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SEP 78 J B VANDER SANDE, N J GRANT DAHC04-75-C-0012

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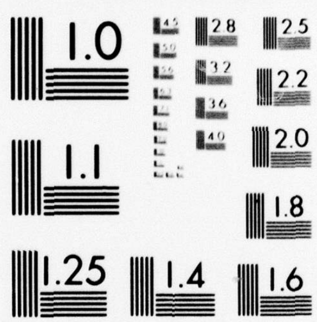

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This is a final report describing research on the devitrification of initially amorphous metallic alloys and the effect of such devitrification on mechanical properties for the Cu-Zr, Ni-Nb, and Pd-Si systems.

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Project 12689-MS, Contract Nos. DAHC04-75-C-0012 and DAAG29-75-C-0012,

THE BEHAVIOR AND PROPERTIES OF SPLAT COOLED AMORPHOUS AND CRYSTALLINE ALLOYS WITH EMPHASIS ON Cu-Zr ALLOYS

I. Statement of the Problem Studied

In the application of a metallic glass as a structural member, it is generally conceded that temperatures near to, and beyond, the crystallization temperature must be avoided. At these temperatures it is presumed that many of the beneficial mechanical properties associated with metallic glasses will be irreversibly lost with the advent of crystallization. However, it has not been shown that structural relaxation and/or partial crystallinity results in degraded mechanical properties. The philosophy developed for this study has been that heat treatments near the glass transition temperature may improve the mechanical properties of initially amorphous metallic alloys and since these temperatures must be avoided in practice, such a treatment does not otherwise limit the application of these materials.

The approach taken in this research is based on the assumption that the phase transformation characteristics of an initially amorphous metallic alloy must be comprehensively understood before an attempt can be made to determine the dependence of mechanical properties on the microstructure. The phase transformations of interest here are those transformations involved in going from the amorphous state to the equilibrium crystalline state. Subsequently this knowledge of the microstructural changes accompanying heat treatment can be correlated with the mechanical properties the alloy exhibits.

This program has concentrated on alloys from the Cu-Zr, Pd-Si, and Ni-Nb systems. The highlights of this program are presented below.

II. Summary of Results

A. Cu-Zr

1. $Cu_{46}Zr_{54}$

The Cu-Zr alloy Cu-54 at% Zr was splat quenched to the noncrystalline state using a piston and anvil device. The glass transition and crystallization temperatures, as well as the enthalpy releases observed during crystallization were measured using differential scanning calorimetry of as-splat specimens and specimens aged below T_g. Transmission electron microscopy and X-ray diffraction experiments were utilized to monitor phase and structural changes in the alloy as it transformed to the crystalline state.

The results of the investigation indicated that the noncrystalline to crystalline transformation in constant heating rate experiments above T_g was a two-step process. The initial step, which is associated with a large exothermic reaction, results in the appearance of crystallites in a matrix of noncrystalline material. The final step, associated with a smaller exothermic reaction, results in the total transformation of glass to the crystalline state and the formation of the equilibrium crystalline phases.

The effect of aging this splat-quenched noncrystalline alloy at temperatures below T_g was also investigated. It was determined from these experiments that crystallization does occur when the noncrystalline alloy is aged $\sim$ 15°C below T_g. It was determined that the thermal stability of the aged glass relative to the spontaneous crystallization observed during the constant heating rate experiments above T_g decreases as a function of aging time.

The room temperature mechanical properties of $Cu_{46}Zr_{54}$ have been investigated as a function of aging time at 375°C (15°C below T_g). The results indicate that the tensile fracture stress and hardness of this material can be changed by such thermal processing. Fracture stress and hardness are increased with short times at temperature by structural relaxation. Also, the presence of a very small volume fraction of crystalline phase causes the shear stiffness of the material to increase markedly providing an additional increase in fracture stress and hardness. Continued devitrification causes embrittlement and the decrease of fracture stress, as predicted by the model of two phase materials; however, hardness continues to increase, reflecting the increasing volume fraction of the harder crystalline phases. Embrittlement and decreasing fracture stress are enhanced by the stress concentration effect at the crystallites which causes void formation and growth.

2. $Cu_{56}Zr_{44}$

The metallic glass $Cu_{56}Zr_{44}$ was examined for its devitrification characteristics at temperatures both above and below T_g utilizing transmission electron microscopy, differential scanning calorimetry, X-ray diffraction, and X-ray energy-dispersive analysis to monitor structural and phase changes. In addition, tensile tests and Knoop microhardness experiments were conducted to determine the effect of devitrification resulting from isothermal aging 14°C below the glass transition temperature on these mechanical properties.

Devitrification above T_g, as determined in constant heating rate experiments, occurs as the sequential formation of the equilibrium crystalline phases, each of which is marked by an exothermic reaction. Devitrification below T_g, resulting from isothermal aging, is observed to occur in a manner resembling a continuous precipitation process. One equilibrium crystalline phase forms first obeying parabolic growth kinetics, followed by the formation of the other equilibrium crystalline phase.

The mechanical properties of $Cu_{56}Zr_{44}$ glass are altered dramatically by isothermal aging which causes structural relaxation of the glass and the nucleation of crystallites. The glass is found to embrittle and tensile fracture stress decreases as the volume fraction of crystalline phase increases. Hardness follows a trend of change with time at temperature similar to tensile fracture stress prior to the formation of ~ 0.02 volume fraction of crystalline phase. With further increases in the volume fraction of crystalline phase, hardness is observed to increase.

