

## Passivity and corrosion resistance of metallic materials

Koji Hashimoto<sup>1</sup> and Katsuhiko Asami<sup>2</sup>

<sup>1</sup>Tohoku Institute of Technology  
6 Futatsuzawa, Taihaku-ku  
Sendai 982-8588  
Japan

<sup>2</sup>Institute for Materials Research, Tohoku University  
2-1-1 Katahira, Aoba-ku  
Sendai 980-8577  
Japan

Passivity and corrosion resistance of metallic materials Koji Hashimoto\* and Katsuhiko Asami\*\* \* Tohoku Institute of Technology, Sendai 982-8588 Japan \*\* Institute for Materials Research, Tohoku University, Sendai 980-8577 Japan

The spontaneous passivity is prerequisite of the use of metallic materials. Spontaneous passivation occurs due to the presence of the air-formed film, unless the material is exposed to highly oxidizing environments where the formation of a passive film is enforced. The corrosion resistance of metallic alloys is determined primarily by the composition of the passive film depending upon the alloy composition. From this point of view, this article looks briefly back the history of the passivity study and compositional and structural analyses of the passive film, and discusses the use of corrosion-resistant materials.

The stable passivity of Fe-Cr alloys containing more than a prescribed minimum amount of chromium was first reported in 1911[1] and led to commercial application of stainless steels. From the engineering point of view the most important passivity was that of stainless steels. The introduction of electrochemical technologies led to a great progress in an understanding of the passivity mostly in the nineteen sixties. The desire of the most corrosion scientists at that time was to know the true character of the passivity of stainless steels. In this connection, the corrosion community was given a shock by Mcbee and Kruger who in applying transmission electron diffraction to anodically formed passive films on binary Fe-Cr alloys reported that the films on stainless steels are amorphous [2]. At that time electron diffraction became newly available to the corrosion scientists but turned out useless for identification of the passive films on stainless steels.

In the nineteen seventies a variety of surface analytical techniques became available to corrosion scientists. Holiday and Frankenthal in applying soft X-ray spectroscopy to analyze the passivating films on Fe-Cr alloys suggested the significant changes in the surface film composition and thickness in the alloy composition range of 10-14report of chromium enrichment in the passive film on a stainless steel was made by Lumsden and Staehle [4]. The change of Fe-Cr alloys into stainless steels at a critical concentration of chromium was demonstrated by X-ray photoelectron spectroscopy [5]. For the Fe-Cr alloys with lower chromium contents the cationic composition of the passive film was the same as the bulk alloy composition. However, at about 13 at enrichment of chromium took place in the passive film, while the composition of the underlying alloy surface is the same as the bulk al-

loy composition, indicating preferential dissolution of iron from the surface film.

The beneficial element next to chromium in enhancing the corrosion resistance of conventional alloys is molybdenum. It has been known that the addition of molybdenum to stainless steels results in a significant decrease in the current density in both the active and passive regions in strong acids. In fact molybdenum forms the protective film in the active region of stainless steels, and prevent the active dissolution. For instance, in a concentrated hydrochloric acid molybdenum shows an active dissolution peak at about -0.3V vs SCE, where the cathodic current is higher than the anodic current for dissolution in the form of Mo<sup>3+</sup>. In the potential region between -0.2 and 0.2 V, molybdenum forms a passive Mo<sup>4+</sup> oxide film but at higher potentials molybdenum dissolves transpassively as Mo<sup>6+</sup> molybdate. On the other hand, tungsten dissolved is not detected at all lower potentials and in the transpassive region WO<sub>3</sub> stays on the metal surface because of its lower solubility in acids.

In pursuit of spontaneously passive alloys in very aggressive concentrated hydrochloric acids, alloys consisting only of corrosion-resistant elements such as chromium-valve metal, molybdenum-valve metal and tungsten-valve metal alloys were prepared by sputter deposition. Almost all these alloys are spontaneously passive in concentrated hydrochloric acids and show higher corrosion resistance than alloy component metals. Among them Cr-Ta alloys exhibit the highest corrosion resistance and are immune to corrosion in 12 M HCl at 30C, forming a passive double oxyhydroxide film of Cr<sup>3+</sup> and Ta<sup>5+</sup>. The corrosion resistance of chromium-valve metal alloys increases with increasing chromium content of the alloys, while that of molybdenum- and tungsten-valve metal alloys increases with increasing valve metal contents. The open circuit potentials of these spontaneously passive alloys in 12 M HCl are vary close to the potentials where transpassivation of molybdenum and tungsten occurs because of high protectiveness of the passive film and because of high cathodic activity. The passive films are composed of an outer valve metal oxyhydroxide layer and an inner tetravalent molybdenum oxide layer. Although molybdenum dissolves transpassively from the outer part of the passive film, if the outer layer prevents oxidation of molybdenum to Mo<sup>6+</sup> the inner molybdenum oxide layer acts as the diffusion barrier for outward diffusion of cations for dissolution. The passive films with the similar structure are formed on tungsten-valve metal alloys. Accordingly, molybdenum- and tungsten-valve metal alloys possess higher corrosion resistance than alloy component metals.

In order to use high corrosion resistance of amorphous alloys, preparation of bulk amorphous alloys has recently been attempted. Since consolidation processing of amorphous alloy powders to form desirable shapes of bulk amorphous alloys can be realized for some alloys by processing in the supercooled liquid state in the interval between glass transition and crystallization temperatures. A variety of amorphous nickel base alloys containing various corrosion-resistant elements were prepared in the form of sheets of a few mm thickness. Their performance against dew point corrosion

was examined in waste incinerators and they showed no corrosion weight change maintaining metallic luster.

The effort to obtain spontaneously passive new corrosion-resistant materials will enable us to apply metallic materials to new industrial fields.

[1] P. Monnartz, *Mettallurgie*, 8 (1911) 161, 193. [2] C. L. Mcbee and J. Kruger, *Electrochim. Acta*, 17 (1972) 1337. [3] J. R. Holliday and R. P. Frankenthal, *J. Electrochem. Soc.* 119 (1972) 1190. [4] J. B. Lumsden and R. W. Staehle, *Scripta Met.* 6 (1972) 1205. [5] K. Asami, K. Hashimoto and S. Shimodaira, *Corros. Sci.* 18 (1978) 151.