Electromagnetic Containerless Processing Facility (TEMPUS)

AC Calorimetry and Thermophysical Properties of Bulk Glass-Forming Metallic Liquids

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Thermo-physical Properties of Undercooled Metallic Glass Forming Alloys

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Abstract

Thermo-physical properties of two bulk metallic glass forming alloys, $Ti_{34}Zr_{11}Cu_{47}Ni_8$ (VIT 101) and $Zr_{57}Nb_5Ni_{12.6}Al_{10}Cu_{15.4}$ (VIT 106), were investigated in the stable and undercooled melt. Our investigation focused on measurements of the specific heat in the stable and undercooled liquid using the method of AC modulation calorimetry. The experiments were conducted in close collaboration with the group of Prof. Samwer, University of Augsburg, for measurement of the specific volume, the groups of Prof. I. Egry , DLR Cologne and Prof. M.G. Frohberg, Technical University of Berlin, for measurements of surface tension and high temperature viscosity, and the group of Prof. H. J. Fecht, University of Ulm, Germany, for coordination of sample selection and specific heat measurements. The VIT 106 exhibited a maximum undercooling of 140 K in free radiative cooling. Specific heat measurements could be performed in stable melt down to an undercooling of 80 K. Analysis of the specific heat data indicate an anomaly near the equilibrium liquidus temperature. This anomaly is also observed in the temperature dependencies of the external relaxation time, the specific volume, and the surface tension; it is tentatively attributed to a phase separation in the liquid state. The VIT 101 specimen exhibited a small undercooling of about 50 K. Specific heat measurements were performed in the stable and undercooled melt. These various results will be combined with ground based work such as the measurement of T-T-T curves in the electrostatic levitator and low temperature viscosity and specific heat measurements for modeling the nucleation kinetics of these alloys.

2. Objectives

The primary scientific objective of the experiments conducted in the MSL-1 spacelab mission was the measurement of the specific heat capacity in the stable and undercooled liquid of the two bulk metallic glass forming alloys

$Ti_{34}Zr_{11}Cu_{47}Ni_8$	VIT 101
$Zr_{57}Nb_5Ni_{12.6}Al_{10}Cu_{15.4}$	VIT 106

From the free temperature decay of the specimen between bias temperature T_1 and T_2, the rate of radiative heat loss was measured from which the total hemispherical emmisivity of the specimen as function of temperature can be inferred if the specific heat is known. Furthermore, the method of AC modulation calorimetry employed for the measurement of the specific heat allows the determination of the effective thermal conductivity of the liquid alloy.

In cooperation with different scientific groups participating in the TEMPUS experiment on MSL-1, it was also planned to share these specimens for the measurement of the temperature dependencies of specific volume, surface tension, and viscosity.

3. Background

In recent years, bulk metallic glass forming alloys, which can be produced with dimensions relevant for their use as structural materials, have attracted considerable attention. This is in part due to their improved mechanical properties, such as increased tensile strength, hardness, and corrosion resistance, making these materials interesting candidates for engineering applications. On the other hand, the exceptional stability of these materials in the metastable undercooled melt makes the undercooled liquid amenable to physical investigations not possible before. The formation of metallic glasses by cooling the liquid alloy from temperatures well above the equilibrium melting point depends critically on the cooling rate, or equivalently on the stability of undercooled melt with regard to crystallization. Following classical nucleation theory,

the nucleation rate is determined by kinetic factors such as the viscosity, expressing the mobility of atoms or groups of atoms, and by thermodynamic factors, expressing the driving force for the formation of a crystalline nucleus in the melt. The latter is composed of a surface energy term and the difference in the Gibbs free energy between the undercooled liquid and the competing crystalline phase. The Gibbs free energy difference can be obtained from measurements of the specific heat capacity, in the metastable liquid and crystalline phase, and the heat of fusion. Combining the specific heat and viscosity data with measurements of the nucleation kinetics, such as T-T-T curves, can serve to model nucleation kinetics. Thus, differences in the nucleation kinetics and glass forming ability of different alloy compositions may be systematically assessed. Investigations of the nucleation kinetics of these alloys have been performed in a ground based program with the electrostatic levitator (ESL). These experiments also allow the determination of the ratio of the specific heat to the total hemispherical emissivity.

