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Titanium Coating on Iron and Steels by Disproportionation Reaction in Molten Salt

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Coating of Ti metal or Ti alloys on steels by a disproportionation reaction of Ti ion in molten chloride has been investigated. An equimolar NaCl-KCl mixture was melted in a quartz crucible under a high-purity Ar atmosphere, and $TiCl_3$ or K_2TiF_6 was added with Ti sponge. Fe, carbon steel (S45C) and stainless steel (SUS304) plates were immersed in the bath at 1100~1250K for scheduled duration. After the immersion, the Fe and carbon steel plates were covered with a dense and adherent layer of Ti-Fe alloy of which thickness was more than 10μm. From the change in the thickness of the Ti layer with the immersion time, it was concluded that the formation rate of the layer was mainly determined by the diffusion of elements in the formed layer. After the immersion, a thin but dense layer, where Ti content was about 90 mass%, was formed on the surface of the stainless steel plate. No Ti alloy phase was seen in it. The Ti deposition on Cr and Ni-Cr alloy plates was also investigated in this study, and the mechanism of Ti deposition on the stainless steel was discussed.

Keywords: *Titanium(Ti), coating, steel, stainless steel, molten salt, disproportionation, corrosion-resistance*

1. Introduction

Coating on steel with Ti metal or its alloys is useful to some purposes, and coating on stainless steel is also effectual to improve its corrosion resistance against seawater. A dense and adherent Ti layer can be formed by PVD and CVD, but an elaborate equipment is required. A thick Ti layer is obtained efficiently by thermal spray, but the layer is usually porous. Electroplating of Ti in molten salt was studied by many researchers[1)], but it has not been made practicable. Surface modification by using a disproportionation reaction of Ti in molten salt is also potential. The coating process by the disproportionation reaction is simple, and high throwing power can be expected. Some researchers have reported the coating of Ti compound by using the disproportionation reaction[2)]. The disproportionation reactions of Ti in molten salt containing $TiC1_3$ and K_2TiF_6 can be written as follows[3,4)];

$$3Ti(II) = 2Ti(III) + Ti \qquad (1)$$

$$4Ti(III) = 3Ti(IV) + Ti \qquad (2)$$

In this study, the coating of Ti and its alloys on steel by using the disproportionation reaction of Ti have been tried. The influence of the operation conditions on the morphology of the layer was discussed, and the change in corrosion resistance by the coating was demonstrated. The behaviors of Ti deposition on Cr and Ni-Cr were also investigated in this study to clarify the peculiar behavior of stainless steel in the process.

2. Experimental

Figure 1 is a schematic illustration of the experimental apparatus. An equimolar mixture of NaCl-KCl (Kanto Chemicals, special grade) was prepared for a bath. The mixture of 200~300g was melted in a quartz crucible in an airtight quartz container filled with high-purity Ar, and dehydrated by dry Cl_2 gas bubbling beforehand. $TiCl_3$ (Wako Pure Chemicals) or K_2TiF_6 (Mitsuwa Chemicals) was added with the excess amount of Ti sponge for the reverse reactions of (1) and (2), and the system was kept for hours to reach equilibrium. The concentration of $TiCl_3$ or K_2TiF_6 in this paper is represented by the values calculated from the added amounts. Fe (Nilaco, 99.8%), carbon steel (S45C) and stainless steel (SUS304) plates of about 15x5x2 mm were used as substrate. They were connected with the wire of the same material covered with mulite sheaths, and immersed in the molten salt.

After the immersion for scheduled duration, the specimen was picked up from the melt and cooled in the container. The specimen was weighted after rinsing with distilled water. Its surface and cross section were observed by SEM and analyzed by EDX. The specimens with/without the coating were immersed in 3% salt water at room temperature for 200 h, and the changes in appearance were observed.

In the research on the Ti deposition on the above substrates, the result of the stainless steel was very different from the others. To clarify the deviation, Ti deposition on Cr and Ni-Cr was also investigated. Cr (Nilaco, 99.9%) and Ni-Cr (Nilaco, 20%-Cr) plates were treated and analyzed by the same procedure mentioned above.

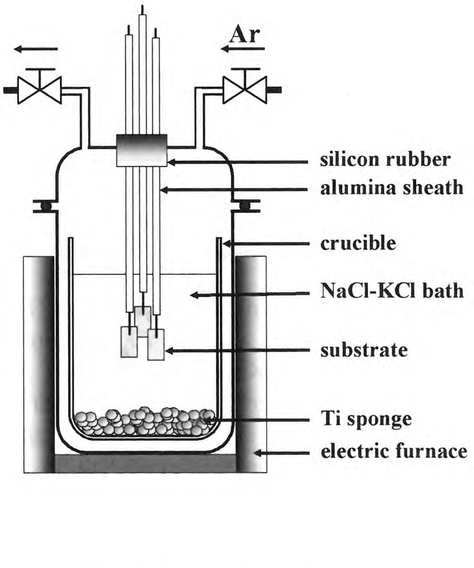

Figure 1. Experimental apparatus.

