Hemispherical total emissivity and specific heat capacity of deeply undercooled $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ melts

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ABSTRACT

High-temperature high-vacuum electrostatic levitation (HTHVESL) and differential scanning calorimetry (DSC) were combined to determine the hemispherical total emissivity, ε_T , and the specific heat capacity , c_p, of the undercooked liquid and throughout the glass transition of the $Zr_{41.2}Ti_{13.8}CU]_{2.5}Ni_{10.0}Be_{22.5}$ bulk metallic glass forming alloy. The ratio of c_p/ε_T as a function of undercooking was determined from radiative cooling curves measured in the HTHVESL. Using specific heat capacity data obtained by DSC investigations close to the glass transition and above the melting point, ε_T and c_p were separated and the specific heat capacity of the whole undercooked liquid region was determined. Furthermore, the hemispherical total emissivity of the liquid was found to be about 0.22 at 980 K. On undercooking the liquid, the emissivity decreases to approximately 0.18 at about 670 K, where the undercooked liquid starts to freeze to a glass. No significant changes of the emissivity are observed as the alloy undergoes the glass transition.

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The hemispherical total emissivity, ε_T, which is the ratio of energy emitted by a material at a temperature T with respect to a black body at the same temperature, has been measured for several solid metals [1,2,3,4], alloys[5], and semi conductors[6]. However, there is a lack of emissivity data on liquid metals and only recently first results were reported for undercooked metallic liquids[7]. Lately, new multicomponent alloy systems have been found such as La-Al-Ni[8], Zr-Ni-Al-Cu[9] and Zr-Ti-Cu-Ni-Be[10] exhibiting an extraordinary thermal stability of the undercooked liquid with respect to crystallization. Cooling rates of less than 100 K/s are usually sufficient to suppress nucleation of crystalline compounds and thus form a bulk metallic glass in these alloy systems. For the particular $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy we even showed that the melt could be undercooled more than 350K below the liquidus temperature, T_{liq}=993K, applying cooling rates lower than 2K/s. The melt then undergoes the glass transition [11]. This deep undercooking of a liquid alloy melt without crystallization was achieved in the high-temperature high-vacuum electrostatic levitator (HTHVESL) at the Jet Propulsion Laboratory. It offers the opportunity to investigate thermophysical properties of undercooked metallic melts in regions which have not been accessible so far. In this paper the hemispherical total emissivity, ε_T, and the specific, heat capacity, cp, of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy are determined in the undercooked liquid state as well as in the glass transition region by measuring c_p/ε_T as a function of temperature in the HTHVESL and combining the data with specific heat capacity measurements in a differential scanning calorimeter (DSC).

Amorphous alloy ingots with a composition $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ were prepared from a mixture of the elements of purity ranging from 99.5% to 99.9% by induction melting on a water-cooled silver boat under a Ti gettered argon atmosphere. Pieces of typically 40 mg were remelted under a 1 mPa vacuum in a radio frequency field (- 2100 kHz) to produce spherical specimens which were introduced into the HTHVESL.

All HTHVESL experiments were performed under ultra high vacuum conditions ($P<7\cdot10^{-3}$ mPa). Sample heating was provided by a] kW UV-rich high pressure xenon

arc lamp. During the melting and solidification process, the sample temperature was measured using an E^2T pyrometer (model 7000ET-1HR) coupled to a readout unit (model E^2T-B) with a nominal sensitivity range of 588K to 1923K. The details of the experimental apparatus are described elsewhere[12]. The main feature and advantage of the HTHVESL compared to electromagnetic levitation is that levitation and heating of the sample are decoupled, so that the sample can be cooled from above the melting point down to room temperature and kept levitated at the same time without significant energy input. Specific heat capacities of the glass, the undercooked liquid, and the crystalline state were measured using a Perkin Elmer DSC7 that was evacuated to a pressure of 1 Pa and purged several times with 99.9999% Ar prior to every experiment. The continuous change in specific heat capacity on heating the glass or cooling the undercooked liquid was measured in both heating and cooling experiments for different rates of temperature change. In addition the absolute values of the specific heat capacity in the amorphous alloys up to 593K and in the crystallized samples up to 893K were determined in reference to a sapphire standard. Details on the DSC experiments can be found elsewhere[13].