In addition to the factors mentioned above, it has been shown that for one alloy composition, ZrTiCuNiBe, phase separation in the stable or slightly undercooled melt strongly influences the undercooling, phase selection, and crystallization microstucture. This effect can be detected as discontinuities in the second derivative of the Gibbs free energy, such as the specific heat and the coefficient of thermal expansion.

Another factor affecting the critical cooling rate for glass formation is the ability of a given alloy composition to either dissolve or passivate possible heterogeneous nucleants present in the melt. This question can be addressed by comparing the Gibbs free energy and viscosity of different alloy compositions together with careful investigation of impurity content on phase selection and undercooling behavior.

4. Methods of data acquisition and analysis

Measurements of the specific heat capacity were performed on 8 mm diameter specimens with the containerless electromagnetic processing device TEMPUS. Specimens are positioned by an radio-frequency (rf) electromagnetic quadrapole field and heated by a dipole field. Containerless conditions are required to avoid heterogeneous nucleation of the undercooled melt

by contact of the specimen with container walls. Furthermore, heating due to the strong levitation forces required for containerless electromagnetic processing would not allow one to perform these experiments under clean ultrahigh vacuum conditions in a 1-g environment.

The heat capacity of the specimen is determined by AC modulation calorimetry. In short, the heating power input to specimen at bias temperature T_o is sinusoidally modulated at frequency ω. This results in a temperature response at ω with amplitude ΔT_{mod} such that $\Delta T_m / T_o << 1$, with c_p given by:

$$c_P = \frac{P_{mod}}{\omega \Delta T_{mod}} f(\omega, \tau_1, \tau_2)$$

P_{mod} is the amplitude of modulated power component. $f(\omega,\tau_1,\tau_2)$ is a correction function accounting for the finite thermal conductivity, with internal relaxation time τ_2, and heat loss, with external relaxation time τ_1 . Due to the typically large difference in the external and internal relaxation times for metallic specimens, there is a frequency where $\Delta T_{mod}(\omega)$ is position independent, characterizing the isothermal regime with $1 - f(\omega,\tau_1,\tau_2) < 10^{-2}$. Experimentally, this regime can be identified by a phase shift of 90° between the heater current modulation and the temperature response. Calibration of P_{mod} is performed by application AC modulation calorimetry to the crystalline phase with known specific heat. The temperature dependence of the calorimeter constant thus obtained can be determined from measurement of the specific volume and the resistivity, as obtained from the current and voltage data from the rf-generator. Fig. 1 shows a typical experimental run with the VIT 106 alloy depicting melting and overheating (1), rapid cooling into the undercooled melt (2), and performing AC modulation calorimetry (3). The sample subsequently recalesces (4), possibly into a metastable crystalline phase.

