

# Effects of Nanocrystallinity on Corrosion Behavior of Amorphous Alloys(アモルファス合金の耐食性に及ぼすナノ結晶性の影響)

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## 論 文 内 容 要 旨

### Chapter 1. Introduction

A highly corrosion-resistant amorphous Fe-Cr-P-C alloy was discovered in 1974. Since then, several amorphous alloys have been developed which exhibit extremely high corrosion resistance in aggressive environments. The high corrosion resistance of the amorphous alloys is partly attributed to an extremely homogeneous nature which provides the formation of protective passive films that are almost free of physical and chemical defects.

On the other hand, several nanocrystalline alloys developed in late 80s and 90s exhibit novel characteristics, e.g., high mechanical strength, excellent soft magnetic properties and improved catalytic activity. Nanocrystallites may also form in the amorphous alloys in case of deviation from the ideal composition or increase in dimensions. These may also form during high temperature applications or heating required for manufacturing of the engineering components.

For interesting characteristics of the nanocrystalline alloys and the possibility of formation of crystallites in the amorphous alloys when the application range is extended, it seems necessary to explore the possibility of maintaining the high corrosion resistance of the amorphous alloys in the nanocrystalline alloys as well.

This study aimed to investigate the effect of nanocrystalline heterogeneity on the corrosion resistance of the amorphous alloys with a particular emphasis to determine the size and the type of alloy heterogeneity which may not have detrimental effects. The effect of alloy heterogeneity has been studied using the sputter-deposited chromium-valve metal (Ti, Nb, Zr, Ta, Al) alloys after heat treatment to introduce nanocrystalline heterogeneity. The role of type of alloy heterogeneity has been emphasized with the help of Cr-Ti and Cr-Nb alloys in chapter 3. The effect of size of alloy heterogeneity has been determined with the help of Cr-Zr and Cr-Ta alloys in chapter 4. The Cr-Al alloys have provided a chance to emphasize the role of type as well as the size of alloy heterogeneity simultaneously. The corrosion behavior of nanocrystalline Cr-Al alloys has been presented in chapter 5. Some of the most significant results included in chapters 3, 4 and 5 have been summarized in chapter 6. The conclusions have been presented in chapter 7.

### Chapter 2. Experimental Methods

This chapter includes the details of the experimental methods.

### Chapter 3. Corrosion Behavior of Nanocrystalline Cr-Ti and Cr-Nb Alloys

The amorphous Cr-Ti and Cr-Nb alloys exhibit higher corrosion resistance in comparison with the alloy constituents due to synergistic interactions between alloy constituents to form more protective passive films composed of double oxyhydroxides.

In spite of the fact that pure chromium and pure titanium undergo active dissolution in 6M HCl, the amorphous Cr-Ti alloys exhibit spontaneous passivity and high corrosion resistance in this environment. After crystallization, the formation of a nanocrystalline mixture of hcp Ti (size ~20-25 nm) and Cr<sub>2</sub>Ti leads to active dissolution in open circuit condition and active-passive transition during anodic polarization. One order of magnitude increase in passive current density is observed with a nanoscopic heterogeneous corrosion damage. By contrast, the formation of a nanocrystalline mixture of Cr<sub>2</sub>Ti and bcc Ti(Cr) (28 nm) containing ~15 at% chromium does not lead to degradation of corrosion resistance of the amorphous alloys and the spontaneously passivating nature of the amorphous alloys is sustained. Similarly, bcc Cr(Ti) containing 7 at% titanium is detrimental for the corrosion resistance, while an as-deposited alloy comprising bcc Cr(Ti) (containing 22 at% titanium in the solid solution) exhibits high corrosion resistance similarly to the amorphous alloys.

Heat treatment of sputter-deposited Cr-Nb alloys leads to the precipitation of bcc Cr (15 nm), bcc Nb (20-25 nm) or an intermetallic compound Cr<sub>2</sub>Nb. At higher temperatures of heat treatment, a mixture of Cr<sub>2</sub>Nb and bcc Cr, or Cr<sub>2</sub>Nb and bcc Nb, is formed. The amorphous or nanocrystalline Cr-Nb alloys exhibit spontaneous passivity in concentrated HCl solutions.

