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ATOM PROBE TOMOGRAPHY STUDIES OF THE DECOMPOSITION OF BULK METALLIC GLASSES

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A systematic study has been conducted on the decomposition of a Pd₄₀Ni₄₀P₂₀ bulk metallic glass that was isothermally pre-annealed at 260° C for 14 h, and then aged at 340°C for various times. The aging temperature is approximately 40°C above the glass-transition temperature but 60°C below the crystallization temperature. Two endothermic peaks develop in the differential scanning calorimetry (DSC) curves of the aged samples. The first peak, at 330°C, is largest in the pre-annealed sample and disappears after 10 min. aging at 340°C. The second peak appears after 20 min. aging and disappears after 320 min. aging. The corresponding x-ray diffraction (XRD) data show no Bragg peaks that could indicate the formation of crystalline embryos. Near-atomic-resolution atom probe tomography (APT) was used to study changes in the atomic spatial distributions as a function of aging time. The chemical environment around each atomic species, and the tendencies for solute clustering and chemical short range ordering, were determined from statistical analysis of the APT data. Clustering and phase separation are identified by APT after only 20 min. annealing, which correlates with the appearance of the second peak in the DSC signal. Crystallization is apparent in the XPT data after 320 min. aging whereas crystallization is seen in the XRD data only after 640 min. aging.

APFIM/TEM/SAXS STUDIES OF EARLY STAGE CRYSTALLIZATION OF BULK-FORMING METALLIC GLASSES

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Recent studies have shown that a variety of crystallization reactions occur from bulk-forming metallic glasses. Although it is expected that nucleation barrier for crystallization is high in bulk-forming metallic glasses, nanocrystalline microstructures were reported in many bulk metallic glasses. In some cases, nano-sized quasicrystalline particles precipitates in early stage of crystallization as a transient stage from amorphous to crystal. Also, in several bulk-forming metallic glasses, phase separation in glassy state is reported prior to the primary crystallization of nanosized crystalline phase.

In order to obtain a better understanding of the crystallization mechanisms of bulk-forming metallic glasses, we have investigated early crystallization stages of $\text{Pd}_{74}\text{Au}_8\text{Si}_{18}$ and $\text{Ni}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ metallic glasses by complementary use of transmission electron microscopy (TEM), atom probe field ion microscopy (APFIM), and small angle scattering (SAXS). The motivation of this work was to obtain experimental evidence as to the possible phase decomposition prior to the crystallization reaction reported in literature^{1,2}.

In both cases, whenever SAXS was detected, we found evidence for primary crystals by TEM observation. The crystallization of $\text{Pd}_{74}\text{Au}_8\text{Si}_{18}$ metallic glass progresses in two stages near T_g , i.e., the primary crystallization of a nanocrystalline fcc phase, followed by the polymorphous crystallization of the remaining amorphous phase. The size of the primary crystals observed by TEM was in good agreement with that estimated by Guiner plot of the SAXS profiles. Prior to the primary crystallization of the fcc phase, no evidence for phase decomposition was found in the amorphous state by HREM/APFIM observations.

The crystallization reaction of the $\text{Ni}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ metallic glass also progresses in two stages near T_g . The first stage was the primary crystallization of nanosized fcc Ni_2Ti -type big cubic phase and Al_2Cu -type $\text{Zr}_2(\text{Cu},\text{Ni})$ phase whose compositions were both close to $\text{Zr}_{67}\text{Ni}_{20}\text{Cu}_{13}$. SAXS appears only after the primary crystallization, and no evidence for phase decomposition prior to the primary crystallization reaction was found by HREM and APFIM. After the second stage of crystallization, a nanocomposite microstructure composed of the big cube phase, $\text{Zr}_2(\text{Cu},\text{Ni})$, and an Al and Ti enriched phase was found. SAXS profiles were consistent with the microstructures observed by TEM.

In this work, we failed to obtain experimental evidence for the proposed phase decomposition in the glassy state prior to the crystallization reaction. By comparing the present results with our previous studies on nanocrystallization of amorphous alloys, we discuss the factors controlling the nanocrystallization of amorphous alloys.

1. H. S. Chen and D. Turnbull, *Acta Metall.* **17**, 1021 (1969).
2. J. F. Löffler, S. Bossuyt, S. C. Glade, W. L. Johnson, W. Wagner, and P. Thiyagarajan, *Appl. Phys. Lett.* **24**, 525 (2000).

STRUCTURAL RELAXATION BEHAVIOR IN Pd-Cu-Ni-P METALLIC GLASSES

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Higher resistance to crystallization in Pd-Cu-Ni-P metallic glasses enables us to investigate whether or not the full-relaxed state appears on annealing for the long-duration at temperatures just below glass transition. Due to the free volume model, the equilibrium free volume in supercooled and equilibrium liquids is proportional to the difference $T-T_K$, where T_K expresses Kautzman temperature. It is well known that the quenched-in free volume can be estimated from DSC exothermic reaction associated with glass transition. Therefore, this DSC behavior directly reflects the equilibrium quantity of free volume in the specimen relaxed fully at a given temperature just below glass transition. In the present study, the full-relaxed state obtained will be discussed from a viewpoint of free volume model. In addition, the kinetics of chemical short range ordering, induced by annealing at about 150 K below glass transition, will be examined by isothermal change in the room temperature resistivity with the progress of annealing. The change in glass structure with the advance in relaxation process will be checked by Mossbauer spectroscopy using the specimen enriched with ^{57}Fe by 1at%.

**COMPOSITION DESIGN AND PREPARATION OF Zr-BASED BULK GLASSY ALLOY
CONTAINING W AND HIGH CONTENT OF Cu**

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New Zr-based quaternary and pentad bulky alloys containing W and high content Cu are designed based on the multicomponent chemical short range order (MCSRO) theory. The MCSRO program which is composed of the Fitbin subroutine for the activity coefficient of constituents, multivariant linear adapting and multielement coexisting equilibrium subroutine for the calculation of all short-range orders is used to optimize the composition of new bulky metallic glass system. The bulk Zr-based metallic glasses with the predicted optimal composition are formed by the copper mold casting method. SEM, XRD DSC and DTA analysis are conducted to determine the microstructure, the supercooled liquid region $\Delta T_x (=T_x - T_g)$, liquidus temperature and the ratio of T_g/T_l . The effects of the addition of W and the increase of Cu content on the glass forming ability are evaluated by MCSRO undercooling and ΔT_x . Tensile and compressive experiments are also conducted to measure the corresponding elastic modulus, fracture strength and elongation etc. The fracture characterization and the mechanism of the bulk metallic glasses are discussed in detail.