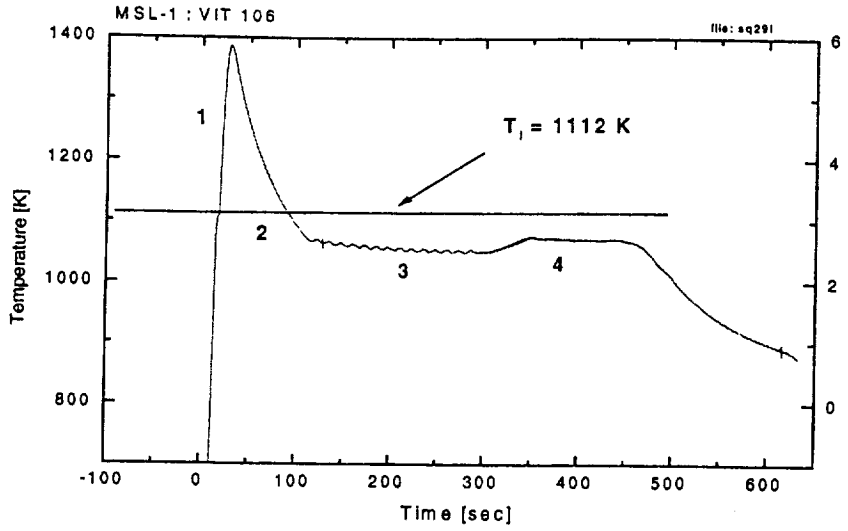

Fig. 1. Typical MSL-1 experiment with VIT 106

Determination of ΔT_{mod} is performed by application of a baseline drift correction, with external relaxation time τ_1, and subsequent Fourier analysis, as shown in Fig.2. The frequency components at 1.2 and 1.5 Hz are due to harmonic motions of the specimen in the potential well of the positioning field and do not represent true temperature variation. Alternatively, a FFT low pass filter is applied to the raw signal and a running average over modulation cycles is performed. The two methods agree within the statistical error of the running average, typically to within 0.1 K. As such, with $\Delta T_{mod} \approx 3$ K, a relative error in c_p determination of $< 4\%$ is obtained. From a step function change in the heating power input, τ_1 can also be determined from the transient behavior of the modulation signal. The data shown in Fig. 3 can be very well represented by a single exponential fit as expected for transients with a small temperature difference.

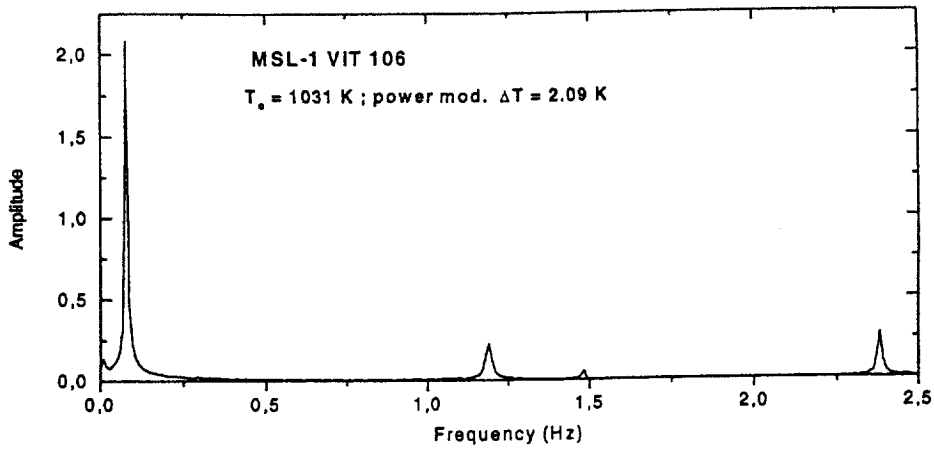

Fig. 2. Fourier transform of temperature signal (3) from Fig.1 after correcting for signal drift

