Effect of Cu on the Corrosion Resistance of a NiMo₂B₂-Dispersed Ni-Based Alloy^{*1}

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Corrosion of NiMo₂B₂-dispersed Ni-based alloy containing Co, Mn, Cr, Fe or Cu was examined by measuring the mass loss and the corrosion potential in 6 mass% HNO₃ aqueous solution and by metallography. The corrosion was accelerated by addition of Co or Mn while it was retarded by addition of Cr, Fe or Cu. In particular, the addition of Cu greatly improved the corrosion resistance. The corrosion proceeded by a mechanism in which the Ni-matrix phase worked as anode while the NiMo₂B₂ phase worked as cathode. The addition of Cu shifted the corrosion potential of the Ni-matrix phase to the noble side by about 15 mV, and consequently the difference in the corrosion potential between the Ni-matrix phase and the NiMo₂B₂ phase decreased. As a result the preferential corrosion of the Ni-matrix phase was extremely retarded.

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1. Introduction

The ternary intermetallic compound, NiMo₂B₂ has a high incongruent melting point of about 1900 K, high hardness and excellent corrosion resistance. Consequently, NiMo₂B₂-dispersed Ni-based alloys have been used as new corrosion-resistant and wear-resistant alloys.¹⁻⁴⁾

In general, hard particle-dispersed alloys corrode by a local cell mechanism in which the matrices work as the anode while the hard particles work as the cathode. In order to improve the corrosion resistance of these alloys, the anodic corrosion of the matrices should be retarded as much as possible. In the present study, we attempted to search alloying elements to retard the preferential corrosion of the Ni-matrix of a NiMo₂B₂-dispersed Ni-based alloy, and measured corrosion potentials of NiMo₂B₂ and the Ni-matrices containing the alloying elements to clarify the driving force of the local cell.

Ni-based alloys containing large amounts of molybdenum generally show excellent corrosion resistance in HCl or H₂SO₄ aqueous solutions whereas they corrode easily in HNO₃ aqueous solutions. The alloys we examined contained large amounts of Mo.⁵⁾ Thus corrosion tests were carried out in 6 mass% HNO₃ aqueous solution.

2. Experimental

2.1 Preparation of the specimens

2.1.1 Preparation of the specimens for the immersion test

A Ni-26.2 mass% Mo-1.5 mass% B alloy and a Ni-26.2 mass% Mo-1.5 mass% B-2.0 mass% M (M = Cr, Mn, Fe, Co or Cu) alloy for the immersion tests were prepared by sintering. The composition of Ni-26.2 mass%-1.5 mass% B

is adjusted in the Ni-NiMo₂B₂ two-phase region in the Ni-Mo-B ternary phase diagram.⁵⁾ Thus, the Ni-26.2 mass%-1.5 mass% B alloy is composed of the Ni-matrix phase and the NiMo₂B₂ phase. As described later, when M is added singly to this alloy by 2 mass%, the M dissolves into the Ni-matrix, and as a result the Ni-26.2 mass%-1.5 mass% B-2.0 mass% M alloy is still two-phase alloy which is composed of the Ni-matrix and NiMo₂B₂. Hereinafter this Ni-26.2 mass%-1.5 mass% B alloy is called the non-addition Ni-NiMo₂B₂ two phase alloy and the Ni-26.2 mass%-1.5 mass% B-2.0 mass% M alloy is called the M-added Ni-NiMo₂B₂ two phase alloy.

Commercial Ni-10 mass% B alloy powder (Fukuda Metal Foil & Powder Co. Ltd.) and pure powders of Mo (purity: 99.9%), Cr (purity: 98%), Mn (purity: 99%), Fe (purity: 98%), Co (purity: 99%) and Cu (purity: 99.85%) were used as starting materials. The powders were weighed in fixed ratio and mixed for 10.8 ks with a ball mill and then compacted at 400 MPa to form $\phi 10 \times 10$ mm³ green compacts. The green compacts were sealed in a silica tube in a vacuum of 10⁻² Pa and then sintered at 1443 K for 14.4 ks. The sintered alloys were examined with X-ray diffraction and the relative densities of the alloys were determined from the measurement of the area of pores on the surface of each sintered specimen.

2.1.2 Preparation of the specimens for the corrosion potential measurement

As described later, the addition of Cu to the non-addition Ni-NiMo₂B₂ alloy retards the preferential corrosion of the Ni-matrix. In order to clarify the reason why Cu retards the preferential corrosion of the Ni-matrix, the corrosion potentials of the Ni-matrices of the non-addition Ni-NiMo₂B₂ two phase alloy and the Cu-added Ni-NiMo₂B₂ two phase alloy were measured. The corrosion potential of NiMo₂B₂ was also measured and compared with them.