3. Results and discussion

3.1 Ti deposition on Fe and carbon steel

The NaCl-KCl melt after $TiCl_3$ and Ti sponge addition changed its color into green, while that after the K_2TiF_6 addition was black. These results indicate that the stable Ti ion was varied with the solutes. However, no remarkable difference in the formed layer described hereinafter was found between the treatments in these baths. K_2TiF_6 can be handled much easier than $TiCl_3$, but F might corrode the substrate or container. $TiCl_3$ and K_2TiF_6 should be chosen to the operation condition appropriately.

The color of the Fe plate changed into gray by the immersion. Very small particles covered the whole surface, and Ti was detected by EDX analysis. The observation of the cross section showed that a dense and adherent Fe-Ti layer of more than 10μm was formed on the Fe surface. No obvious structure related with the surface particles was observed. The Ti content around the surface was above 50 at%, and a layer containing about 30at% Ti was formed inside. Considering the phase diagram of Fe-Ti system, the surface and inside layers should be FeTi and Fe_2Ti, respectively.

The surface of the carbon steel plate was also covered with Ti-Fe layer. A typical SEM image of its cross section is shown in Fig.2, and the contents of Ti and Fe are shown in Fig.3. The result was similar to that on the Fe plate, namely Fe_2Ti and FeTi layers seemed to be formed.

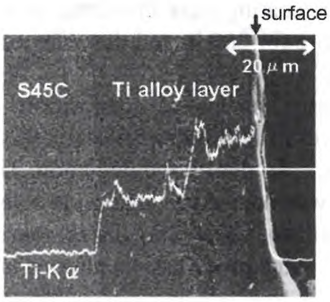

Figure 2. SEM image of cross section of carbon steel after immersion in bath with 2mol% $TiCl_3$ for 72h at 1203K.

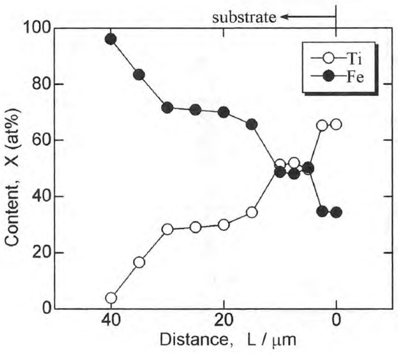

Figure 3. Fe and Ti contents in deposited layer on carbon steel after immersion in bath with 2mol% $TiCl_3$ for 72h at 1203K.

However, the top surface was covered with the layer where the Ti content was about 60 at%, though Ti-Fe compounds containing more than 50 at% Ti are not seen in its phase diagram. Carbides of Ti and Fe were not observed in the formed layers in this study.

If the Ti alloy layer was formed uniformly on the whole surface of the specimen, the thickness of the layer is in proportion to the weight gain. The weight of the specimen always increased by the immersion actually, and the thickness estimated from the weight gain was consistent with that directly observed by SEM. Furthermore, the weight gain of the Fe and carbon steel plates was in proportion to the square root of the immersion time. Their weights increased faster when the temperature rose. These results suggest that the reaction rate was determined by the diffusion of the elements in the formed layer. The driving force of the coating should be the difference in Ti activity between the specimen and Ti sponge in the system.

The corrosion resistance of the Fe and carbon steel plates were improved very much by the coating as shown in Fig.4. The whole surfaces without the coating were rusted furiously after the immersion in 3 wt% NaCl solution for 200 hours, while obvious change in appearance was rarely seen on the specimens with the coating. However, corrosion sometimes occurred from the edge of the specimen with the coating. Pre-treatment, such as chamfering, should be necessary to prevent such corrosion.

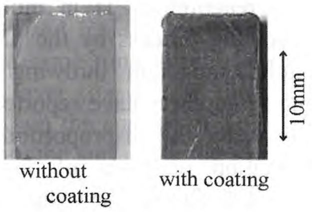

Figure 4. Appearances of carbon steel with/without coating (1203K, 48h, 2mol%-$TiCl_3$) after immersion in 3%-NaCl solution for 200h.