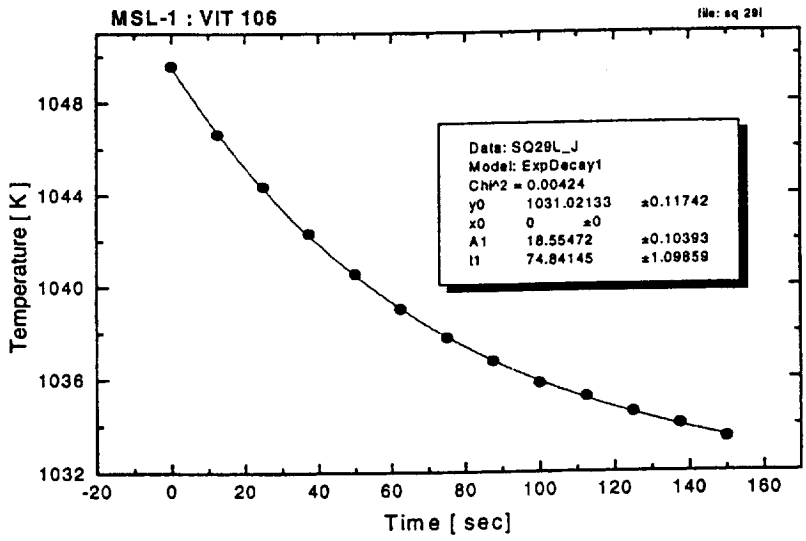

Fig3. Position of modulation maxima as function of time for τ_1 determination. ● data points, — single exponential fit

5. Flight results compared with ground results

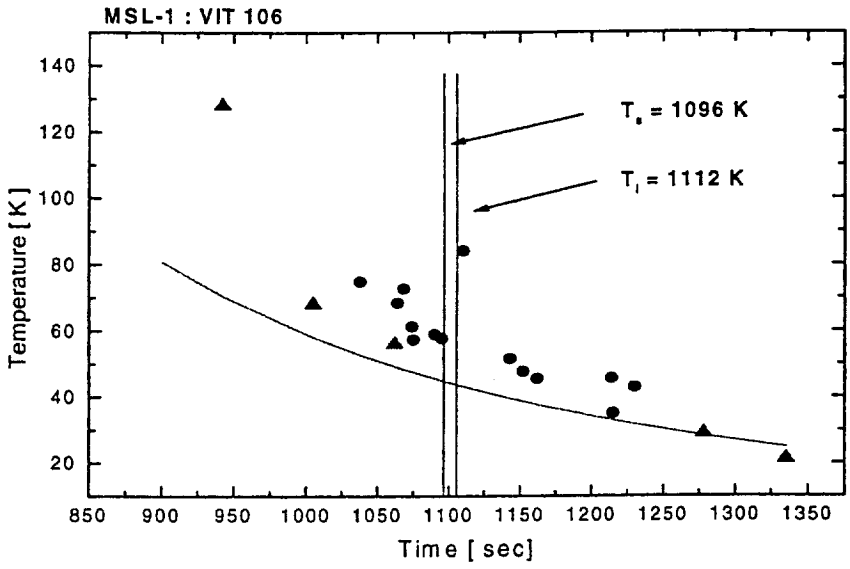

Fig. 4. External relaxation time as a function of temperature for VIT 106
●: MSL-1, Δ : ESL- ground based results.

Fig. 4 shows results for the external relaxation time τ_l obtained in the flight experiment for VIT 106 together with similar values obtained in the ESL. The good agreement between these values demonstrates the consistency of the experimental approach. The solid line represents a T^{-3} scaling of τ_l for constant specific heat capacity. As such, the deviation of the experimental data from this scaling reflects the strong increase of the specific heat with decreasing temperature for the undercooled melt. Furthermore, a singular point near T_l is observed suggesting an unusual behavior in c_p. Further evidence is provided in Fig. 5, with values of the specific heat from AC modulation calorimetry normalized to the heater coupling coefficient. The temperature dependence of the coupling coefficient has not yet been taken into account. Nonetheless, the anomaly exhibited in the external relaxation time is also present in the specific heat in the same temperature range. Furthermore, the temperature dependence of the specific volume also appears to change in this temperature range. This behavior is suggestive of a phase separation just above the liquidus temperature. In order to test this hypothesis further, laboratory experiments to analyze the solidification microstructure after rapidly quenching the liquid from different

temperatures are under way. AC modulation calorimetry could be performed for this alloy up to an undercooling of 70 K. The agreement of data points at similar temperatures is very good and demonstrates the precision of this method.

