Extremely Corrosion-Resistant Bulk Amorphous Ni-Cr-Ta-Mo-Nb-5P Alloys

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Introduction

The use of corrosion-resistant amorphous alloys is restricted by their limited thickness of ribbon or film. Thus, the establishment of the processing technology of bulk amorphous alloys with extremely corrosion resistance will open a new era for their wide applications. This can be realized by consolidation of amorphous alloy powders, prepared by gas atomization, in the temperature interval of supercooled liquid, ΔT_x, defined by the difference between glass-transition temperature, T_g, and crystallization temperature, T_x, $\Delta T_x = T_x - Tg$. However, the gas atomization for preparation of amorphous alloy powders and processing in the temperature interval of the supercooled liquid are laborious, complicated, time-consuming and expensive technologies and are not suitable for trial to prepare bulk amorphous alloys. As simpler and easier methods copper mold casting of alloy rods of 1-2 mm diameter can be applied for preparation of bulk amorphous alloys when the alloy compositions are carefully selected. If the bulk alloy rods are formed by copper mold casting, such alloys can form amorphous alloy powders and be processed in the temperature interval of the supercooled liquids into desirable shapes. Using the copper mold casting technology, we prepared various corrosion-resistant bulk amorphous alloys such as Ni-Cr-Ta-Mo-P-B [1], Ni-15Cr-10Mo-16P-4B [2], Ni-(10-15)Cr-5Ta-16P-4B [2], Ni-(40-x)Nb-xTa-(3-5)P [3] and Ni-Cr-Nb-16P-4B [4] alloys. These alloys are spontaneously passive in concentrated hydrochloric acids.

The composition of alloys amorphizable in the bulk form is seriously restricted particularly when corrosion-resistant elements are added. The most effective combination of corrosion-resistant elements by small additions in providing extremely high corrosion resistance is Cr, Ta and Mo [5]. In the present work an attempt at preparing Ni-Cr-Ta-Mo-Nb-P alloys corrosion-resistant in concentrated hydrochloric acids was performed by copper mold casting.

Experimental Procedures

Crystalline alloy ingots were prepared by argon arc melting. These ingots were used for copper mold casting and melt spinning. Copper mold casting was carried out for preparation of rod-shaped amorphous alloys of 1 mm diameter. Single roller melt-spinning was used for preparation of amorphous alloy ribbons of about 1 mm width and 20-30 μm thickness. Glass-transition temperature, T_g, and crystallization temperature, T_x, of ribbon-shaped specimens were measured by a differential scanning calorimeter with a heating rate of 0.33 Ks^{-1}. The structure of specimens was identified by X-ray diffraction with Cu $K\alpha$ radiation.

Prior to immersion tests and electrochemical measurements the surface of specimens was polished in cyclohexane with silicon carbide paper up to No. 1500, degreased in acetone and dried in air. Immersion tests and electrochemical measurements were carried out in 6 and 12 M HCl open to air at 303K. Corrosion rates were estimated from the weight loss after immersion for 168 h. Potentiodynamic polarization curves were measured with a potential sweep rate of 0.5 mVs^{-1}. The potential was swept from the open-circuit potential to anodic and cathodic directions using different specimens after immersion in hydrochloric acids for about 10 min. The morphology of the alloy rods before and after immersion was examined using an atomic force microscope in the contact mode for the specimens polished with diamond paste before immersion.

Results and Discussion

Melt-spun amorphous alloys were used for examination of thermal properties and corrosion rates. The alloys which exhibited wide temperature intervals of supercooled liquid of about 50 K were used for copper mold casting. Alloys were prepared by adding Cr and/or Mo substituting Ta and Nb of the Ni-25at%Ta-15at%Nb-5at%P alloy and by maintaining an almost constant ratio of Ta/Nb. Ni-25Ta-15Nb-5P, Ni-22Ta-5Mo-13Nb-5P and Ni-19Ta-10Mo-11Nb-5P alloy rods were identified as amorphous single phase alloys by X-ray diffraction. However, substitution Ta and Nb of Ni-25Ta-15Nb-5P alloy by 5 at% or more Cr resulted in the mixture of the major amorphous and minor crystalline phases. Among about 10 alloys substituted by both Cr and Mo only Ni-2.5Cr-22Ta-2.5Mo-13Nb-5P alloy rod was identified as the amorphous single phase alloy by X-ray diffraction.

All amorphous alloy rods show high corrosion resistance in concentrated hydrochloric acids. In particular, the alloy containing Cr and Mo in addition to Ta and Nb did not show detectable corrosion weight loss after immersion for 168 h in 6 and 12 M HCl at 303 K.

All these alloys are spontaneously passive in both 6 and 12 M HCl at 303K. Potentiodynamic polarization curves of the Ni-2.5Cr-22Ta-2.5Mo-13Nb-5P alloy rod measured in 6 M HCl at 303 K was almost the same as the melt-spun ribbon-shaped counterpart. However, the anodic current density of the passive region for the alloy rod measured in 12 M HCl at 303 K was slightly higher than that for the melt-spun counterpart which is completely amorphous. This fact suggests the presence of minor less corrosion-resistant nanocrystalline phases which are undetectable by X-ray diffraction. In this connection, AFM and SEM observations of all three alloys after immersion in 6 M HCl revealed the presence of very minor nanocrystalline phases which have higher corrosion resistance than the amorphous matrix.

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