Fig. 1. presents a typical cooling curve for a spherical sample of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy obtained in the HTHVESL after removing the heat source. Due to the unique design of the HTHVESL the heat transfer resulting from conductive and convective cooling in a gas, and any heat input Qi_n from an external source can be neglected, in contrast to electromagnetic levitation (see also ref. [14]). Hence, the cooling process is purely radiative and determined by the following equation

$$m \cdot c_p(T)\frac{dT}{dt} = -\varepsilon_T(T) \cdot A \cdot \sigma \cdot (T^4 - T_s^4) \qquad (1)$$

where m is the mass of the sample with a surface area, A, T is the temperature of the sample, Ts is the temperature of the surroundings, and σ is the Stephan-Boltzmann constant. Since the cooling curve T(t) of the spherical sample with a known mass and density is only a function of c_p and ε_T, the ratio c_p/ε_T as a function of temperature can be

determined from the shape of the cooling curve[7]. The density of the liquid sample is assumed to be constant. Fig 2 shows the c_p/T curve obtained by averaging 14 different cooling curves. The uncertainty of the calculated c_p/ε_T values is ±20 J/g-atom·K at any given temperature. Fig.2 indicates that c_p/ε_T rises with increasing undercooking and starts to drop at about 670K. This temperature is the. beginning of the glass transition for cooling at the present cooling rate, as determined by DSC experiments. At about 750 K an anomaly in the c_p/ε_T curve is observed. It is due to a very small recalesence effect, that is barely visible in each cooling curve (see Fig. 1) representing a small heat release. This exothermic effect can be either due to nucleation of crystalline compounds or to the beginning of a decomposition reaction of the alloy in the undercooked liquid state. Based on x-ray diffraction and DSC experiments, comparing the sample processed in the levitator with an amorphous reference sample, we showed that the upper limit for crystalline parts in the sample is less than **2°/0]** [1]. This favors the latter explanation. Decomposition in the amorphous or undercooked liquid state was also found in the ZrAlCuNi[15] system and even Appears in binary metallic glasses where different short range orders can develop depending on composition[16]. In addition, if the decomposition proceeds via a spinodal unmixing process it can be favored compared to nucleation of crystalline compounds as there is no nucleation barrier to overcome[17].

The hemispherical total emissivity is evaluated using specific heat capacity data obtained by the DSC experiments[13]. In Fig.3 the measured specific heat capacities are displayed. Specific heat capacities of the metastable undercooked liquid are marked as circles. These data were obtained by measuring the track of the specific heat capacity from the amorphous alloy throughout the glass transition into the undercooked liquid with different heating rates between 0.0167 K/s and 6.67 K/s[13]. The specific heat capacity of the liquid above the eutectic temperature is marked as a diamond [18]. The dashed curve represents the specific heat capacity of the undercooled liquid fitted to the experimental data according to a $1/T^2$ law[11,19,20]. The curve is extrapolated down to the Kauzmann

temperature, TK, which represents the lower bound for the glass transition for thermodynamical reasons (see ref. [13]). However, the specific heat capacity values of the undercooled liquid below about 620 K are only accessible for heating and cooling rates below 0.0167 K/s. In contrast, the cooling rates in the HTHVESL experiment are of the order of 2 K/s. For this cooling rate the undercooled liquid falls out of metastable equilibrium far above the Kauzmann temperature and the specific heat capacity starts to drop. This is shown in Fig.3 as well. The open triangles in Fig.3 show the track of the specific heat capacity of a sample cooled in the DSC with a rate of 1.667 K/s throughout the glass transition. The curve starts to deviate from the specific heat capacity curve of the undercooled liquid below about 670 K, that corresponds to the temperature below which c_p/ε_T measured in the HTHVESL starts to drop as well.

