Investigation on the Binary Organic Components TRIS-NPG as Suitable Model Substances for Metal-Like Solidification

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Abstract. Metallic solidification structures show a huge variation of patterns, which may be observed in many solidification processes such as casting and welding. To improve our understanding of the formation of these patterns, directional solidification experiments are carried out by using the Bridgman-technique. Hereby, not only metal alloys are investigated, model substances are also considered for this purpose. Such model substances consist of transparent organic components with a non-facetted high temperature (simply called plastic) phase. These organic components solidify like metals, which have the advantage of being able to observe the formation as well as the dynamics of solidification patterns with a standard light microscope. Studies on the formation of layered peritectic solidification structures have been carried out by using the model system TRIS-NPG. So far only very few binary organic systems reveal a peritectic region which is suitable for such experiments. For these rare systems, and especially for the TRIS-NPG system, there is insufficient knowledge of corresponding physical and chemical properties. As further studies on peritectic layered structures are planned on board of the ISS for 2019, it is of utmost importance to discover more about the specific properties of this type of material. Therefore, partial complimentary studies on thermal conductivity, vapor pressure, and viscosity for peritectic concentrations were conducted. The corresponding values are needed for the correct interpretation of the dynamics of peritectic pattern formation, within a temperature gradient in a Bridgman furnace using this model system.

Introduction

Only organic components that display the formation of a non-facetted (nf) high-temperature (plastic) phase [1], as opposed to the facetted low-temperature phase, are suitable as model systems for metal-like solidification behavior. Such organic substances are optically isotropic and consist of molecules with a globular shape, which act as stacked spherical objects with weak interactions; usually by hydrogen bonds. In the plastic phase, the molecules are more or less free to rotate around their center [2, 3, 4]. Therefore, organic compounds which show a plastic phase are quite attractive to study metal-like solidification morphologies by means of in-situ observation techniques. Investigations on peritectic solidification morphologies require model systems, which show a peritectic reaction within a suitable concentration and temperature range. Currently, only few systems are known which meet the necessary requirements [5]. One of them, the model system NPG (Neopentylglycol)-TRIS (Tris[hydroxymenthyl]aminomethane) has been selected by the authors for investigation on peritectic layered structures [6-14]. This system was thermodynamically studied by [5, 15, 16] and the pure substances NPG and/or TRIS investigated by [17-22]. In contrast to metals, organic compounds consist of molecules, therefore, they may have properties in the solidification temperature range which do not occur in metals. Since NPG and TRIS are commercial used at room temperature, there properties at higher temperatures are not well-studied. From publications and material data sheets, it is well-established that NPG is hydroscopic and has the tendency to sublimate [23], whereas, the plastic phase stability of TRIS correlates with the selected annealing temperature [26] and is relatively sensitive to impurities [3, 24, 25]. Investigations on peritectic layered structures with a concentration of $x = 0.5$ mol fraction NPG are to be conducted aboard the International Space

Station (ISS) for 2019. To carry out the in-situ observations under μg conditions with the model system TRIS-NPG European Space Agency (ESA) designed a Bridgman furnace. One prerequisite for the construction of the device was to design a glass sample which would withstand the mechanical stress of the experiments. Therefore, extensive literature studies on the two pure substances were performed and selected properties of the molecular alloy in the melting range were determined; namely the thermal conductivity, the vapor pressure and the viscosity in the area of the peritectic plateau ($0.46 \leq x \leq 53$ mol fraction NPG). The findings of this research are published in this article.

Experimental

The experimental setups are described here only briefly. A detailed description of the different scientific investigations is provided in [27].

Alloy Preparation: NPG and TRIS, as delivered from Aldrich [28], have a purity of 99 % and 99.9+ %, respectively. An additional treatment process for NPG was applied to reduce the water content by dehydration, as shown in [5]. Since TRIS, as delivered, already has a purity of 99.9+ %, and is thermally sensitive [3, 24, 25], it was used as delivered. The alloys were prepared in an inert atmosphere by mixing the powders of both organic substances and heated up shortly above the melting point [26]. Since NPG has a tendency to sublimate, the alloys were prepared in closed glass containers to avoid a shift of concentration by vaporization. The alloy was cooled down to room temperature and subsequently stored in an inert atmosphere until use for further studies.

Thermal Conductivity: The measurement of the thermal conductivity was performed with the heat conductivity measuring device: type K-system II, according to ASTM D5930-97 standard at normal atmospheric pressure. Further details are in [27]. The measurements were carried out within a temperature range from 373 K to 443 K, for both pure substances and $x = 0.5$ mol fraction NPG.