3.2 Ti deposition on stainless steel

The color of the stainless steel also changed into gray by the immersion. Very small particles covered the whole surface, and Ti was detected by EDX analysis. Figure 5

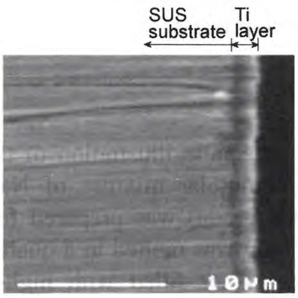

Figure 5. SEM image of cross section of SUS304 after immersion in bath with 2mol% K_2TiF_6 for 72h at 1103K.

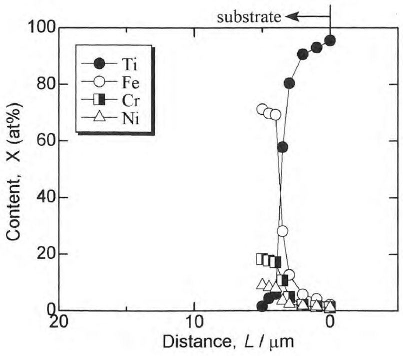

Figure 6. Contents in deposited layer on SUS304 after immersion in bath with 2mol% K_2TiF_6 for 72h at 1103K.

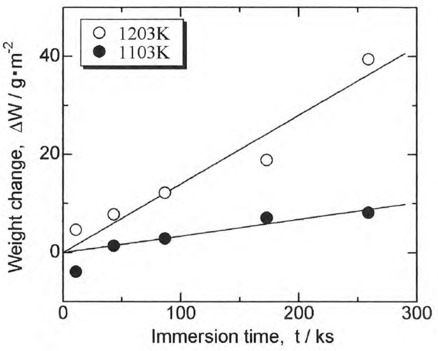

Figure 7. Weight change of SUS304 specimen by immersion in bath with 2mol% K_2TiF_6.

shows the SEM image of the cross section of the stainless steel after the immersion. A dense and adherent layer containing Ti was formed on the surface. The layer was very thin, a few μm, but the Ti content reached more than 90 at% as shown in Fig. 6. A particular element in stainless steel wasn't enriched in the Ti layer, and intermetallic compounds of Ti with Fe, Cr and Ni seemed not to be formed. These results were reproductive under the experimental conditions in this study.

Figure 7 shows the weight change of the stainless steel plate with the immersion time. The weight of the stainless steel tended to increase with the immersion time, though it sometimes decreased in the beginning of the immersion. The higher the immersion temperature was, the bigger the weight gain was. The weight gain of the stainless steel wasn't necessarily in proportion to the square root of the immersion time in contrast to the cases of the Fe and carbon steel mentioned above. This result suggests that the reaction rate of the Ti-layer formation on the stainless steel wasn't determined by the diffusion of the elements in the formed layer.

The mechanism of the Ti-layer formation on stainless steel should be different from those on Fe and carbon steel; The formation of the Ti layer on the stainless steel cannot be explained only by the deviation in the Ti activities, and the reaction rate wasn't determined by the diffusion of the elements in the formed layer. The thinness of the Ti layer on stainless steel in comparison with those on Fe and carbon steel must be related to the difference in the mechanism. It was shown that Ti alloy was formed on Fe and Ni substrate[5,6], which are main ingredients of the stainless steel(SUS304). Cr in the stainless steel might affect the Ti deposition.

3.3 Ti deposition on Cr and Ni-Cr

The surface of the Cr plate after the immersion was fully covered with particles, but rougher than the other metals. Figure 8 shows the SEM image of the cross section of the Cr plate after the immersion. The surface was covered with a dense and adherent layer of deposit, but the layer was uneven. Figure 9 shows the contents of Cr and Ti in the cross section shown in Fig.8. The deposit was almost pure Ti metal, and the Cr content was very low in the deposit. Cr-Ti alloy wasn't found, nor were vestiges of its thermal decomposition seen.

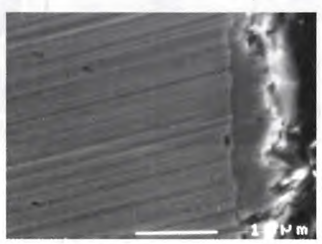

Figure 8. SEM image of cross section. of Cr after immersion in bath with 2mol% K_2TiF_6 for 72h at 1103K.

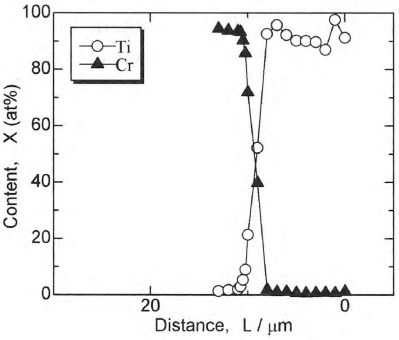

Figure 9. Contents in deposited layer on Cr after immersion in bath with 2mol% K_2TiF_6 for 72h at 1103K.