Judging from the phase diagram of the Ni-Mo-B ternary system,⁵⁾ the composition of the Ni-matrix of the non-addition Ni-NiMo₂B₂ two phase alloy is Ni-15.8 mass% Mo. Also, because Cu does not dissolve into NiMo₂B₂ as described later, the composition of the Ni-matrix of the Cu-

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added Ni–NiMo₂B₂ two phase alloy is Ni–15.8 mass%Mo–2.5 mass%Cu. A specimen with this composition was prepared by mixing pure Ni, Mo and Cu powders described in Section 2.1(1) for 10.8 ks with a ball mill and then compacting the mixtures at 400 MPa into a $\phi 10 \times 10 \text{ mm}^3$ green compact. The green compact was melted in an Ar arc furnace and then subjected to the homogenizing treatment at 1473 K for 24 h.

A single phase specimen of NiMo₂B₂ was prepared using Ni–10 mass%B, pure Ni and MoB (Japan New Metals Co. Ltd.) powders. Boron was weighed 1 mass% more than the amount calculated from the stoichiometric composition of NiMo₂B₂ because boron was oxidized during the sintering of the mixture of the powders. The value of 1 mass% was determined by a trial and error experiment. The powders were mixed for 10.8 ks with a ball mill and then compacted at 400 MPa into a $\phi 10 \times 10 \text{ mm}^3$ green compact. The green compact was sealed in a silica tube in a vacuum of 10^{-2} Pa and then sintered at 1473 K for 20 ks. After sintering, homogenizing treatment was carried out at 1273 K for 10 h. The formation of the single phase specimen was confirmed by X-ray diffraction.

2.2 Immersion test

The specimens were polished with #600 emery paper and degreased in acetone using an ultrasonic cleaning apparatus. Immersion tests were performed in an aerated 6 mass%HNO₃ aqueous solution at 308 K. After the elapse of fixed times, the specimens were taken out of the solution, weighed to determine the mass losses by corrosion, cut perpendicular to the surfaces, and then submitted to EPMA.

2.3 Measurements of polarization curves

In order to interpret the result of the immersion test, polarization curves were measured. One surface of each sintered specimen was polished with #600 emery paper and degreased in acetone with an ultrasonic cleaning apparatus, and then mounted in epoxy resin as shown in Fig. 1. The specimen mounted in epoxy resin was settled in a rubber holder and a copper conductor wire was attached to it along with a copper chip and a spring as shown in Fig. 2. Leaving an area of $5 \times 5 \text{ mm}^2$ of the polished surface, the residual specimen surface, the copper wire, chip, spring, resin and rubber were insulated with a fluorine resin. Polarization curves were measured in 6 mass%HNO₃ solution at 308 K. A calomel half-cell electrode (saturated with KCl, SCE) was used for the reference electrode. After the solution was degassed by Ar for 1.8 ks, the specimen was held for about 3.6 ks before starting measurements so that the corrosion potential was stabilized. Polarization tests were then conducted under a sweep rate of $0.5 \text{ mV} \cdot \text{s}^{-1}$ in a deaerated atmosphere.

2.4 Measurements of corrosion potential

The intermetallic compound, NiMo₂B₂, and the single phases of the Ni-matrices of the non-addition Ni–NiMo₂B₂ two phase alloy and the Cu-added Ni–NiMo₂B₂ two phase alloy were polished with #600 emery paper and degreased in acetone with ultrasonic cleaning apparatus. The working electrodes were constructed from these specimens in the same

Fig. 1 Schematic sketch of sample mounted in the epoxy resin.

Fig. 2 Schematic sketch of working electrode assembly.

Fig. 3 X-ray diffraction pattern of Ni–26.2%Mo–1.5%B alloy sintered at 1473 K for 14.4 ks.

way as for the working electrode for the measurements of the polarization curves. After degassing by Ar for 1.8 ks, the corrosion potentials were measured in a deaerated atmosphere.

3. Results and Discussion

Figure 3 shows the result of X-ray diffraction of the non-addition Ni–NiMo₂B₂ two phase alloy. Rieger's data⁶⁾ were adopted to identify NiMo₂B₂. The alloy was found to be composed of a Ni-matrix and NiMo₂B₂. The alloys containing 2 mass% alloying elements, M, also gave the same X-ray

diffraction pattern as Fig. 3.

