Mechanical properties of ductile Fe–Ni–Zr and Fe–Ni–Zr (Nb or Ta) amorphous alloys containing fine crystalline particles

A. INOUE,* H. TOMIOKA,† T. MASUMOTO
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan

Melt-quenched Fe$_{60-30}$Ni$_{10-30}$Zr$_{10}$ and Fe$_{70}$Ni$_{20}$Zr$_{10-x}$ (Nb or Ta)$_x$ (x ≤ 2 at%) alloy ribbons with the duplex structure consisting of amorphous and bcc phases were found to exhibit hardness and tensile strengths higher than those of the totally amorphous alloys. The volume fraction of the bcc phase was intentionally allowed to alter in the range 0% to 60% by changing the composition and sample thickness. The bcc phase has an average particle size of 75 nm for the Fe–Ni–Zr alloys and 50 nm for the Fe–Ni–Zr–Nb alloys, and the lattice parameter is much larger than that of pure α-Fe because of the dissolution of large amounts of zirconium, niobium and/or tantalum. The hardness and tensile strength of the duplex alloys increase with amount of bcc phase and reach about 880 DPN and 2580 MPa, which are higher by about 20% to 30% than those of the amorphous single state, at an appropriate volume fraction of bcc phase. As the volume fraction of the bcc phase increases further, the duplex alloys become brittle and the tensile strength decreases significantly. The enhancement of strength was considered to be due to the suppression of shear slip caused by fine bcc particles dispersed uniformly in the amorphous matrix. It was thus demonstrated that an optimum control of melt-quenched structure results in the formation of ductile Fe-based amorphous alloys containing fine crystalline particles.

1. Introduction
It is well known that an amorphous alloy possesses high strength combined with rather good ductility. However, almost all the iron-based amorphous alloys become rapidly brittle on annealing at temperatures much lower than crystallization temperature [1] as well as upon crystallization and such a catastrophic loss of ductility prevents practical applications as an engineering material. The appearance of iron-based amorphous alloys in which the ductile nature remains almost unchanged even by introducing crystalline phases has been fervently desired from the engineering point of view. Recently, it has been found that melt-quenched Fe–Ni–Zr alloys are so ductile that no cracks are observed even after a 180° bend test in a duplex state containing fine crystalline particles in an amorphous matrix as well as in an amorphous single state. It is also noticeable that the duplex alloys exhibit tensile strengths and hardness higher than those of the amorphous single phase. The aim of this paper is to present the conditions in which the amorphous alloys containing numerous fine crystalline particles form and the mechanical properties of the duplex alloys.

2. Experimental methods
Master alloys of Fe–Zr, Fe–Ni–Zr, Fe–Co–Zr, Fe–Cr–Zr and Fe–Ni–Zr–X (X = Ti, V, Nb, Nb, Ta) were prepared by arc melting in an Ar atmosphere. The melts were poured onto a water-cooled copper wheel to form ribbons with a width of 0.5 mm and a thickness of 10-12 μm. The ribbon samples were annealed at various temperatures in the range of 200-700°C for 10 minutes.
Ta, Cr, Mo, W, Al or Si) systems were prealloyed using high-purity metals under argon atmosphere in an arc furnace. The ingots were repeatedly turned over and remelted to ensure homogeneity of composition. Each ingot was then used to produce rapidly quenched ribbons from the melt by chill block melt-spinning in air. Typically, the amount of alloys melted in one run was about 1 g and the rotation speed of the steel roller (20 cm diameter) was controlled in the range 2000 to 6500 rpm in order to change the resultant sample thickness. The ribbons were subjected to bend ductility testing and samples able to bend through 180° were designated as being ductile. The as-quenched phase was examined by conventional X-ray diffraction and transmission electron microscopy techniques. The transmission electron microscope samples were electrolytically thinned in a solution of 90 parts ethyl alcohol and 10 parts perchloric acid, immersed in ice water. The crystallization temperature (Tx) and the heat of crystallization (∆H) were measured using differential scanning calorimetry (Perkin Elmer DSC II) at a heat rate of 40 K min⁻¹. The heat of crystallization of Fe₆₀Ni₃₀Zr₁₀ amorphous alloys is roughly independent of composition, and hence the crystalline fraction (V_f) of the specimens was determined from the ratio of the amount of heat released on being heated from room temperature to 900 K to the amount of heat evolved from a totally amorphous specimen on crystallization, using the following equation.

\[
V_f = \frac{\Delta H_{T, Am} - \Delta H_{T, PAm}}{\Delta H_{T, Am}}
\]

Here, \(\Delta H_{T, Am}\) is the total enthalpy released upon crystallization of a totally amorphous sample and \(\Delta H_{T, PAm}\) is the total enthalpy released upon crystallization of a partially amorphous sample. Hardness and strength of the specimens were measured by a Vickers microhardness tester with a 100 g load and an Instron-type tensile testing machine at a strain rate of \(1.7 \times 10^{-4}\) sec⁻¹, respectively. Eight to ten symmetrical indentations and eight tensile test data were used to determine an average microhardness value or tensile strength. Tensile specimens were cut from as-quenched ribbon into strips having a gauge dimension of 10 mm long. Subsequent to tensile testing, the cross-sectional area at the fracture site of each specimen was measured using optical microscopy in order to minimize error in the estimation of the tensile strength. Fracture surfaces were examined in the scanning electron microscope (SEM) to determine the effect of crystalline particle dispersion on the fracture surface morphology and the mode of fracture under uniaxial tension.

3. Results
3.1. Melt-quenched structure
The change in the melt-quenched structure of Fe₇₀Ni₃₀Zr₁₀ alloy is shown in Fig. 1 as a function of rotation speed of the roller. With decreasing rotation speed, the structure changes from homogeneously amorphous phase to duplex phases consisting of fine crystalline particles embedded in an amorphous matrix. The corresponding diffraction patterns shown in Fig. 1d and f clearly indicate that the crystalline particles have a bcc structure with a lattice parameter of \(a = 0.2910\) nm which corresponds to ferrite phase containing rather large amounts of zirconium and/or nickel. Hence, its composition appears to be fairly close to the nominal composition of the alloy. The bcc particles precipitate very uniformly and have an elliptical or a globular shape with a diameter as small as about 75 nm. Furthermore, one can see in Fig. 1c and e that the interfaces between bcc and amorphous phases are not perfectly spherical but develop outgrowths or cusps. The particle size appears to increase with decreasing rotation speed, but the degree of change is very slight. It is therefore inferred that the mechanical properties of the duplex alloys depend strongly on the amount of precipitation of the bcc particles.

Surprisingly, the duplex alloys consisting of bcc and amorphous phases shown in Fig. 1c exhibit a highly ductile nature and are able to sustain a 180° bend. As an example, the deformation structure of a Fe₇₀Ni₃₀Zr₁₀ duplex alloy subjected to a 180° bend is shown in Fig. 2. While numerous deformation markings can be seen near the bent edge, no cracks are observed, in good agreement with the deformation structure of homogeneously amorphous alloys. The similar duplex structures consisting of amorphous and bcc phases were also observed in melt-quenched Fe₉₀Zrₓ, Fe₆₀₆₀Cr₁₀₋₂₀Zr₁₀ and Fe₆₀₆₀Co₁₀₋₃₀Zr₁₀ alloys. However, the duplex phases in these alloys are brittle and fracture occurs during the bend test, indicating that the addition of nickel