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Surface Tension and Viscosity of Quasicrystal-Forming Ti–Zr–Ni Alloys[1]

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Recent X-ray scattering measurements show that icosahedral short-range order in Ti–Zr–Ni alloys is responsible for a change in phase selection from the stable C14 Laves phase to the quasicrystalline icosahedral phase, and that icosahedral short-range order increases at deeper undercoolings. This change in short-range order should be reflected in changes in the thermophysical properties of the melt. The surface tension and viscosity of quasicrystal-forming Ti–Zr–Ni alloys were measured over a range of temperature, including both stable and undercooled liquids, by an electrostatic levitation (ESL) technique. ESL is a containerless technique which allows processing of samples without contact, greatly reducing contamination and increasing access to the metastable undercooled liquid. The measured viscosity is typical of glass-forming alloys of similar composition to the quasicrystal-forming alloys studied here; however, the surface tension shows an anomaly at deep undercoolings.

KEY WORDS: electrostatic levitation; quasicrystal; surface tension; Ti–Zr–Ni alloys; viscosity.

1. INTRODUCTION

Quasicrystals are a symmetric but non-periodic arrangement of atoms, discovered in 1984 in Al–Mn alloys [1] and since in many different alloy

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systems, including Ti-based and Zr-based systems. Quasicrystals have unique physical and electronic properties that make them promising for such diverse applications as infrared sensors, non-stick coatings for bearings and cookware, and hydrogen storage.

Quasicrystal-forming systems seem ideal to test Frank's hypothesis [2] that the undercoolability of liquid metals is caused by significant icosahedral short-range order in the liquid. These icosahedral clusters are incompatible with crystalline periodicity; however, *extended* icosahedral order is found in quasicrystals. Recent results by Kelton et al. [3], show that icosahedral ordering in liquid quasicrystal-forming Ti–Zr–Ni alloys increases as undercooling increases. This clustering should be reflected in a change in thermophysical properties of the liquid.

2. MEASUREMENTS

The surface tension and viscosity of quasicrystal-forming Ti–Zr–Ni alloys were measured over a range of temperature, including both stable and undercooled liquids. Because these alloys are highly reactive and the quasicrystal formation is suppressed by oxygen, the tests were performed in high vacuum ($\sim 10^{-7}$ Torr) using NASA/MSFCs Electrostatic Levitation (ESL) Facility [4]. ESL is a containerless technique which allows processing of samples without contact, greatly reducing contamination and increasing access to the metastable undercooled liquid.

In ESL, spherical samples of approximately 2–3 mm diameter are charged and supported in a strong electric field. There is no minimum in the electric field, so the sample position is inherently unstable. However, a computer-controlled active feedback loop continuously adjusts the levitation voltage to maintain the sample position. The sample is melted with a YAG laser, and its temperature is monitored with an optical pyrometer (InGaAs detector, 1.45–1.8 μm, Impac GmbH).

Because of the need for noncontact processing, the measurements were made with the oscillating drop technique, described in detail elsewhere [5–7]. The dc electrostatic levitation field is modulated at a frequency near the resonant frequency of the levitated liquid drop, exciting surface oscillations. When the excitation is interrupted, the oscillations continue at the natural frequency of the drop, which is determined by the surface tension [8], decaying at a rate determined by the viscosity [9].

The oscillations are monitored by high-speed digital video (up to 512×512 pixels at 1000 frames/s). The oscillation video is transformed by image analysis into a curve of amplitude versus time. A bandpass Fourier filter is applied to the curve to remove low-frequency oscillations caused by movement of the sample, and then the filtered area–time data are fitted with a model waveform to determine the frequency and damping constant of the oscillations. Fitting frequency in the time domain provides better resolution than taking the frequency peak in the power spectrum because the time-domain fit does not suffer bin-width limitations from the finite sample size.

In order for the droplet oscillations to reveal the properties of the liquid, certain conditions must be met. First, the internal flow must be laminar, or turbulent dissipation will dominate viscosity in the damping of oscillations. This limitation has prevented ground-based measurements of viscosity of metals by the oscillating drop technique by electromagnetic levitation (EML). In electrostatic levitation (ESL), the positioning force does not drive fluid flow, so Marangoni or natural convection determines the internal flow velocity, and the constraint of laminar flow is easily met for many materials.

Second, the viscosity must be low enough that Rayleigh's analysis, developed for inviscid drops, is still valid. Suryanarayana and Bayazitoglu [10] provided a numerical analysis of the oscillations of drops with finite viscosity, and characterized the effect of viscosity by the parameter α^2. For mode $l=2$ oscillations, $\alpha^2 = \sqrt{8\gamma\rho R_o}/\mu$, where γ is the surface tension, ρ the density, μ the viscosity, and R_o is the undeformed spherical radius of the drop. They determine that for $\alpha^2 > 59$ there is less than a 1% deviation of the resonant frequency from Rayleigh's [8] analysis for inviscid droplets. For the samples and conditions presented, α^2 ranges from about 60 at the lowest temperatures to over 2000 at the highest, so the effect of viscosity on the measured surface tension can be neglected in these measurements.

Two further corrections to the natural oscillation frequency are required due to the net charge of ESL samples. The first, by Rayleigh [11] accounts for the mutual repulsion of surface charges, which opposes the surface tension, while the second, by Feng and Beard [12] accounts for the gradient in the imposed electric field. For the conditions of these experiments, each correction is of the order of 1%.

