Alloy systems with critical cooling rates for glass formation below 100 K/s, i.e., with good glass forming ability (GFA), are a relatively recent development. Because of their resistance to crystallization, alloys such as Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5} (Vit1) and Pd_{49}Cu_{39}Ni_{10}P_{20} (PCNP)\(^{2}\) can be examined in the deeply undercooled liquid region on accessible laboratory time scales. As shown by Turnbull,\(^{3}\) GFA (represented by critical cooling rate) scales with the reduced glass transition temperature \(T_g^\ast\) defined as the glass transition temperature \(T_g\) divided by the liquidus temperature \(T_l\). This correlation has been confirmed in many experiments (see Ref. 4 for summary). Thermal stability in metallic glasses is usually quantified by measuring the temperature difference \(\Delta T\) between the glass transition and the first crystallization event upon heating at a constant rate. For some systems, it has been demonstrated that larger values of \(\Delta T\) tend to be associated with lower values of critical cooling rate \(R_c\).\(^{5,6}\) As a result, the thermal stability has served as an indicator of GFA in these alloys.

In recent years, the crystallization of Vit1 has been extensively examined.\(^{7-11}\) Several studies of this alloy have revealed a tendency to undergo chemical decomposition in the undercooled liquid,\(^{7-10}\) which has a direct influence on the subsequent nucleation and growth of crystalline phases. Since the decomposition occurs at a temperature close to \(T_g\), the isothermal crystallization behavior of Vit1 for low undercooling is quite different from its behavior when deeply undercooled.\(^{11}\) In addition, a study by Schroers \textit{et al.}\(^{12}\) involving constant heating and cooling experiments has shown that Vit1 crystallizes in a different manner upon heating from the amorphous solid than upon cooling from the melt. In this study, a cooling rate of approximately 1 K/s was required to bypass crystallization during cooling, whereas a heating rate of 200 K/s was necessary to avoid crystallization of a detectable volume fraction. Chemical decomposition has also been observed in a series of alloys which lie along the tie line between Vit1 and Zr_{46.25}Ti_{42.5}Cu_{25}Ni_{10}Be_{27.5} (Vit4).\(^{13}\) These alloys, Zr_{53.5}Ti_{12.3}Cu_{11.25}Ni_{10}Be_{23.75} (Vit1a), Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25} (Vit1b), and Zr_{53.5}Ti_{12.3}Cu_{11.25}Ni_{10}Be_{23.75} (Vit1c), show increased \(\Delta T\) values compared to Vit1.\(^{14}\)

The present work is focused on a seven alloy series which lies along the tie line described by (Zr_{37.5}Ti_{2.5}Cu_{10}Ni_{10}P_{10}Cu_{30}Ni_{10}P_{10})~(Zr_{37.5}Ti_{2.5}Cu_{10}Ni_{10}P_{10}Cu_{30}Ni_{10}P_{10})\(_{2}\) \(_{2}\) \(_{2}\), show in-...
profiles measured for Vit1b. For each measurement, the sample is cooled at a controlled rate from its initial temperature to some temperature below the glass transition. During cooling, crystallization in the sample manifests as an abrupt decrease in the magnitude of the cooling rate due to a release of the heat of fusion, as shown in the curves labeled (a), (b), and (c). The size of the crystallization peak decreases as the cooling rate magnitude increases in each subsequent measurement, and a crystallization event becomes undetectable, i.e., the sample has been rendered amorphous for the purposes of this study, after the cooling rate exceeds a certain value. Curve (d) represents such a measurement. Variations in cooling rate prior to crystallization can be attributed to limitations in the control algorithm used to modulate power during cooling. Thus, to determine a cooling rate value for each measurement, an average of the rate between 1200 and 900 K was calculated.

Also shown in Fig. 1 are data taken while free cooling the sample from its initial temperature. These data show another limitation of the experimental apparatus; as the temperature decreases, the maximum constant cooling rate that can be maintained decreases dramatically because the rate of heat loss from the crucible exterior limits the overall cooling rate of the sample/crucible combination. Therefore, as the constant cooling rate measurements approach the temperature where they intersect the free-cooling curve, they begin to follow the latter. In order to take measurements of cooling rates in excess of 10 K/s for Vit1c and Vit4, samples were cooled with a flow of ultrahigh purity argon. Only the downstream pressure could be varied to produce different cooling rates for samples of these alloys, and estimates of \( R_c \) have greater error as a result.

Table I lists the results of DTA scans of each alloy. For all seven alloy compositions, the glass transition temperature \( T_g \) remains essentially constant, with an average value of 625 K. The solidus temperature fluctuates to some degree, but \( T_l \) changes by a much greater amount between Vit1 and Vit4, reaching a maximum value of 1239 K in Vit1c. \( T_l \) for Vit1, 996 K, agrees well with previous results.\(^{17}\)

The relationship between the experimentally determined \( \Delta T \), \( T_g \), and \( R_c \) values is shown for all the alloys in Fig. 2. \( T_g \), the reduced glass transition temperature, was calculated using \( T_g / T_l \). As shown in the top portion of Fig. 2, \( \Delta T \) and \( T_g \) show a negative correlation as a function of composition. Both values remain fairly constant for Vit1(b) through Vit1 but change dramatically from Vit1a to Vit4, reaching a maximum in \( \Delta T \) and a minimum in \( T_g \) at Vit4c. Since \( T_g \) does not vary significantly between the seven alloys studied, this means that as \( \Delta T \) increases, \( T_l \) increases as well in this alloy series.