Figure 4 shows EPMA photographs of a cross section of the non-addition $\text{Ni-NiMo}_2\text{B}_2$ two phase alloy. (a) is a SEM photograph. (b), (c) and (d) are X-ray images of B-K_α , Mo-L_α and Ni-K_α , respectively. From (b) and (c), it was found that the particles of NiMo_2B_2 were homogeneously dispersed in the Ni-matrix. The relative density of the alloy was 96%. In the case of the alloys containing 2 mass% alloying elements, M, each M was found to be perfectly soluble into the Ni-matrix from the EPMA observation. Therefore, it can be said

Fig. 4 EPMA photographs of $\text{Ni-26.2\%Mo-1.5\%B}$ alloy sintered at 1473 K for 14.4 ks. (a) SEM image, (b) B-K_α image, (c) Mo-L_α image, (d) Ni-K_α image.

that the alloys containing alloying elements, M, are also composed of the Ni-matrix phase and the NiMo_2B_2 phase. Their relative densities were also 96%.

Figure 5 shows the results of the immersion tests of the sintered alloys. The corrosion resistance of the alloy was decreased by the addition of Co or Mn. On the other hand, the corrosion resistance was improved by the addition of Cr, Fe or Cu. In particular, Cu was found to be very useful alloying element to improve the corrosion resistance. Accordingly further detailed investigation for the Cu effect on the corrosion resistance was carried out.

Figure 6 shows the effect of the Cu content on the corrosion resistance of the $\text{Ni-NiMo}_2\text{B}_2$ two phase alloy. The corrosion resistance was increased as the Cu content was increased, and almost saturated at the addition of 2 mass%. Therefore, the 2 mass% addition of Cu was adopted as the optimum content of Cu.

Figure 7 shows EPMA photographs of a cross section of

Fig. 5 Effects of alloying elements on corrosion resistance of $\text{Ni-26.2\%Mo-1.5\%B}$ alloy in 6% HNO_3 aqueous solution at 308 K.

Fig. 6 Effects of the content of Cu on corrosion resistance of $\text{Ni-26.2\%Mo-1.5\%B}$ alloy in 6% HNO_3 aqueous solution at 308 K.

Fig. 7 EPMA photographs of Ni-26.2%Mo-1.5%B alloy after corrosion test. (a) SEM image, (b) B- K_{α} image, (c) Mo- L_{α} image, (d) Ni- K_{α} image.

the non-addition Ni-NiMo₂B₂ two phase alloy after the immersion test (Fig. 5). It was presumed that the corrosion proceeded by a local cell mechanism in which the Ni-matrix phase worked as the anode while the NiMo₂B₂ phase worked as the cathode. On the other hand, Figure 8 shows EPMA photographs of a cross section of the Cu-added Ni-NiMo₂B₂ two phase alloy after the immersion test (Fig. 5). From these photographs, Cu was found to dissolve in the Ni-matrix and effectively retard its preferential corrosion.

Fig. 8 EPMA photographs of Ni-26.2%Mo-1.5%B-2%Cu alloy after corrosion test. (a) SEM image, (b) Mo- L_{α} image, (c) B- K_{α} image, (c) Mo- L_{α} image, (d) Cu- K_{α} image.

To clarify the reason for the improvement of the corrosion resistance by the Cu addition, polarization curves of the non-addition and the Cu-added Ni-NiMo₂B₂ two phase alloys were measured. Figure 9 shows their results. The anodic polarization curve of the non-addition Ni-NiMo₂B₂ two phase alloy showed that its corrosion proceeded by the active dissolution of the Ni-matrix, indicating that its corrosion potential was 15 mV (vs.SCE). In the case of the Cu-added Ni-NiMo₂B₂ two phase alloy, active dissolution was

Fig. 9 Polarization curves of Ni-26.2%Mo-1.5%B and Ni-26.2%Mo-1.5%B-2%Cu alloys in 6% HNO_3 aqueous solution at 308 K.

also found to be caused. However, its corrosion potential was 25 mV (vs.SCE) and 10 mV nobler than that of the non-addition alloy. Furthermore, the corrosion current density of the Cu-added Ni- NiMo_2B_2 two phase alloy was smaller than that of the non-addition alloy.