Taking the c_p/ε_T data from Fig.2, the hemispherical total emissivity is calculated for each measured specific heat capacity value. Below 670 K the specific heat capacity data of the sample cooled in the DSC with 1.67 K/s are used. The resulting hemispherical total emissivity as a function of temperature is shown in Fig.4. Duc to the lack of direct C_p measurements between 7 10K and 980K, the ernissivity is interpolated as a straight line. This is most likely a good first approximation since, in general, there is a virtually linear relationship between the electrical resistivity and the hemispherical total emissivity for pure metals[4]. Furthermore the temperature dependence of the resistivity in liquid metals and alloys is weak and linear as well[21,22]. As can be observed in Fig.4, the emissivity of the melt is 0.22 at 980 K and decreases to a value of 0.18 in the deeply undercooled melt just above the glass transition, When the sample starts to freeze to a glass at about 670 K no significant change of the hemispherical total emissivit y is observed within the experimental error. This is in good agreement with results of Geyer[23], who showed that the dc resistivity of the amorphous $Zr_41.2Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy changes only slightly as the sample is heated above the glass transition.

In contrast to solidification by crystallization, significant changes in the surface morphology that affect the emittance do not appear during solidification by freezing the undercooled $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ liquid to a glass. It was shown by atomic force microscopy[24], that the free surfaces of the amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy exhibit an extraordinary smoothness of ±5 nm on a typical length scale of more than 1μm. So we assume that artifacts produced by a change of the surface morphology can be neglected in this particular case.

The emissivity data as a function ofternperature were used to determine the specific heat capacity of the undercooked liquid by multiplying them with the c_p/ε_T curve. The calculated specific heat capacity from the undercooking experiment is added in Fig.3 (dashed-dotted line). The specific heat capacity data throughout the glass transition fits the experimental data obtained in the DSC on cooling, since those were used to calculate the emissivity. For the undercooked liquid region the specific heat capacity obtained from the levitation experiments is in good agreement with the $1/T^2$ law (dashed) until the metastable undercooked melt falls out of metastable equilibrium at 670 K and starts to undergo the glass transition, Only at 750 K, where a weak recalesence effect occurred, as discussed above, the deviations are larger.

In this paper we described an experimental approach to determine the hemispherical total emissivity of a material by combining cooling experiments in the HTHVESL with specific heat capacity measurements in a DSC. Hence, it was possible to obtain emissivities of a deeply undercooled liquid down to the glass transition and we presented the hemispherical total emissivity for the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ bulk metallic glass forming alloy. The hemispherical total emissivity depends linearly on the temperature in the undercooked liquid. In the glass transition region no significant deviations from this behavior are observed, which is due to the fact that the glass transition neither significantly affects the dc resistivity nor the surface morphology of the sample. Furthermore, the specific heat capacity of the whole undercooked liquid region was determined. The results

are consistent with the present picture of the temperature dependence of the specific heat capacity in the undercooled liquid.