B. Ni-Nb

A Ni-40 at% Nb alloy was rapidly quenched into its amorphous state; the properties and crystallization behavior of this alloy were studied by means of calorimetry, X-ray diffraction, hardness, and mechanical testing. Calorimetry indicated four transformations occurred upon heating, one endothermic and three exothermic. The glass transition temperature was found to be about 901°K with peak crystallization transformations occurring at 964, 1005, and 1028°K. From X-ray diffraction, corresponding crystallization structures were fcc-1, fcc-2, and stable phases of orthorhombic Ni_3Nb and rhombohedral μ-NiNb.

The hardness value (Vickers diamond pyramid) of the amorphous state was about 865 and increased with crystallization to 1270. The corresponding stress for the amorphous state was 194 kg/mm^2.

Ni-15 at% Nb was also rapidly quenched and was found to be a face-centered-cubic solid solution structure. Its fracture behavior was purely elastic with a fracture stress of 110 kg/mm^2 for a crystal size of 165 Å. Upon heating samples to 800°C, there was a slight increase in crystal size to 170 Å and an unknown second phase became present along with the fcc solid solution.

C. Pd-Si

The fracture process in amorphous $Pd_{80}Si_{20}$ has been investigated and can be described as consisting of shearing on a plane at an angle 39° between the tension axis and, usually, the thickness vector, with the fracture path at 90° to the tension axis. It was observed that shearing sometimes occurs on a plane at 39° between the tension axis and the width vector, with the thickness fracture at 90° to the tension axis and with the corresponding fracture morphology consisting of a featureless zone(s) and a vein pattern zone. *In situ* observations within an SEM revealed that the initial shear leads to the featureless areas. The advancement of the crack into amorphous material is accompanied by the formation and growth of multiple shear bands in front of the main crack and with some divergence in angle. Separation of the fracture surfaces occurs through complex opening of multiple shear bands. A comparison of shear offsets on the front and the back (thickness direction) of the specimen confirmed the shear fracture mechanism. There was no evidence of necking for the conditions of testing. A wavy form of crack propagation is revealed on a microscale and is controlled by the interaction between the direction of crack propagation and the directions of shear band formation. Matching sharp cusps, in contrast to veins, were observed on the fracture surfaces when viewed at 90° to the fracture surface, in agreement with the meniscus theory of Argon and Salama. Ridging might be a better description of the pattern rather than veining.

III. List of Publications Stemming from this Program

A. J. Megusar, J. B. Vander Sande, and N. J. Grant, "Crystallinity and Mechanical Properties of Metallic Glasses," *Rapidly Quenched Metals*, edited by N. J. Grant and B. C. Giessen, M.I.T. Press (1976), p. 401.

B. J. Megusar, C. Clay, and N. J. Grant, "Fracture Behavior of Amorphous $Pd_{80}Si_{20}$," submitted for publication.

C. C. Clay and N. J. Grant, "The Properties of Amorphous $Ni_{60}Nb_{40}$," submitted for publication.

D. C. Clay and N. J. Grant, "Crystallization Characterization of Amorphous $Ni_{60}Nb_{40}$," submitted for publication.

E. R. L. Freed and J. B. Vander Sande, "A Study of the Crystallization of Two Noncrystalline Cu-Zr Alloys," J. Non-Cryst. Sol. 27, 9 (1978).

F. R. L. Freed and J. B. Vander Sande, "The Metallic Glass $Cu_{56}Zr_{44}$: Devitrification and the Effects of Devitrification on Mechanical Properties," submitted to Acta Met.

G. R. L. Freed and J. B. Vander Sande, "The Effects of Devitrification on the Mechanical Properties of $Cu_{46}Zr_{54}$ Metallic Glass," submitted to Met. Trans.

H. A. Calka, M. Madhava, D. E. Polk, B. C. Giessen, H. Matyja, and J. Vander Sande, "A Transition-Metal-Free Amorphous Alloy: $Mg_{.70}Zr_{.30}$," Scripta Met. 11, 65 (1977).

I. B. C. Giessen, M. Madhava, D. E. Polk, and J. Vander Sande, "Refractory Amorphous Inter-Transition Metal Alloys," Materials Science and Engineering 23, 145 (1976).

IV. Participating Scientific Personnel and Degrees Granted

A. Robert L. Freed, Ph.D. Thesis entitled "Devitrification and Mechanical Properties of Cu-Zr Metallic Glasses," awarded by the Department of Materials Science and Engineering, June 1978.

B. Carolyne Clay, Metallurgical Engineer Thesis entitled "The Properties of Amorphous and Microcrystalline Ni-Nb Alloys," awarded by the Department of Materials Science and Engineering, February 1978.

C. Professor N. J. Grant, Department of Materials Science and Engineering.

D. Professor J. B. Vander Sande, Department of Materials Science and Engineering.

E. Professor K. H. Johnson, Department of Materials Science and Engineering (1975-6 only).

F. Dr. J. Megusar, Center for Materials Science and Engineering (partial support 1975-6 only).