welded part, but similarly there was no crack observed by DPT result.

Figure 12 and Figure 13 show the cross-sectional views at the location where the galvanized steel plate was placed directly on top of the austenitic stainless steel plate specimen. Zinc was observed on the specimen surface. However, there was no cracking and no grain attack by molten zinc observed even at around the welded part.

Based on the Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) analysis result, zinc was oxidized and grain boundary penetration of the austenitic stainless steel was not observed (Figure 14).

DISCUSSION

a) Heating Test of Galvanized Steel Plates

Even though the galvanized steel plates were heated in atmospheric condition with low concentration of O₂, and the heating temperature was raised above melting point of zinc, no molten zinc drops were observed. From the results of external visual observation and cross-sectional microscopic observation, though the zinc melted, the molten zinc did not drop due to the effects of oxidation and surface tension of the melted zinc.

In addition, similarly no molten zinc droplet was observed even though the heating was done by simulating actual fire condition.

The iron-zinc layer did not melt when heated by gas burner because the heating temperature did not reach the iron-zinc alloy melting temperature, which is approximately 700°C.

b) Pool Fire Simulation Test

From the experimental results, during the fire, the dropping of molten zinc from the melted galvanized steel plate is very limited and does not easily occur. Even though the presence of zinc adhesion was detected at the edge of the austenitic stainless steel plate where galvanized steel plate was placed directly on top of it, there was no intergranular penetration and no zinc-iron alloy formed on the stainless steel. It can be presumed that the austenitic stainless steel oxide layer prevents the zinc penetration by molten zinc.

Therefore, even if the molten zinc dropped, the diffusion of zinc is hindered by the growth of the austenitic stainless steel oxide layer due to the heat from the fire, preventing the intergranular penetration by molten zinc and alloying from happening. Thus, zinc embrittlement does not occur.

In addition, another study that evaluated the potential for liquid metal embrittlement of stainless steel by galvanized fasteners in an industrial fire scenario⁹ had been conducted, and the outcome was similar to this study.