The intermetallic compound Cr<sub>2</sub>Nb exhibits a similar corrosion resistance to that of the amorphous alloys. By contrast, the metallic precipitates of bcc Cr and bcc Nb are responsible for increase in the passive current density. Nevertheless, the preferential dissolution of bcc Nb leaving behind mostly the amorphous phase or the intermetallic Cr<sub>2</sub>Nb during potentiostatic polarization results in a similar current density to that of the amorphous counterparts. Accordingly, the corrosion resistance of the amorphous alloys is sustained in spite of the formation of nanocrystalline heterogeneity.

The corrosion behavior of nanocrystalline Cr-Ti and Cr-Nb alloys reveals the fact that all type of alloy heterogeneity is not detrimental for corrosion resistance of the amorphous alloys. The metallic precipitates of bcc Cr, bcc Nb and hcp Ti are observed to cause detrimental effects. The nanocrystalline alloys exhibit high corrosion resistance similarly to the amorphous alloys when only intermetallic phases are formed. Similarly, the preferential dissolution of less corrosion-resistant metallic phases leaving behind mostly the intermetallic phases leads to similar corrosion resistance to that of the amorphous alloys.

### Chapter 4. Corrosion Behavior of Nanocrystalline Cr-Zr and Cr-Ta Alloys

Heat treatment of Cr-Zr and Cr-Ta alloys results in the precipitation of less corrosion-resistant metallic phases in the matrices of corrosion-resistant amorphous or intermetallic nanocrystalline phases. The size of the less corrosion-resistant precipitates is small.

Figure 1 presents the polarization curves of as-deposited (amorphous) and heat-treated (nanocrystalline) Cr-60Zr and Cr-67Zr alloy samples in 6M HCl. The heat-treated alloy samples contain precipitates of hcp Zr in the matrices of chromium-rich amorphous phase or the intermetallic compound Cr<sub>2</sub>Zr. Interestingly, an ennoblement of pitting potential takes place with increasing heat treatment temperature as long as the size of hcp Zr precipitates is less than 20 nm. This happens due to enrichment of chromium in the matrix phase as a consequence of precipitation of hcp Zr. The chromium-rich matrix phase is responsible for the formation of a protective passive film. This film can completely cover the whole alloy surface including the less corrosion-resistant hcp Zr precipitates due to small size. When the precipitate size exceeds the critical limit of 20 nm, the protective passive film cannot completely cover the grown precipitates and a defective surface film is formed. This leads to a less noble pitting potential of the alloys.

The corrosion behavior of nanocrystalline Cr-Ta and Cr-Zr alloys extends the findings made in the chapter 3, in terms of the size of alloy heterogeneity. The corrosion-resistant matrices determine the corrosion resistance of the nanocrystalline alloys if the size of less corrosion-resistant precipitates is less than a critical limit, i.e., ~20 nm. This is due to the formation of protective passive films which can completely cover the whole alloy surface. The

less corrosion-resistant precipitates lead to a decrease in the corrosion resistance if their size exceeds the critical limit. This is due to the formation of defective surface film.

## **Chapter 5. Corrosion Behavior of Nanocrystalline Cr-Al Alloys**

In contrast to additions of titanium, zirconium, niobium and tantalum, the addition of aluminum to chromium is detrimental from corrosion point of view. The aluminum has an active nature in acidic environments and does not seem to contribute to the passivity of the Cr-Al alloys. Nevertheless, several nanocrystalline Cr-Al alloys maintain high corrosion resistance of the amorphous alloys, similarly to the other chromium-valve metal alloys with high passivating abilities. The alloys containing more than 35 at% chromium undergo spontaneous passivation in 0.1M HCl with the formation of thin protective passive films, in spite of the development of nanocrystalline heterogeneity. The nanocrystalline intermetallic phases are able to sustain the high corrosion resistance of the amorphous counterparts. The detrimental and beneficial effects of alloy heterogeneity depend on the size as well as the type of the alloy heterogeneity. A few of the results have been emphasized in the following paragraph.

As-deposited Al-43Cr and Al-51Cr alloys crystallize to a two phase mixture of  $Al_{17}Cr_9$  (35 at% chromium) and bcc Cr(Al) (>60 at% chromium) by heat treatment at 550 and 600°C for Al-43Cr alloy and 450-600°C for Al-51Cr alloy. The grain size of the alloys depends on the heat treatment temperature. An enhancement of pitting corrosion resistance is observed by heat treatment due to increased passivating ability of chromium-rich bcc Cr(Al), as long as the grain size is less than 20 nm. An increase in the grain size above 20 nm results in a decrease in the pitting potential. Heat treatment of Al-43Cr alloy at 425-500°C results in the formation of an aluminum-rich metastable phase in addition to the above mentioned phases. This leads to a decrease in the pitting potential of the alloys, although grain size is less than 15 nm.

