Composition Effects on Phase Formation and Stability

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Standard methods for obtaining accurate values for the temperature-dependent nucleation and growth rates are laborious and time consuming. More rapid techniques are needed for materials development so that small changes in stability due to composition shifts or the introduction of heterogeneous nucleation agents can be assessed quickly, and for remote experiments, such as in a microgravity environment, where the data are often taken under conditions that preclude the possibility of multiple experiments for different times at different temperatures. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are ideally suited for these cases, yielding estimates of phase transition temperatures and enthalpies of transformation. When coupled with microstructural studies they can also give information about the mode and kinetics of transformation. Nonisothermal DSC and DTA studies, in particular, are easily made in little time, require small quantities of sample, and allow the transformation kinetics to be probed over a wide temperature range. Further, research staff can be easily trained and automation is relatively easy, allowing measurements to be made at remote locations.

These advantages and the low apparatus weight make such studies ideal for supporting investigations in a reduced gravity environment. Samples processed in space, for example, can quickly be screened and modifications can be made to experimental procedures during flight, greatly increasing the probability of positive results. However, DSC/DTA techniques, particularly nonisothermal ones, suffer from a lack of quantitative methods for the data analysis. Existing methods are based on erroneous assumptions for the temperature dependence of the effective rate constants and generally lead to misinformation about the transformations studied. Further, no account is taken of the transformation microstructure, which is known to dramatically influence the isothermal phase transformation kinetics.

Under continuing NASA support within the Microgravity Division, we have developed realistic numerical models for first order phase transformations proceeding by nucleation and growth, including time-dependent nucleation rates and cluster-size-dependent growth rates in a natural way. Surface crystallization and heterogeneous nucleation have been studied. The importance of sample-size in evaluating DSC/DTA results was emphasized and the first quantitative methods for including those effects in data analysis were developed. Model predictions were shown to agree quantitatively with experimental crystallization data for powders of lithium-disilicate glasses. Based on those studies, we demonstrated that all existing methods of analysis for DSC/DTA data were flawed. New numerical techniques were proposed.

These past studies have focused on polymorphic crystallization, where the composition of the initial and final phases are identical. Only a limited number of phase transformations are approximately polymorphic. Under current NASA support, we are therefore extending the techniques developed for modeling DSC/DTA data to include nucleation and growth in primary crystallizing glasses and precipitation processes. Growth in these cases, involving solute redistribution, has been investigated extensively by others; methods for taking account of overlapping diffusion fields are available. The correct methods for nonstoichiometric nucleation, however, are less clear. Previous experimental studies are few and interpretations of the data are difficult; no previous measurements of the composition dependence of the time-dependent

nucleation rates exist. Such studies are essential to guide the development of a model for nucleation that can be included in the numerical calculations of the DSC/DTA peak profiles.

Previous measurements of the steady-state nucleation rate as a function of alloy compositions have typically indicated a changing driving free energy. Our first measurements of the composition dependence of the time-dependent nucleation rate in any system, made in $Na_2O.2CaO.3SiO_2$ glasses as a function of [SiO_2] and [Na_2O], indicate instead a composition-dependent interfacial free energy. Further, numerical calculations of the time-dependent nucleation rates following multistep annealing treatments are in good agreement with experimental data, supporting the essential validity of the kinetic model from the classical theory of nucleation. Some discrepancies for small preannealing times, and a slight "ringing" in the number of nuclei produced as a function of preannealing are difficult to reconcile within the classical theory, however. Undercooling values as a function of composition in TiFeSiO alloys (made in collaboration with D. Herlach and D. Holland-Moritz from the DLR in Germany) are minimum at the stoichiometric composition of α(TiFeSiO), a crystal phase with significant local icosahedral order. That the undercooling limit does not track with the liquidus temperature and the presumed similarity in the local structures of the stoichiometric α-phase and the liquid, also suggest a composition-dependence of the α-phase/liquid interfacial free energy.

As observed by others, many Al-rare earth (RE) glasses devitrify to an extremely fine-grained nanostructured material. We recently demonstrated that Al-Y-Fe glasses form a dense microstructure α-Al with a uniform grain size of approximately 20 nm, independent of any preannealing treatments. This likely signals a change in the kinetic model of the classical theory. We have developed a new model for homogeneous nucleation in these glasses, that takes account of the linked fluxes of interface attachment and diffusion in the glass to the cluster neighborhood. Numerical results show that the high nucleation rates, slow growth rates, and insensitivity to preannealing treatments are naturally explained within this model.

Led by these experimental and theoretical results, we have established criteria for primary nucleation behavior. These insights and the new kinetic model for nucleation are being incorporated into the computer models previously developed to model DSC/DTA studies of polymorphic transformations.