Vapor Pressure: The experimental equipment consists of an autoclave, the heating system, a thermal Fe-Cu-Ni sensor, a pump, and a digital pressure gauge. For measurements 50 g of the substance was filled into the autoclave and the inner pressure was reduced to -80 k·Pa. Afterwards, the temperature was raised in incremental steps from room temperature up to 500 K. Three independent experiments were carried out for TRIS, NPG, $x = 0.3$, $x = 0.5$, and $x = 0.7$.

Dynamic Viscosity. The measurement of the dynamic viscosity was conducted by using a Brookfield programmable rheometer DV-III Ultra [29]. The prepared alloy (TRIS, NPG, $x = 0.4$, $x = 0.5$, or $x = 0.6$) is placed in a 250 ml beakers and heated until the sample had completely liquefied. To avoid vaporization during the melting process, the beakers were sealed with a foil until the measurements of the viscosity with the rheometer had taken place under normal atmospheric conditions.

Results and Discussion

Thermal Conductivity. In general, the thermal conductivity, λ, as a function of temperature shows a non-linear correlation. In fact, it depends on the corresponding phase, namely melt, faceted- or plastic phase. To compare the accuracy of the measurement the obtained experimental results and the published values [18, 19] are shown in Fig. 1. The values measured at Montanuniversitaet Leoben (MUL) for the temperature range of the melting point of NPG (401.3 ± 1.0 K), are within the range of the published results [18, 19]. For the plastic phase, the trend towards thermal conductivity diverges between [18] and [19]. Whereby, the results of MUL correlates with the trend presented in [18], which shows a drop in thermal conductivity at lower temperatures. For TRIS, the experimental data indicate a nearly constant thermal conductivity over the entire investigated temperature range. However, in this case the conductivity slightly increases in the faceted phase with a drop in temperature, and in the melt once the temperature rises. The alloy $x = 0.5$ shows a correlation between an increasing thermal conductivity and a falling temperature.

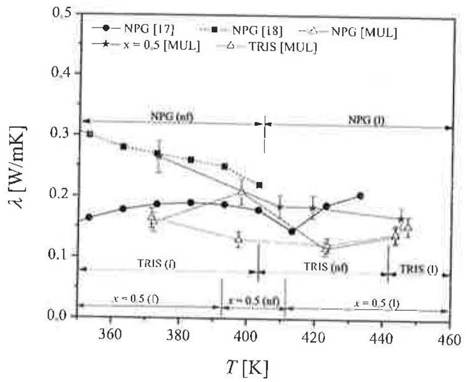

Figure 1. The graph shows the experimentally obtained values for the thermal conductivity of NPG, TRIS and the alloy of $x = 0.5$ (observed at MUL), compared to the results published by [18,19].

Vapor Pressure. With the determination of the vapor pressure, p_v, the enthalpy, ΔH_V, and the entropy, ΔS_V, were determined by using the Clausius-Clapeyron relation [30]. This equation can be derived to a simpler first order equation, where the slope multiplied by the gas constant R is equal to the enthalpy ΔH_V. The relation between the logarithm of the vapor pressure and the reciprocal of the temperature, taken from the experimental results, is shown in Fig. 2.

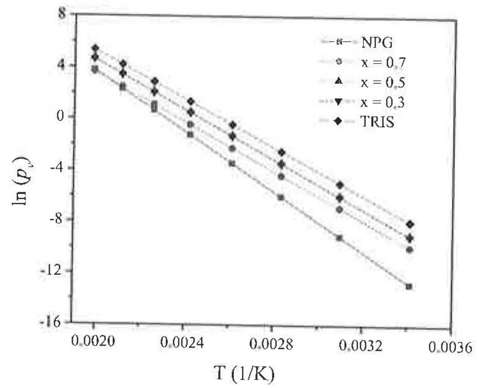

Figure 2. Natural logarithm of the vapor pressure at 293 K to 503 K in $\Delta T = 30$ K steps (dots). The lines are the regression analysis for the vapor pressure.

The expected vapor pressure for the entire concentration range is calculated according to Ra-oult's law [30] and compared with the experimental results (Fig. 3). As a comparison, the study of [13] was used, where ΔH_V for NPG is given with 74.7 kJ/mol. The results do not confirm the expected values, but show nearly constant values for NPG and all other alloys with $\Delta H_V = 78.4 \pm 1.6$ kJ/mol. An exception is TRIS which has a significantly higher ΔH_V of 96.4 ± 2.3 kJ/mol. ΔS_V has been calculated from ΔH_V, divided by the corresponding boiling temperature T_b. According to Trouton's rule, all alloys and both organic compounds TRIS and NPG show a vaporization entropy value ΔS_V above 88 J/K mol, which proves that the organic compounds are associated in the liquid state by hydrogen bonds, irrespective of the specific molecular structure [30].