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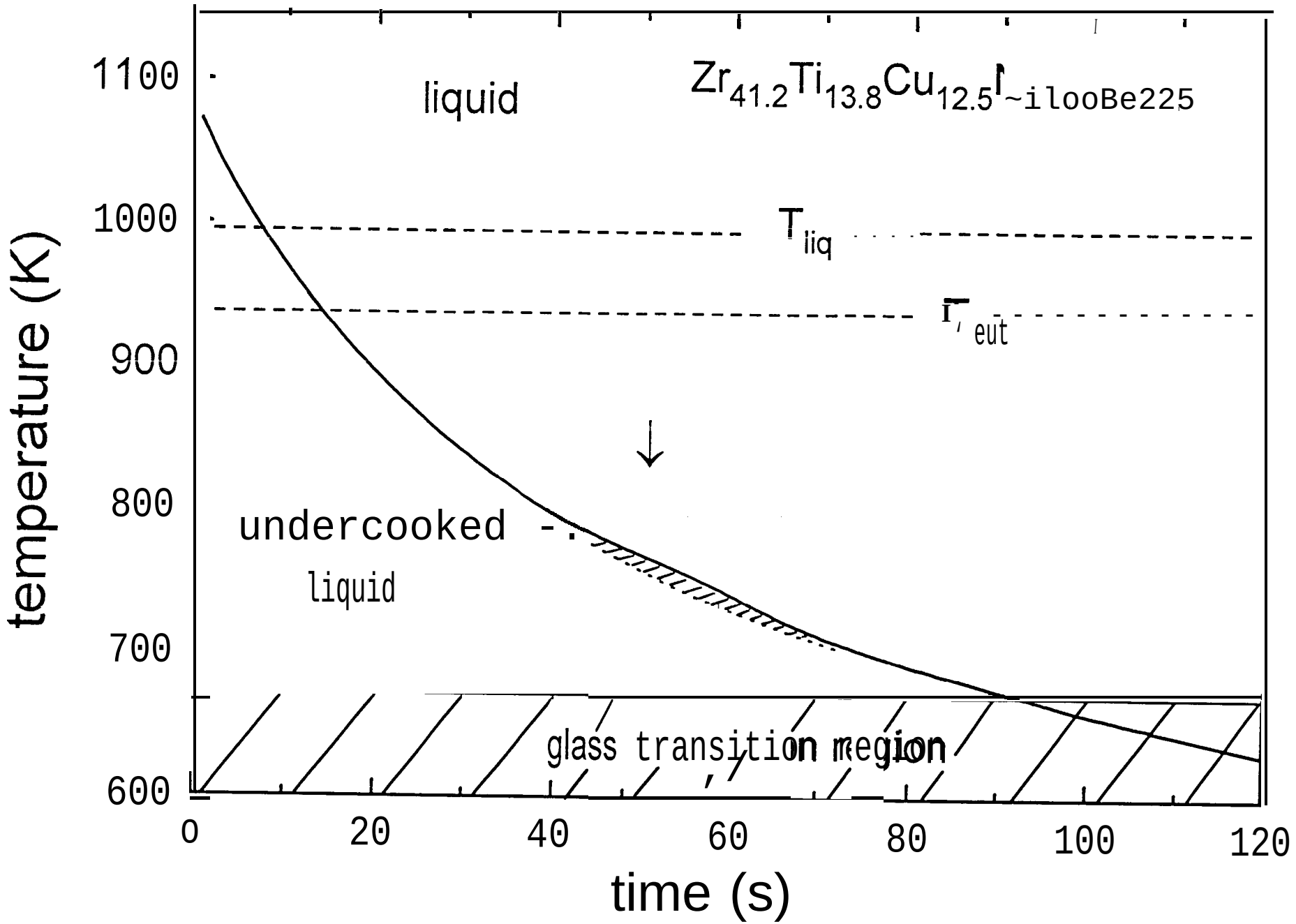
FIGURE CAPTIONS