These observations in combination with several other results lead to a conclusion that the high corrosion resistance and existence of critical size of heterogeneity is not peculiar to the chromium-valve metal alloys with high passivating ability, and it could be a general phenomenon for most of the alloy systems containing chromium. However, the critical size of alloy heterogeneity also depends on the type of the alloy heterogeneity. For example, the critical size for a less corrosion-resistant  $Al_{17}Cr_9$  in the corrosion-resistant matrix of Cr(Al) is ~20 nm (similar to that for hcp Zr in Cr-Zr alloys), while it is less than 15 nm for the aluminum-rich metastable phase.

## **Chapter 6. The Role of Nanocrystalline Heterogeneity in Determining the Corrosion Resistance of Amorphous Alloys**

Heat treatment of amorphous chromium-valve metal alloys results in precipitation of either chromium-deficient phase leading to an enrichment of chromium in the matrix phase or a chromium-rich phase (e.g., bcc Cr) leading to a decrease in the chromium content of the matrix phase. The corrosion resistance of the chromium-valve metal phases increases with the chromium content. On the other hand, bcc Cr itself is not corrosion-resistant in strong acids.

When the precipitates are a less chromium phase and less than critical size, i.e., 20 nm, the precipitation leads to an increase in the corrosion resistance because the entire alloy surface can be covered by the more protective and stable passive film due to an increase in the chromium content of the matrix phase (Fig. 2(a)).

However, when the size of the less chromium phase exceeds the critical limit, the corrosion resistance decreases because the protective passive film cannot cover completely the grown less corrosion-resistant precipitates any longer and hence passivity breakdown tends to occur easily (Fig. 2(b)).

When bcc Cr is precipitated, the corrosion resistance decreases in strong acids regardless of the size of the precipitates. This happens due to a decrease in the passivating ability of the matrix phase in addition to low corrosion resistance of bcc Cr, itself. (Fig. 2(c)).

## **Chapter 7. Conclusions**

This chapter presents the conclusions of the thesis. The nanocrystalline alloy heterogeneity is not always detrimental to the corrosion resistance of the amorphous alloys. Its beneficial or detrimental effects depend on the size as well as the type of the heterogeneity.

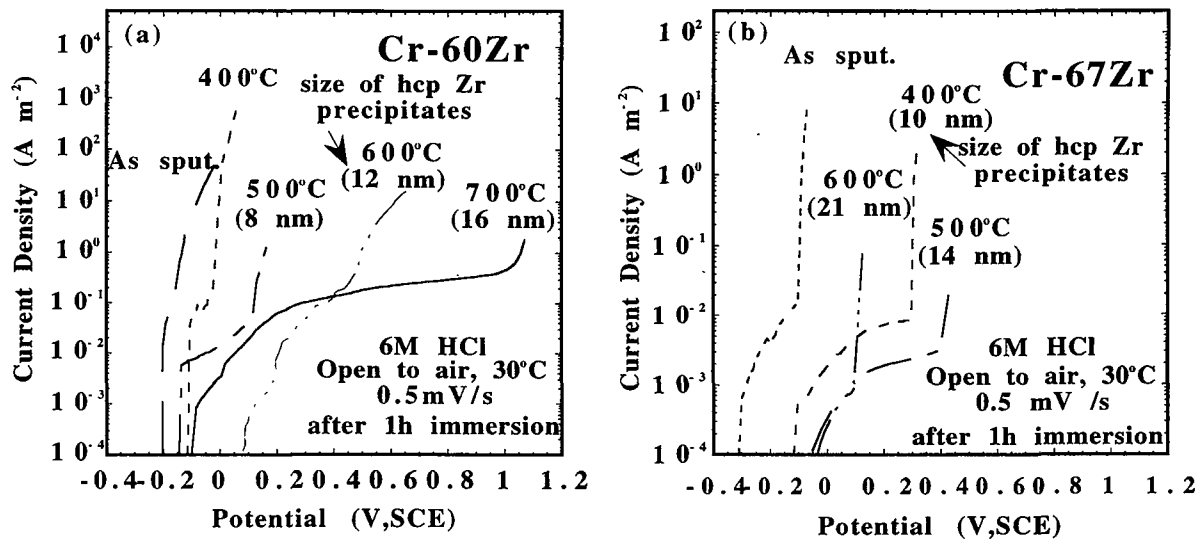


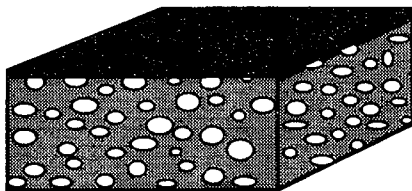
Fig. 1. Polarization curves of heat-treated Cr-60Zr (a) and Cr-67Zr alloy samples (b) in 6M HCl open to air at 30°C.