In order to clarify the reason why the Cu-added alloy showed the nobler corrosion potential and the smaller corrosion current density than the non-addition alloy, the corrosion potentials of the single phases of the non-addition and Cu-added Ni-matrices and NiMo_2B_2 were measured. Figure 10 shows the X-ray diffraction pattern of the NiMo_2B_2 single phase which was prepared for the measurement of corrosion potential. As can be seen from the pattern, the specimen was found to be composed of NiMo_2B_2 alone. Figure 11 shows the results of the measurements of the corrosion potentials of the single phases of the non-addition and the Cu-added Ni-matrices and also NiMo_2B_2 . The corrosion potential of the NiMo_2B_2 single phase was 50 mV (vs.SCE) at the moment when the specimen was dipped into the solution, and shifted to 60 mV (vs.SCE) after 10 minute and afterwards became constant. The corrosion potential of the Ni-matrix of the non-addition alloy was -12 mV (vs.SCE) at the moment when the specimen was dipped into the solution, and shifted to -5 mV (vs.SCE) after 1 hour and then became constant. That is, NiMo_2B_2 was nobler than the non-addition Ni-matrix. Therefore, it can be considered that the preferential corrosion of the Ni-matrix of the non-addition alloy proceeds by a local cell mechanism. On the other hand, the corrosion potential of the Ni-matrix of the Cu-added alloy was 5 mV (vs.SCE) at the moment when the specimen was dipped into the solution, and shifted to 10 mV (vs.SCE) after 1 hour and became constant. That is, the addition of Cu made the Ni-matrix nobler and decreased the difference in the corrosion potential between the Ni-matrix and NiMo_2B_2 . As a result, it is presumed that the corrosion rate of the Cu-added alloy decreased by the decrease of the corrosion potential difference.

The decrease of the corrosion current density with the in-

Fig. 10 X-ray diffraction pattern of NiMo_2B_2 prepared by sintering at 1473 K for 20 ks followed by the heat treatment at 1273 K for 369 ks.

Fig. 11 Corrosion potential of NiMo_2B_2 , Ni-15.8%Mo and Ni-15.8%Mo-2.5%Cu alloys in 6% HNO_3 aqueous solution at 308 K.

crease of the corrosion potential can be explained using the schematic diagram shown in Fig. 12. In the case of the non-addition Ni- NiMo_2B_2 two phase alloy, the corrosion potential, E_{COR} , and the corrosion current density, i_{COR} , are the coordinates of the intersection of the cathodic polarization curve of NiMo_2B_2 starting from E_C and the anodic polarization curve of the Ni-matrix starting from E_A . On the other hand, when Cu is added to the Ni-matrix, its corrosion potential increases up to E'_A . Therefore, the corrosion potential, E'_{COR} , and the corrosion current density, i'_{COR} , of the Cu-added Ni- NiMo_2B_2 two phase alloy are the coordinates of the intersection of the cathodic polarization curve of NiMo_2B_2 starting from E_C and the anodic polarization curve of the Cu-added Ni-matrix starting from E'_A . Because E'_A is nobler than E_A , E'_{COR} is nobler than E_{COR} . As a result, i'_{COR} is smaller than i_{COR} . This is the reason for the improvement of the corrosion resistance by the addition of Cu.

4. Conclusion

Alloying elements which retarded the preferential corrosion of the Ni-matrix of the NiMo_2B_2 -Ni two phase alloy in the 6 mass% HNO_3 aqueous solution were searched and the

Fig. 12 Schematic diagram of corrosion resistance increased by addition of Cu. E_A : corrosion potential of non-addition Ni-matrix, E_C : corrosion potential of NiMo_2B_2 , E'_A : corrosion potential of Cu-added Ni-matrix, E_{cor} and i_{cor} : corrosion potential and corrosion current density of non-addition Ni- NiMo_2B_2 two phase alloy, respectively, E'_{cor} and i'_{cor} : corrosion potential and corrosion current density of Cu-added Ni- NiMo_2B_2 two phase alloy, respectively.

following results were obtained.

- (1) The corrosion was accelerated by the addition of Co

or Mn while it was retarded by the addition of Cr, Fe or Cu. In particular, the addition of Cu greatly improved the corrosion resistance.

(2) The corrosion proceeded by a mechanism in which the Ni-matrix phase worked as the anode while the NiMo_2B_2 phase worked as the cathode. Cu retarded the preferential corrosion of the Ni-matrix.

(3) The addition of Cu made the corrosion potential of the Ni-matrix phase nobler and decreased the difference in the corrosion potential between the Ni-matrix phase and the NiMo_2B_2 phase. This is reason for the retardation of the preferential corrosion of the Ni-matrix phase by the addition of Cu.

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