

# Corrosion Behavior of Copper-Mold Cast and Sheath-Rolled Ni-Cr-Nb-P-B Bulk Amorphous Alloys in HCl Solutions

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Since extremely corrosion-resistant amorphous Fe-Cr-P-C alloys in hydrochloric acid solution were found in 1974 [1], various amorphous alloys showing high corrosion resistance even in aggressive environments have been tailored. However, because of the requirement of rapid quenching for amorphization, most of such materials are in the shape of ribbons or thin films, which limits their practical applications as corrosion-resistant materials. Recently, practically important bulk amorphous alloys with excellent mechanical properties have been prepared even by a conventional casting technique, since amorphous alloys with extremely high glass forming ability have been found [2].

Corrosion-resistant bulk amorphous alloys have also been successfully prepared by some of the present authors using copper mold casting [3]; cylindrical amorphous Ni-Cr-P-B alloys containing Mo or Ta are spontaneously passive in 6 mol dm<sup>-3</sup> HCl solution at 303 K. Nb is also a corrosion-resistant element and its addition is expected to improve the glass forming ability of Ni-Cr-P-B alloys, since Nb is the same group as Ta in the periodic table. In the present study, the bulk amorphous Ni-Cr-Nb-P-B alloys are prepared by copper mold casting. Further, a larger size of the amorphous alloy plate of 2 mm thickness is prepared by He gas atomization and subsequent sheath rolling of the atomized powders. Their corrosion behavior has been examined in various concentrations of HCl solutions.

## Experimental

Cylindrical bulk Ni-Cr-Nb-16 at% P-4 at% B alloys of 1 and 2 mm in diameter with various Cr and Nb contents were prepared by copper mold casting. Their structure was identified by using micro-area X-ray diffraction analysis. Corresponding melt-spun amorphous alloy ribbons were also prepared for comparison. Preparation of a Ni-10Cr-5Nb-16p-4B alloy plate of 2 mm thickness was performed by sheath rolling of He gas-atomized powders at 708 K, at which the alloy was in the supercooled liquid state.

The corrosion behavior of the alloys prepared was examined in 1, 6 and 12 mol dm<sup>-3</sup> HCl solutions open to air at 303 K. Corrosion rates were estimated from the weight loss after immersion in the 6 and 12 mol dm<sup>-3</sup> HCl solutions for one week. After immersion, the surface of the specimens was observed by SEM. Potentiodynamic polarization curves were obtained with a potential sweep

rate of 0.5 mV s<sup>-1</sup>.

## Results and Discussion

From X-ray diffraction patterns, as-cast Ni-5Cr-5Nb-16P-4B, Ni-10Cr-5Nb-16P-4B and Ni-5Cr-10Nb-16P-4B alloys of 1 mm diameter are amorphous. The Ni-5Cr-10Nb-16P-4B alloy of 2 mm diameter is also amorphous. The other as-cast alloys contain crystalline phases. The major phase is an fcc Ni so that the alloys containing this phase dissolved activity in aggressive HCl solutions. The as-cast amorphous alloys are spontaneously passive even in 12 mol dm<sup>-3</sup> HCl solution, showing high corrosion resistance. Among the three amorphous alloys, Ni-10Cr-5Nb-6P-4B alloy reveals lowest passive current density in 6 mol dm<sup>-3</sup> HCl solution. This is consistent with the fact that the corrosion rates of the sputter-deposited Cr-Nb binary alloys decrease with an increase in the Cr content [4]. The potentiodynamic polarization curves of the as-cast Ni-5Cr-5Nb-16P-4B and Ni-5Cr-10Nb-16P-4B alloys of 1 mm diameter in all HCl solutions used in the present study are similar to those of the corresponding melt-spun amorphous alloy ribbons, indicating that significant difference of cooling rates for amorphous alloy formation does not affect their corrosion resistance. In contrast, the passive current density of the as-cast Ni-10Cr-5Nb-16P-4B alloy of 1 mm diameter is higher than the corresponding amorphous alloy ribbon in 12 mol dm<sup>-3</sup> HCl solution, although in 6 mol dm<sup>-3</sup> HCl solution the polarization curves of both specimens are similar. High resolution transmission electron microscopy observation reveals that the as-cast specimen contains nanocrystals, probably an fcc Ni phase, of about 1 nm size, in the amorphous matrix. Although the population density of the nanocrystalline precipitates is relatively low, the presence of such actively dissolving crystalline phase may result in the slight increase in the passive current density.

The sheath-rolled Ni-10Cr-5Nb-16P-4B alloy is also amorphous and shows spontaneous passivation in HCl solutions. The corrosion rates of the sheath-rolled and melt-spun Ni-10Cr-5Nb-16P-4B alloy specimens in 6 mol dm<sup>-3</sup> HCl solution at 303 K are similar, being about 5-7 x 10<sup>-3</sup> mm y<sup>-1</sup>. However, in 12 mol dm<sup>-3</sup> HCl solution, the sheath-rolled specimen reveals about 4 times higher corrosion rate than the melt-spun specimen. Similarly, the passive current density in the potentiodynamic polarization curve for the sheath-rolled specimen is higher than that for the melt-spun ribbon in 12 mol dm<sup>-3</sup> HCl solution. From surface observation by SEM, preferential corrosion attack appears to occur at boundaries between the original gas-atomized powders. Such preferential attack may result from the oxide growth during heating of the powders for rolling. The thermally formed oxide may dissolve more easily than the passive films, since the thermally formed oxide probably contains phosphorus and boron species.

## References

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