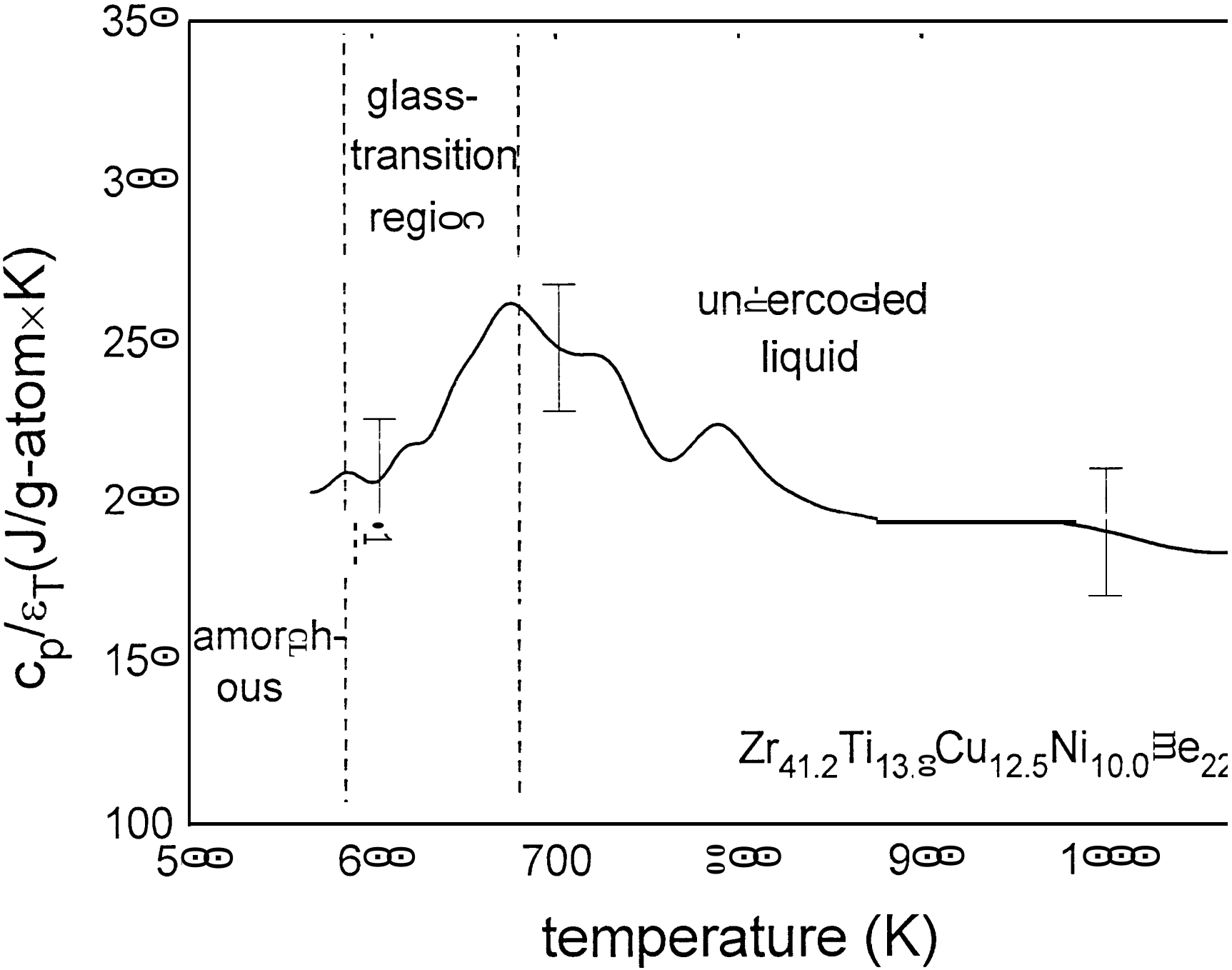
Fig. 1. Temperature-time profile of a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ sample alloy, which is undercooled below the liquidus temperature, T_{liq}, and eutectic temperature, T_{eut}. The undercooled liquid freezes to a glass in the glass transition region (hatched). A small exothermic effect is observed at about 750 K (arrow).

