TA Instruments

Thermal Analysis & Rheology

Thermal Analysis Application Brief

Detection Of The Glass Transition in Metal Glasses By Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA)

Number TA-137

SUMMARY

Metal glasses, or amorphous metals, are a new class of electronic and engineering materials. Although their existence has been known for some time, it is only in the last few years that extensive research in universities and industry (1,2) has been directed towards finding commercial applications, such as components in economic energy conversion cells which generate electrical energy from sunlight or waste heat. Thermal analysis techniques, particularly DSC and DMA, provide a convenient way to characterize these materials.

INTRODUCTION

Metal glasses are known to have a disordered, non-crystalline structure in the solid phase, similar to that of a glass. They are currently produced by spraying a molten alloy onto a cooled, rapidly rotating copper drum so that the metal is quenched extremely rapidly (at about one million degrees per second). This causes the random atomic structure of the liquid to be retained in the solid at ordinary temperatures. However, unlike ordinary glasses, metal glasses are not brittle and may be used in applications where impact resistance and mechanical strength are important. Metal glasses can be produced in the form of ribbons and wires much more economically than ordinary metals since processes such as casting, rolling, and drawing are not necessary. Metal glass ribbons and wire can currently be made at a rate of approximately 1.5 kilometers per minute. (3)

The non-crystalline structure of these materials means that they do not have the grain boundaries found in normal crystalline metals. These grain boundaries are responsible for weakening ordinary metals and making them susceptible to chemical attack and corrosion. The properties of metal glasses, therefore, are different than those of the alloys from which they are made, and frequently their electrical conductivity, magnetic susceptibility, and resistance to corrosion are superior.

Like common glasses, metal glasses have glass transitions (Tg) at elevated temperatures, but unlike common glasses many metal glasses devitrify (crystallize) almost immediately after the glass transition is passed. Since the unique properties of metal glasses are observed only while the material remains amorphous, the glass transition defines the maximum use temperature for such materials. The working temperature is usually kept well below the Tg.

Differential Scanning Calorimetry (DSC) which measures heat flow in materials as a function of time and temperature can be used to evaluate the glass transition, the devitrification temperature and the heat of devitrification for metal glasses. Dynamic Mechanical Analysis (DMA) which measures the modulus (stiffness) and energy dissipation properties of a material is also valuable in determining these transition temperatures, as well as the metal glass' mechanical integrity at different temperatures.

EXPERIMENTAL

The metal glasses evaluated here were thin ribbons. Samples of appropriate size (approximately 0.06 (T) x 3.0 (W) x 7 (L) millimeters) and weight (nominally 20 mg) were cut for DMA and DSC respectively. The DSC runs were obtained in crimped aluminum pans at 20°C/minute in nitrogen. The DMA runs were obtained with the ribbon clamped horizontally and oscillating at its natural resonance frequency.

RESULTS

Many metal glasses have a general formula which is approximately $M_{80}X_{20}$ where M may be one element or combination of elements from the group iron, cobalt, nickel, chromium, palladium and copper. X may be one or more from the group of phosphorous, boron, carbon, aluminum and silicon. Metal glasses are formed by rapid cooling from the melt to give amorphous metals.

Common formulations are Fe-Ni-Co-B and Pd-Cu-Si, but many other elements may be included in the alloy formulation such as titanium, molybdenum and zirconium. The amorphous materials currently being investigated for solar energy applications are based largely on silicon with up to 50% of transition elements. It is the ability to "Chemically modify" the composition of the metal glasses to optimize certain specific properties that makes this class of materials subject to so much research work. Other potential applications include their use as reinforcing elements in polymers and elastomers, corrosion resistant cables, magnetic shields, tape recorder heads and transformer cores. These last three are due to the unusually high magnetic susceptability of these materials.

DMA and DSC analyses of a metal glass formed from an alloy of palladium, copper and silicon are seen in Figures 1 and 2 respectively.