Since Ti was deposited both on the stainless steel and Cr, it is obvious that Cr strongly affects the deposition of Ti. However, there were some differences. The boundary between the deposit and substate was clearer on the Cr palte than on the stainless steel plate. The overall thickness of the deposited layer on the Cr plate seemed bigger than that on the stainless steel plate under the same condition. In contrast with the thickness, the weght of the Cr plate decreased by the immersion, while the weight of the stainless steel plate tended to increase.

The substitution reaction of Ti for Cr might have occurred in the system. The weight decrease and the surface roughness can be explained by assuming the substitution reaction. However, it is hard to attribute the formation of Ti layer on the stainless steel plate to only the substitution reaction; The weight decrease of the stainless steel wasn't reproductive, and was observed only in the begining of the immersion. The ratios of Cr to Fe and Ni didn't change remarkably around the boundary between the deposit and substrate.

Figure 10 shows the SEM image of the cross section of the Ni-Cr plate after the immersion. The surface was covered with three dense layers. The layers adhered to the substrate or the inner layer, and the thickness reached more than 30 µm totally. The weight of the Ni-Cr plate increased remarkably by the immersion.

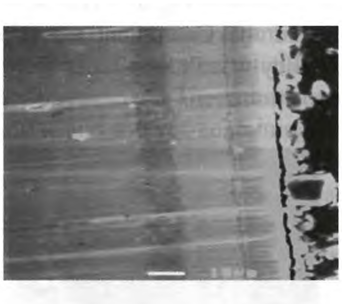

Figure 10. SEM image of cross section of Ni-Cr after immersion in bath with 2mol% K_2TiF_6 for 72h at 1103K.

Figure 11 shows the contents of Cr and Ti in the cross section shown in Fig.10. The two outer layers seemed Ti-Ni alloys. These layers were similar to those formed on Ni substrate[5,6], and the Cr content in these layers was very low. A Cr-condensed layer was seen inside the Ti-Ni alloy layers, and the contents of the elements changed continuously in this layer. This result indicates that Ni migrated from the substrate to the deposit preferentially, and the migration of Ni proceeded even through the Cr-condensed layer. The Cr content in the Ni-Cr plate was almost the same as that in the stainless steel, but the formed layers by the immersion were quite different. Although Cr strongly affects the Ti depostion, the mechanism should not be simple.

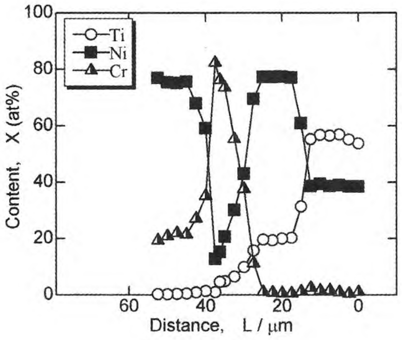

Figure 11. Contents in deposited layer on Ni-Cr after immersion in bath with 2mol% K_2TiF_6 for 72h at 1103K.

The results of the Ti deposition on Cr and Ni-Cr gave valuable information on Ti deposition on stainless steel; Some mechanisms assumed beforehand were denied. However, the accurate mechanism is still being investigated.

4. Conclusion

In equimolar NaCl-KCl melt containing $TiCl_3$ or K_2TiF_6 with Ti sponge, Ti alloy layers were formed on the surfaces of Fe and carbon steel by the disproportionation reaction of Ti. The layer was dense and adherent, and the thickness was more than 10µm. It was suggested that the driving force of the coating was the difference in the Ti activity between the specimen and Ti sponge, and that the reaction rate was determined by the diffusion in the formed layer. The corrosion resistance of Fe and carbon steel was remarkably improved by the coating.

A Ti metal layer was formed on the surface of the stainless steel. The layer was dense and adherent, but much thinner than those on Fe and carbon steel under the same condition. The mechanism of the Ti deposition on the stainless steel seemed different from those on Fe and carbon steel; The driving force of the reaction should not be the difference in Ti activity, and the reaction rate wasn't determined by the diffusion of the elements in the deposited layer.

Ti metal was also deposited on Cr plate, and Ti-Ni alloy layer was formed on Ni-Cr plate. These results gave valuable information on the Ti deposition on stainless steel, but the accurate mechanism still remains unclear. Becasuse the formation of a Ti metal layer should be effective in some purposes, the further investigation on the mechanism is desired to perform the efficient treatment.

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