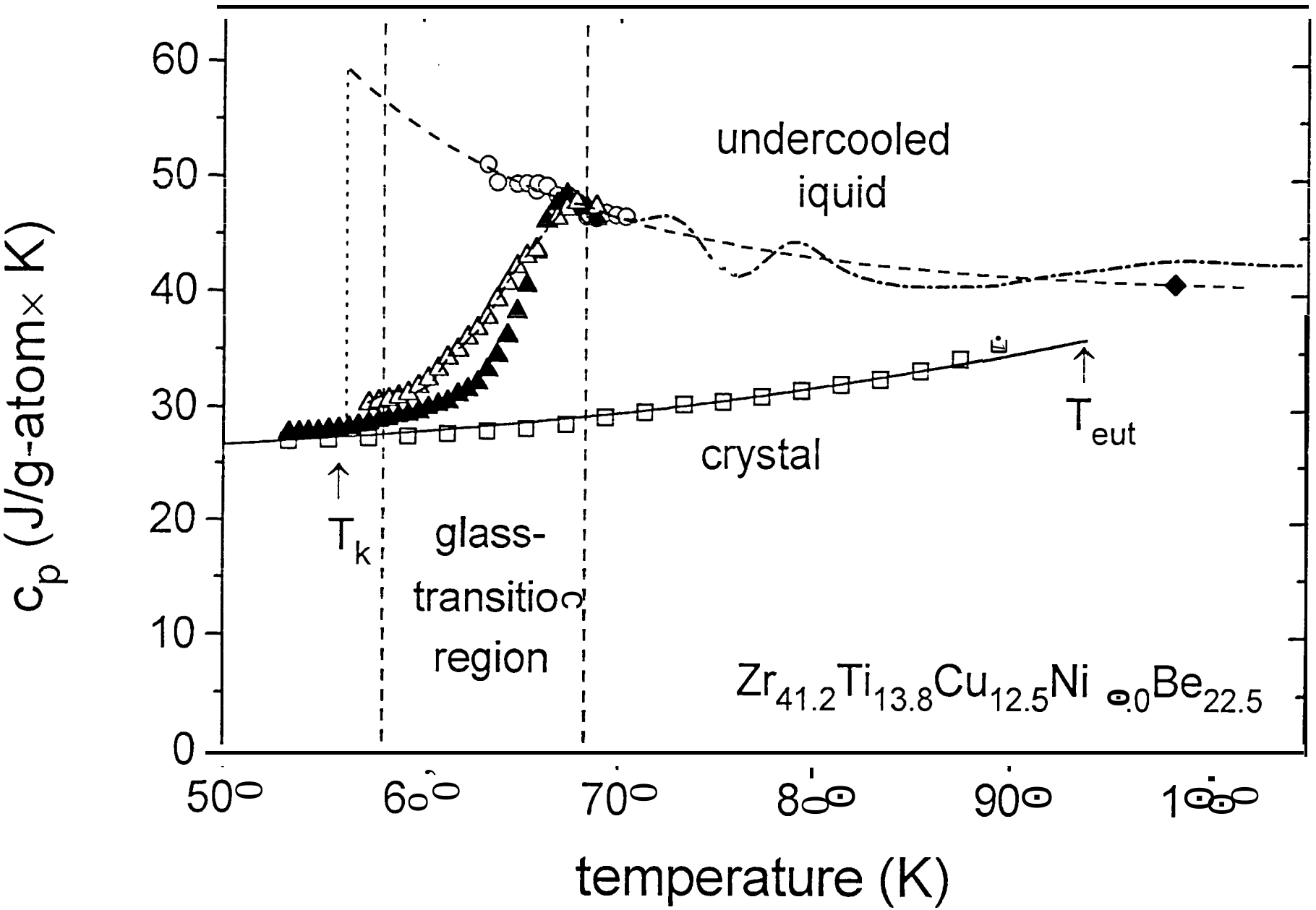
Fig.2. The measured ratio c_p/ε_T as a function of temperature during radiative cooling. c_p/ε_T rises with decreasing temperature and to drops as soon as the undercooled liquid starts to freeze to a glass. The anomaly observed at 750 K reflects the small recalesence effect observed in the cooling curve.