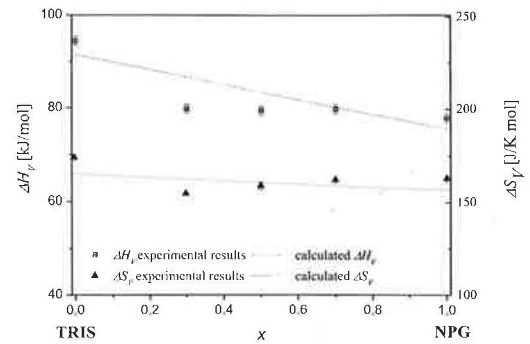

Figure 3. The graph shows the experimental results enthalpy (squares) and entropy (triangles) of vaporization in comparison with the calculated results (broken lines).

Dynamic Viscosity: Viscous flow in a homogeneous temperature field is described by the Arrhenius-Andrade equation [30]. A logarithmic application of viscosity, η, and temperature result in a linear correlation, which is depicted in Fig. 4.

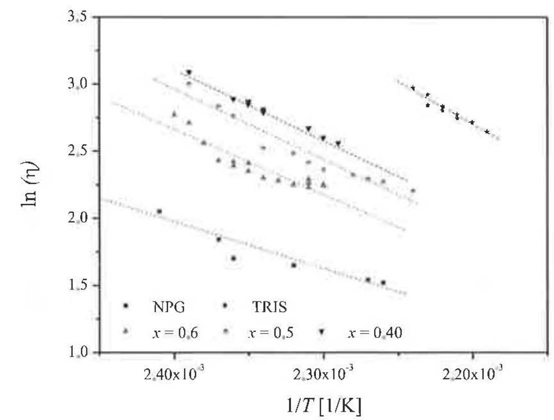

Figure 4. The figure displays the linear correlation between the logarithms of the measured dynamic viscosity of selective concentrations from organic compounds TRIS and NPG and the reciprocal of temperature. The left end of the regression line is equal to the freezing point.

Based on the experimental viscosity data, the activation energy E_a can be roughly estimated by applying the Arrhenius-Andrade equation. The energy is in the order of $E_a = 58.6 \pm 0.2$ kJ/mol for TRIS constantly decreasing to 27 ± 0.3 kJ/mol for NPG.

Conclusions

It is essential to consider two peculiarities if the TRIS-NPG binary organic system is to be selected as a model substance; the tendency for NPG to sublimate and the limited thermal stability of TRIS near the melting point. The thermal stability of TRIS has already been investigated and published by the authors [26]. The sublimation tendency for NPG was taken into account in the sample preparation insofar as the smallest possible gas volume was available above the liquid level.

Concerning thermal conductivity, a decreasing thermal conductivity was measured for the peritectic alloy (x = 0.5), with an increasing temperature. It should be noted that this trend does not apply to the two pure substances. Both exhibit an increasing thermal conductivity with increasing temperature in the respective liquid phase(s). By comparing the obtained measured values with the published ones, the thermal conductivity of the liquid phase for the model system TRIS-NPG can be assumed as being in the range of $\lambda = 0.15 \pm 0.5$ W/m K.
The determination of the vaporization-enthalpy and entropy for the selected alloys follows Raoult's law, exhibiting $\Delta H_V \sim 80$ J/mol for pure NPG and the investigated alloys. Pure TRIS turns out to be an exception is in that it exhibits a vaporization enthalpy of 94.4 KJ/mol. The study confirms that the molecules are also connected in the liquid phase via hydrogen bonds, since $\Delta S_V > 90$ J/K mol.
The viscosity of the liquid is in the magnitude of 1.0 ± 0.5 mPa·s, comparable with salad vinegar. The investigations facilitate an estimation for the activation energy potential, which is one third of the vaporization enthalpy for NPG; up to one and a half times that value for TRIS. This is a well-established empirical indication and proved to be true for the NPG values. In summary, it can be stated that the different, independent methods of investigation have been able to determine a general tendency of the alloy to behave as both the experimental and simulation data have managed to indicate, and confirm each other in their order of magnitude. For exact determination of the values, it will be necessary to conduct further extensive investigations under both experimental (in-situ) and simulation conditions.

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