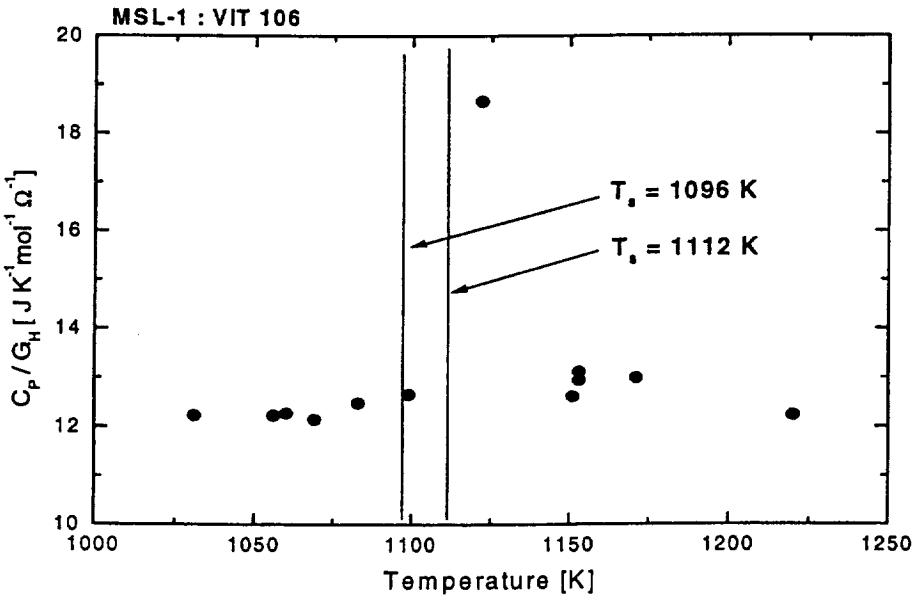

Fig 5. Specific heat capacity of VIT 106 normalized to heater coupling coefficient G_H.

As compared to ESL ground based experiments where undercooling of over 200 K could be obtained, the VIT 101 flight specimen showed only an undercooling of 45 K, which is attributed to the presence of minor impurities. Specific heat capacity data in the stable melt and the slightly undercooled melt were obtained. It should be pointed out that no anomaly in τ_1 or c_p similar to VIT 106 could be observed. The same holds for the measurements performed by the Fecht group on two bulk glass forming alloys of different composition.

Other ground based work includes analysis of solidification microstructure and phase selection in the flight specimen (VIT 101) solidified from the undercooled liquid under μg conditions. Comparison will be made with a 1-g reference specimen, as well with those phases crystallizing at high undercooling by heating the glass into the undercooled melt. Results of an

electron microprobe analysis are shown in Table 1, exhibiting two phases of almost complementary composition in (ZrTi) ≈ 50 at% and (NiCu) ≈ 50 at%. We will further identify the structure of these phases and investigate the dependence of their formation on impurity levels.

Tab. 1 EDX spot analysis of $Ti_{34}Zr_{11}Cu_{47}Ni_8$ (VIT 101) flight specimen

Phase	Zr at%	Ti at%	Ni at%	Cu at%
1	7.45	36	12.97	36.42
2	18.99	22.44	8.12	50.44
3	3.27	47.44	3.05	46.24

6. Conclusions

The specific heat capacity of two glass forming metallic alloys was measured by AC modulation calorimetry in the stable and undercooled (for VIT 106) melt. The temperature dependence of the specific heat as well of the external relaxation time and the specific volume appear to exhibit an anomaly tentatively identified as phase separation in the liquid. This would constitute an important finding as phase separation is suggested to occur frequently in glass forming metallic melts. However, with a few exceptions, experimental evidence of this is rare.

Further work will include investigation of the phase selection in these alloys as well as viscosity measurements at high undercooling. These data can be combined with high temperature viscosity data and undercooling experiments with the ESL to model the nucleation kinetics in these alloys. Future perspectives also include the implementation of AC modulation calorimetry in the ESL.