The \( R_c \) values depicted in the lower portion of Fig. 2 show a different behavior. At one extreme, they approach a limit of approximately 1.4 K/s in Vit1(b) and Vit1(a), but from Vit1a to Vit4 they increase steadily, reaching a maximum of 28 K/s in Vit4. The increase in \( R_c \) from Vit1a to Vit1c follows the trend toward smaller values of \( T_g \). The GFA of these alloys, however, does not seem to correlate well with the width of the supercooled liquid region, \( \Delta T \). As the critical cooling rate increases in this alloy series, the width of the supercooled liquid region also increases; those glass compositions with the largest \( \Delta T \) are actually the poorest glass formers.

As shown above, the results tend to confirm Turnbull’s criterion, which predicts that glass forming ability should decrease with decreasing reduced glass transition temperature.
ture. However, contrary to results published for other glass forming systems, the thermal stability and GFA do not show a positive correlation for the alloy series examined in this study. This suggests that different mechanisms influence crystallization upon heating and upon cooling. It has been demonstrated that decomposition in Vit1 influences the nucleation and growth of crystalline phases in the alloy. In addition, small-angle neutron scattering research on Vit1a–Vit4 has revealed the existence of spatially correlated inhomogeneities in some of these alloys after annealing. This research has resulted in the determination of an effective critical temperature \( T_c \) for Vit1, Vit1a, and Vit1b, and has established that \( T_c \) decreases from Vit1 to Vit1c, eventually reaching the glass transition temperature between Vit1c and Vit4.

It can be expected, given the trend in critical temperature for Vit1–Vit4, that decomposition plays an important role in determining thermal stability in this alloy series (this phenomenon has also been recently observed for Zr–Ti–Cu–Ni–Al alloys). For Vit1, the critical temperature is significantly higher (\( \sim 60 \) K) than the glass transition temperature, allowing a diffusion-controlled decomposition mechanism to effect significant changes in the alloy composition during heating through the temperature range from \( T_g \) to \( T_c \). In essence, the decomposition sets the time scale for crystallization in these alloys, increasing in amplitude until certain of the decomposed regions have a composition which favors nucleation and growth. For Vit1a, Vit1b, and Vit1c, the critical temperature shifts progressively lower and closer to \( T_g \). Thus, the effects of decomposition on subsequent crystallization behavior in each alloy are mitigated by the increasingly more sluggish kinetics of each alloy at temperatures below its respective critical temperature. This results in a dramatic increase in apparent thermal stability as the time scale for the diffusion-controlled decomposition process increases. It is unclear whether \( T_c \) for Vit4 lies above or below \( T_g \), but, given the decrease in \( \Delta T \) observed between Vit1c and Vit4, it seems likely that the crystallization of Vit4 upon heating proceeds through different mechanisms than the six alloys preceding it in the series. This may also account for the abrupt increase in \( T_g \) between Vit1c and Vit4 despite the fact that \( R_c \) also increases, but further study is necessary to elucidate the reasons for this departure from the Turnbull criterion. It is important to note that the critical temperature for all studied alloys is lower than the crystallization temperature measured upon cooling. Therefore, this decomposition process cannot influence the crystallization upon cooling.

In conclusion, results of continuous cooling and differential thermal analysis experiments have been presented. The critical cooling rate was directly measured with a high accuracy. A continuous increase in \( R_c \) and a concomitant decrease in GFA for each successive alloy in the series from Vit1-(b) to Vit4 was observed. The DTA results confirm, for the most part, the assessment of GFA for each alloy, because \( T_g \) also decreases as \( R_c \) increases between Vit1 and Vit1c. The thermal stability does not follow this trend, however. \( \Delta T \) values for the alloys tend to be largest for the poorest glass formers. Vit4 appears to be the exception to the observed trends in \( \Delta T \) and \( T_g \), and the author speculates that a change in crystallization mechanism is responsible for the observed results for this alloy. Between Vit1-(b) and Vit1c, changes in thermal stability upon heating can be attributed to a decomposition process in the undercooled liquid. The critical temperature decreases from Vit1 to Vit1c, approaching the glass transition temperature near Vit4. As a result, crystallization upon heating is influenced directly by the time scale for decomposition in each alloy, and this time scale increases from Vit1 to Vit1c, increasing the apparent thermal stability. This decomposition process does not influence the crystallization upon cooling, which is evidenced by the fact that the critical temperature is always lower than the crystallization temperature.

This work was supported by the National Aeronautics and Space Administration (Grant No. NAG8-1744) and the Department of Energy (Grant No. DEFG-03086ER45242).

---