The devitrification or crystallization exotherm in the DSC scan at about 420°C is characteristically sharp and easily identifiable as the major feature of the thermogram. For this particular sample a second, smaller exotherm was observed at about 450°C and is thought to be due to a second phase crystallizing at a higher temperature. DSC can therefore give information on the rather complex phase diagrams of such metal glasses. The baseline change at 370°C would normally be attributed to the glass transition. However, the results of a DMA run on the same metal glass, shown in Figure 1, would indicate that in this case that assumption is incorrect. The most prominant feature of the scan is the rapid drop in frequency between 390° and 410°C which is associated with the rapid decrease in sample strength (modulus) at the glass transition. This is also shown by a broad damping peak and means that the baseline step in the DSC scan at 370°C is not the glass transition of the metal glass.

The true position of the glass transition is the much smaller step indicated on the figure at about 400°C, just before the onset of devitrification. The DMA scan shows devitrification by a rise in frequency as the sample becomes more brittle and its modulus increases. A further important point is that this particular sample loses very little of its mechanical strength up to a temperature of about 350°C.

Figure 3 shows the DSC thermogram of a metal glass which has the appropriate chemical formula of $Fe_{40}Ni_{40}P_{14}B_6$ and Figure 4 shows the DMA results for the same material. In this case Tg deduced from DSC is confirmed by DMA, both techniques showing a transition at 380°C and devitrification at 400°C. The DMA results, however, show that this material steadily looses its mechanical strength above a temperature of about 250°C and therefore has a lower working temperature range than the first sample described.

The DSC scan can also be used to calculate the heat of devitrification (by integrating the area under the curve) which can be characteristic of the composition of the glass and which can give information on the degree of crystallinity of the material.

REFERENCES

1. N.J. Grant and B.C. Giessen (ed), *Rapidly Quenched Metals*, MIT Press, 1970.
2. Proceedings of the Second International Conference on Rapidly Quenched Metals, *Material Science and Engineering*, 23, 83-322 (1976).
3. "METGLAS® MATERIALS", Materials Research Report, Allied Chemical Corporation, Morristown, NJ.