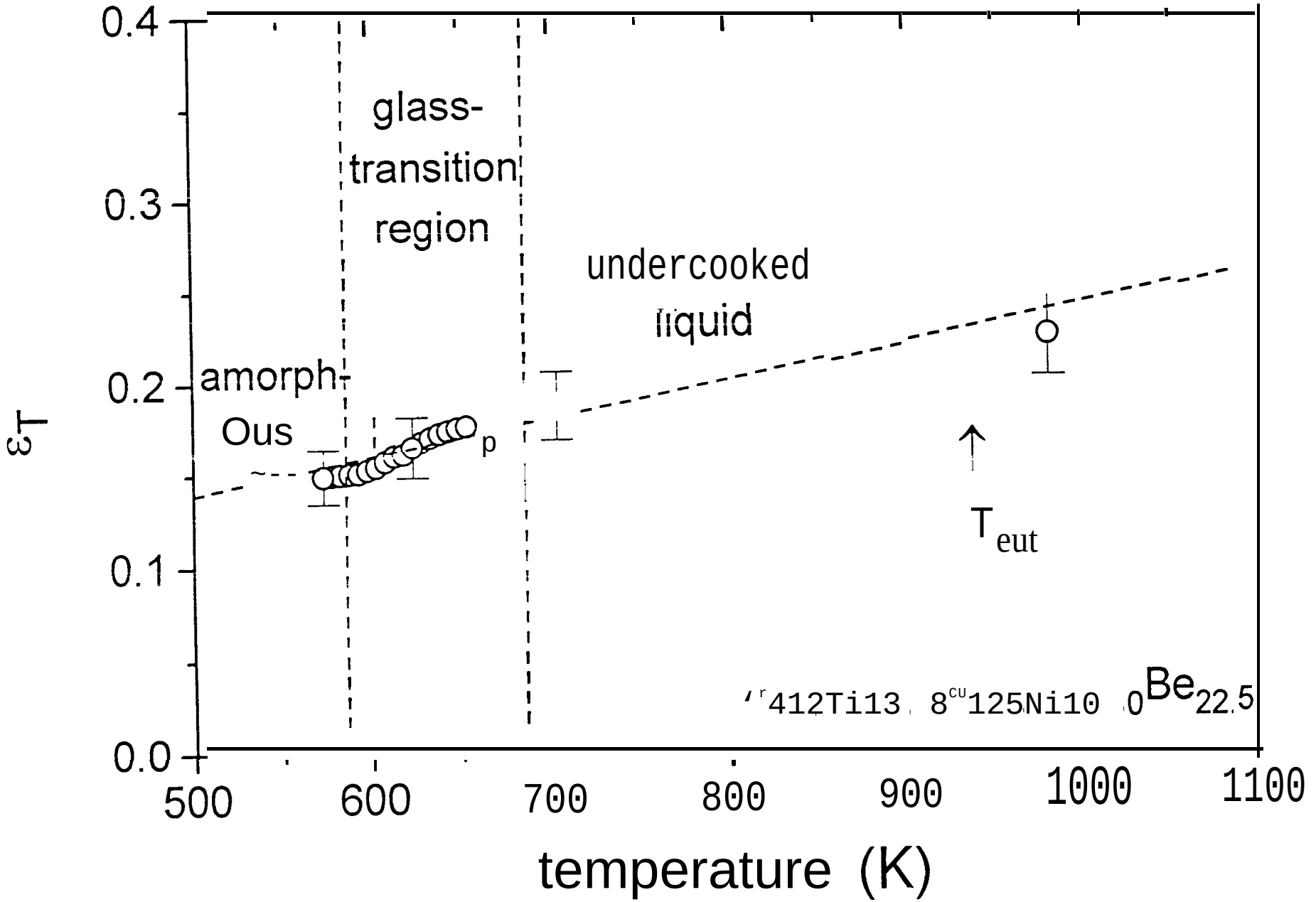
Fig.3. Specific heat capacity of the undercooled liquid (○ ●), throughout the glass transition on heating (▲) and cooling (A) with 1.67 K/s , and of the crystal (0), measured with a DSC. The specific heat capacity curve determined by the $c_p/\varepsilon_T(T)$ curve is plotted as a dashed- dotted line. Additionally drawn is a fit to the specific heat capacity data of the undercooled liquid according to a $1/T^2$ law (dashed)[13].

Fig.4. Hemispherical total emissivity of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy in the undercooled liquid and throughout the glass transition.


liquid
$Zr_{41.2}Ti_{13.8}Cu_{12.5}$
T_{liq}
T_{eut}
undercooked liquid
glass transition region
temperature (K)
time (s)
1100
1000
900
800
700
600
0
20
40
60
80
100
120


glass-
transition
region
undercooled
liquid
amorph-
ous
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22}$
c_p/ε_T(J/g-atom×K)
temperature (K)
350
300
250
200
150
100
500
600
700
800
900
1000


60
50
40
30
20
10
0
c_p (J/g-atom× K)
undercooled
iquid
crystal
T_k
T_{eut}
glass-
transitio
region
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$
50
60
70
80
90
100
temperature (K)


0.4
0.3
0.2
0.1
0.0
glass-
transition
region
undercooked
liquid
amorph-
Ous
p
T_{eut}
ε_T
$(Ti_{41.2}Cu_{38.8}Ni_{10.0}Be_{22.5})_{99}Fe_1$
500
600
700
800
900
1000
1100
temperature (K)