### Passivation based on the presence of chromium-containing phase

Nanocrystalline alloy structure and corrosion resistance

Size of precipitates

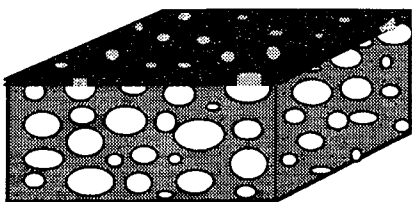
Chromium concentration in the matrix



(a) Increase in corrosion resistance

less than critical size (chromium-deficient)

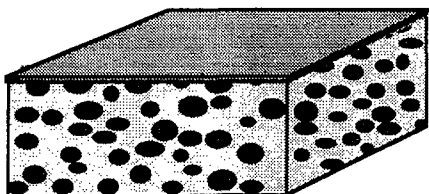
increase



(b) Decrease in corrosion resistance

more than critical size (chromium-deficient)

increase



(c) Decrease in corrosion resistance

regardless of size decrease (bcc Cr)

Fig. 2. Schematic representation of the effects of nanocrystalline precipitates in amorphous or nanocrystalline matrix on the corrosion resistance of the alloys in strong acids.

# 審査結果の要旨

本論文は、均一固溶体中に生じるナノスケールの化学的不均一性が耐食性に及ぼす影響を明らかにする目的で、合金構成元素より優れた耐食性を示すアモルファスクロム-バルブメタル合金にナノ結晶が析出する熱処理を施し、耐食性の変化を調べたものであって7章よりなる。

第1章は緒論であり、本研究の背景と目的を述べている。

第2章では、実験方法を述べている。

第3章では、析出物のタイプと耐食性の関係を明らかにする目的で、主としてアモルファスCr-Ti合金を用い、両元素を含む金属間化合物相の析出は6 M HCl中における耐食性に影響しないが、bcc Crあるいはhcp Tiのような単体相が生じると耐食性が低下することを見いだしている。

第4章では、析出物の大きさが耐食性に及ぼす影響を明らかにするため、主としてアモルファスCr-Zr合金を用い、平均粒径が20 nm未満のhcp Zr相の析出は、母相のクロム濃度を上昇させて不働態化能を向上させ、クロムに富む不働態皮膜でhcp Zr相表面を含む合金全表面を覆うため、12 M HCl中における耐食性を向上させること、しかし hcp Zr はアノード分極によって孔食を受けるため、hcp Zr相の平均粒径が20 nmを越えると、大きなhcp Zr相表面をクロムに富む安定な不働態皮膜で完全には覆いきれなくなるため、耐食性が低下し始めることを見いだしている。

第5章では、クロム濃度が高いほど耐食性が向上するAl-Cr合金を用い、耐食性が低いアルミニウムに富んだ相が析出すると粒径が十数nmであっても、0.1MHCl中における耐食性が低下するが、さらに高い温度で熱処理し、アルミニウムに富んだ相が金属間化合物相に吸収されると、化合物相は大きくても耐食性は向上すること、特に、最も耐食性が高いbcc Cr相が化合物相と共に生じると、合金の不働態化能が上がり製造のままの合金より高い耐食性を示すことなどを明らかにしている。

第6章では、析出物の性質と大きさが耐食性に及ぼす影響を類型化し考察している。

第7章では、本研究で得られた成果を総括している。

以上要するに、本論文は、合金の耐食性は、化学的不均一性のタイプと大きさによって影響を受け、母相の不働態化能を向上させる析出物の粒径が20 nm未満であるときは、返って耐食性が向上するが、析出物の大きさが臨界サイズを越えると、不働態皮膜が不完全になって耐食性が低下することなど、これまで予想もされなかった事実を明らかにしたものであって、材料物性学の発展に寄与するところ少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。