Local Icosahedral Ordering in Undercooled Metallic Liquids and the Nucleation Barrier: Confirmation of a Half-century-old Hypothesis

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Introduction

Many people are familiar with the observation, first made by Fahrenheit, that liquid water can be cooled significantly below its freezing temperature before ice forms. In 1952, David Turnbull showed that this ability to undercool was a common property, occurring even in metallic liquids [1]. To explain this, Charles Frank proposed that the atoms in the liquid metal are locally packed with an icosahedral symmetry [2]. Since this hypothesis is incompatible with long-range periodicity, a barrier naturally arises to the nucleation of crystal phases. Recently, we obtained the first experimental proof of this hypothesis based on *in situ* synchrotron x-ray diffraction and nucleation studies of electrostatically levitated droplets of TiZrNi liquid alloys [3]. Data from these studies demonstrate that icosahedral short-range atomic order exists, becoming better developed with decreasing temperature below the liquidus temperature. This increased icosahedral order favors the transformation of the liquid to a metastable icosahedral quasicrystal phase (i-phase) instead of the polytetrahedral C14 Laves phase, which is the thermodynamically favored phase, thereby demonstrating a clear connection between the nucleation barrier and the local structure of the liquid and giving the first verification of Frank's hypothesis.

Methods and Materials

The experimental data were obtained through a joint collaboration between researchers from Washington University, NASA's MSFC, and the MU-CAT sector at the APS. The x-ray structural studies were made on 2.5-mm-diameter samples of highly reactive $Ti_{39.5}Zr_{39.5}Ni_{21}$ alloys by using the NASA electrostatic levitation (ESL) facility, temporarily moved from MSFC to beamline station 6-ID-D at the APS. Samples were melted by using a 30-W CO_2 laser; the sample temperature was measured to better than ±1K by using optical pyrometers with a wavelength range of 1.2 to 1.4 µm. Two Be windows were installed in the ESL at diametrically opposite ends of the chamber for the incident and diffracted x-ray. The diffracted beam was detected over a large q-range in less than 1 second by using a MAR3450 image plate, allowing studies of the metastable liquid in the deeply undercooled state as well as the structural identification of the transient solid phases that form during nucleation. The high-energy x-rays used (125 keV, 0.099 Å) provided a scattering range of $0 \leq q \leq 9$ Å. Figure 1 shows a levitated liquid sample in the beamline ESL (BESL) chamber.

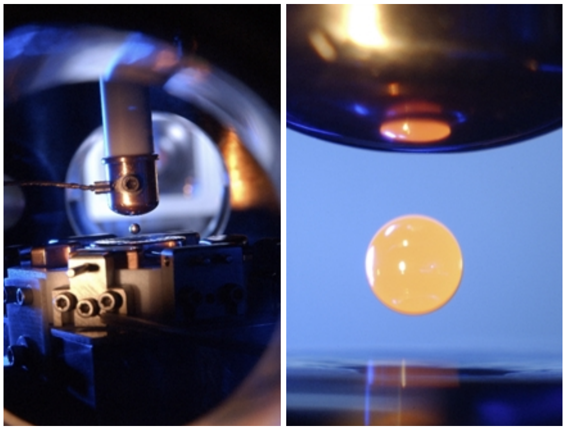

FIG. 1. Left shows levitated TiZrNi solid sphere in BESL chamber; right shows liquid TiZrNi sample.

Results

The diffraction pattern from liquid droplets of $Ti_{39.5}Zr_{39.5}Ni_{21}$ at a temperature of 1029K (liquidus is 1083K) is shown in Fig. 2 (top curve). Two abrupt increases in the sample temperature were observed during free radiation cooling of the liquid droplets. The first, with the temperature rising from 953K to a plateau temperature of 1058K, was due to the evolved heat of fusion during the liquid solidification to the metastable i-phase (Fig. 2, middle curve). This was followed within a few seconds by a second rise from 1058 to 1083K, corresponding to the transformation to the C14

Laves phase (Fig. 2, bottom curve), indicating that the i-phase is metastable; C14 is the stable phase. The fact that the i-phase is the first phase to nucleate, even though the driving free energy is less than that for the C14 phase, demonstrates that the nucleation barrier for the icosahedral quasicrystal is less.

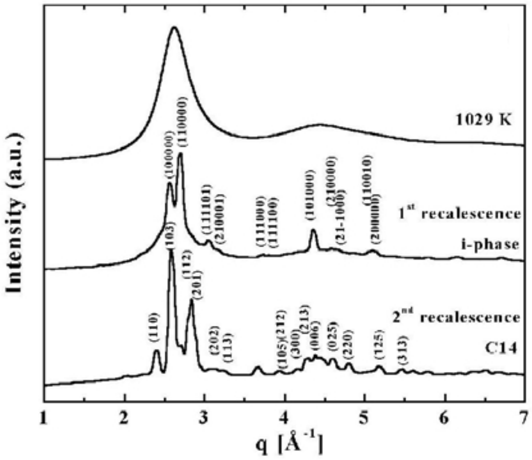

FIG. 2. X-ray diffraction patterns as a function of q for the undercooled liquid (top), during the first recalescence to the i-phase (middle) and during the second recalescence to the C14 phase (bottom) (taken from Ref. 3). © 2003 by the American Physical Society.

Figure 3 shows the x-ray structure S(q) for the $Ti_{39.5}Zr_{39.5}Ni_{21}$ liquid, measured as a function of temperature. A shoulder on the high-q side of the second peak in S(q) (marked by an arrow) is consistent with local icosahedral order in the liquid. It becomes more visible with increased undercooling, indicating that the liquid order is better defined at lower temperatures. The relative locations of the first two peaks in S(q), $q_2/q_1 = 1.72$, and the location of the shoulder on the second peak, $q_{shoulder}/q_1 = 1.97$, are in good agreement with those expected for a perfect icosahedron [4]. S(q) calculated from a 13-atom icosahedral cluster fits well to the diffraction data, supporting these conclusions.

Discussion

Collectively, these data demonstrate a correlation between growing icosahedral order in the undercooled liquid and the preferential nucleation of a metastable phase that also has icosahedral order, providing the first verification of Frank's hypothesis in any metallic liquid. The fact that structural fluctuations in the liquid act as a template, decreasing the nucleation barrier of the icosahedral phase, blurs the distinction between homogenous and heterogeneous nucleation. Nucleation theories based on a local order parameter (e.g., density functional models) are best-suited for describing such processes.

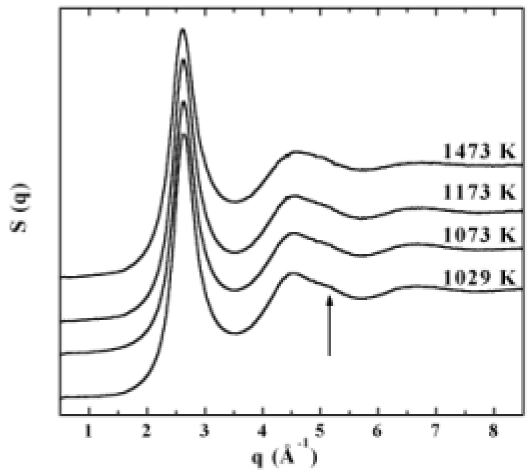

FIG. 3. S(q) for a $Ti_{39.5}Zr_{39.5}Ni_{21}$ liquid as a function of temperature (taken from Ref. 3). © 2003 by the American Physical Society.

Acknowledgments

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