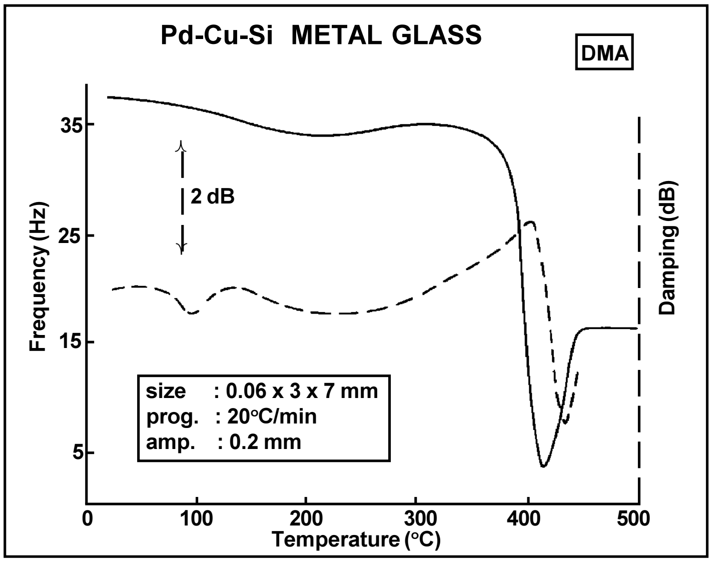

Figure 1

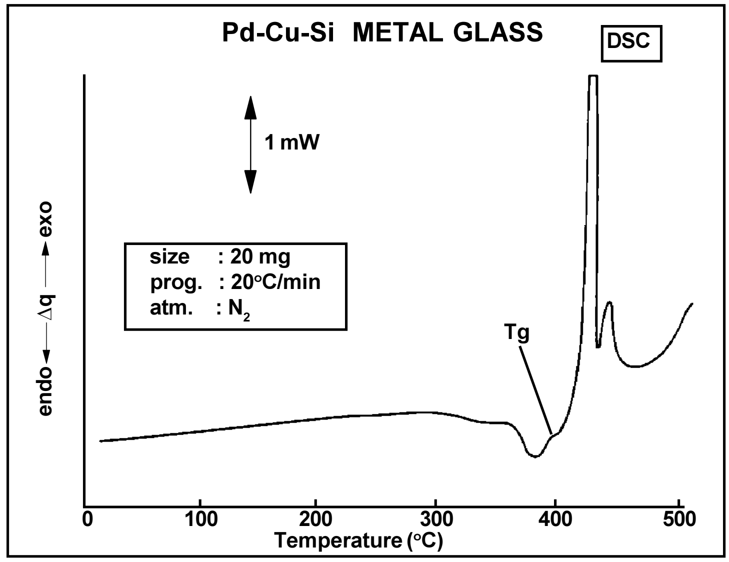

Figure 2

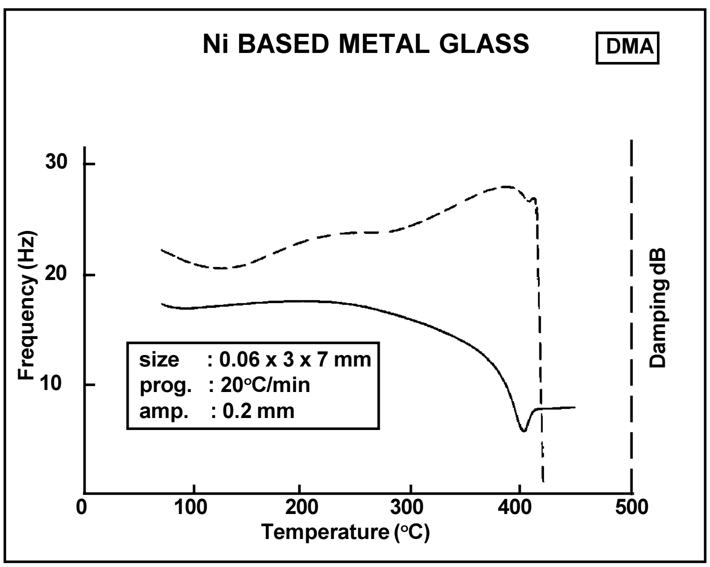

Figure 3

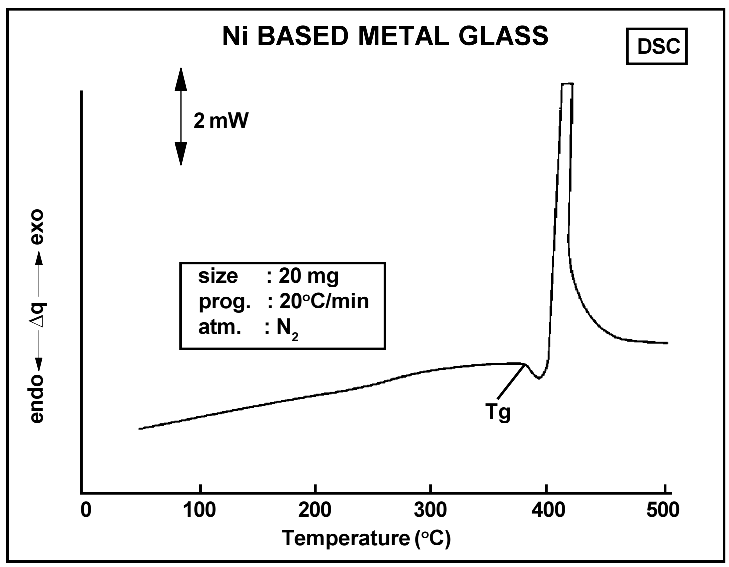

Figure 4

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