Samples of 30–113 mg of $Ti_{37}Zr_{42}Ni_{21}$ were prepared using high-purity elements Ti (99.995%), Zr (99.9%), and Ni (99.995%). First, the elements were arc-melted into master ingots of approximately 0.5 g. The master ingots were flipped and remelted five times to homogenize the composition. Pieces of the proper size for ESL experiments were cut from the master ingot and arc-melted again to achieve an approximately spherical shape. Special attention was paid to maintain the nonmetallic impurities as low as possible ($C < 95$ ppm, $N < 20$ ppm, $O < 166$ ppm). The samples were melted repeatedly in ESL in vacuum to homogenize them and allow maximum undercooling, then one measurement per melt cycle was made on succeeding cycles.

3. RESULTS AND DISCUSSION

3.1. Viscosity

The oscillations of a viscous droplet not subject to excitation decay exponentially. The exponential time constant τ is given by Lamb's formula [9] for mode l:

$$\tau_l = \frac{\rho R_o^2}{(l-1)(2l+1)\mu}, \tag{1}$$

where ρ is the density, R_o is the undeformed spherical radius (calculated from the mass and density), and μ is the viscosity. The measurements presented here were made on mode $l = 2$ oscillations.

This formula requires the density of the liquid sample to be known, unlike the equation for surface tension (Eq. (2)). Noncontact optical measurements of the density of liquid Ti–Zr–Ni alloys are currently underway, but results are not available. However, given the scatter in viscosity data, a reasonable estimate of the density of $Ti_{37}Zr_{42}Ni_{21}$ is easily obtained. The room temperature density was estimated at $6.21\,g\cdot cm^{-3}$ from the radius measurement of a 3.05 mm diameter sphere processed in the ESL. Assuming that the thermal expansion coefficient is comparable to that of a glass of similar composition of $Ti_{20}Zr_{60}Ni_{20}$ (8×10^{-6} /K), and a 5% expansion occurs on melting, the density was estimated to be 5.79–$5.80\,g\cdot cm^{-3}$ for the liquid over the temperature region of interest.

The viscosity of the quasicrystal-forming composition $Ti_{37}Zr_{42}Ni_{21}$ was measured in both the stable and undercooled liquid states. The measurements ranged from about 600 K above the solidus temperature to about 110 K undercooled, only 7 K above the recalescence temperature. In this temperature range, the viscosity changes by more than 1.5 orders of magnitude. Ninety-five measurements on five samples of masses 30.4–113 mg are presented in a semilog plot in Fig. 1.

The data in Fig. 1 all lie within the scatter of the data and follow the Arrhenius law, as shown by the straight line. The activation energy calculated from the slope of the straight line is $69\,kJ\cdot mol^{-1}$. This value is much higher than in transition metals ($50.2\,kJ\cdot mol^{-1}$ for Ni and $41.4\,kJ\cdot mol^{-1}$ for Fe [13]), suggesting the formation of a network of clusters in the liquid. Interestingly, this is the first measurement of viscosity of any Ti–Zr–Ni alloy in the liquid and undercooled state. Measurements of other compositions which nucleate β(Ti/Zr) (low Ni) and the C14 Laves phase (27at.% < Ni < 33at.%) are in progress.

Because this alloy is close in composition to bulk metallic glass forming alloys, the viscosity should be expected to follow the Vogel–Tammann–Fulcher (VTF) law [14–16] $\mu = \mu_o \exp(B/(T - T_o))$ where μ_o, B, and T_o

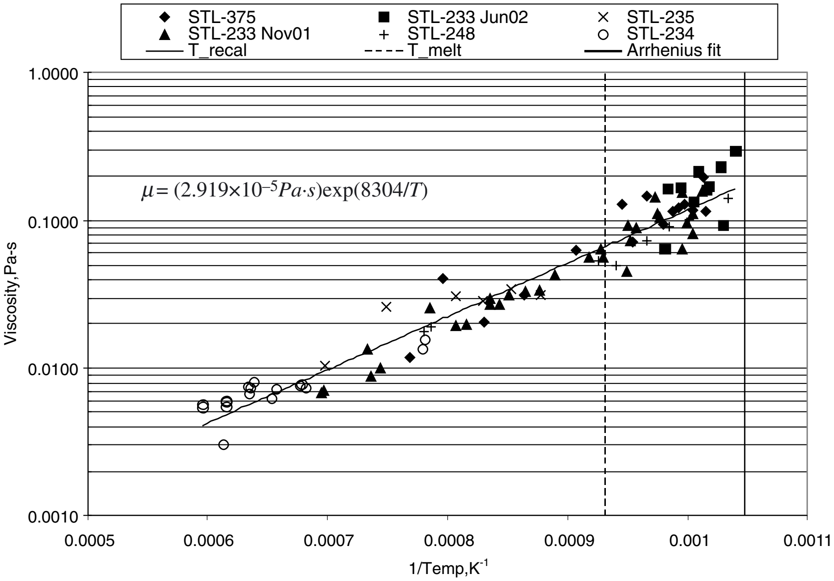

Fig. 1. Viscosity of $Ti_{37}Zr_{42}Ni_{21}$ in the stable and undercooled liquid shows a good fit to a single Arrhenius equation from 110 K below to 600 K above the solidus temperature.

are the constants whose physical significance is discussed further in terms of fragility in [17]. However, even with the wide temperature range measured, it is not possible to distinguish between Arrhenius and VTF fits for these data.

3.2. Surface Tension

The natural frequency f_l of surface oscillations of a liquid droplet in mode l are given by Rayleigh's equation [8]:

$$f_l = \sqrt{\frac{l\,(l-1)\,(l+2)\,\gamma}{3\pi m}}, \qquad (2)$$

where γ is the surface tension and m is the mass of the droplet.

The surface tension results presented in Fig. 2 show several remarkable features. First, the upper band shows measurements from about 50 K undercooled to over 600 K above the melting point. These measurements on five different samples of masses ranging from 30.4–113 mg show a standard error of only ± 1.5%. The slope of surface tension versus temperature in this range is very small, with indeterminate sign.

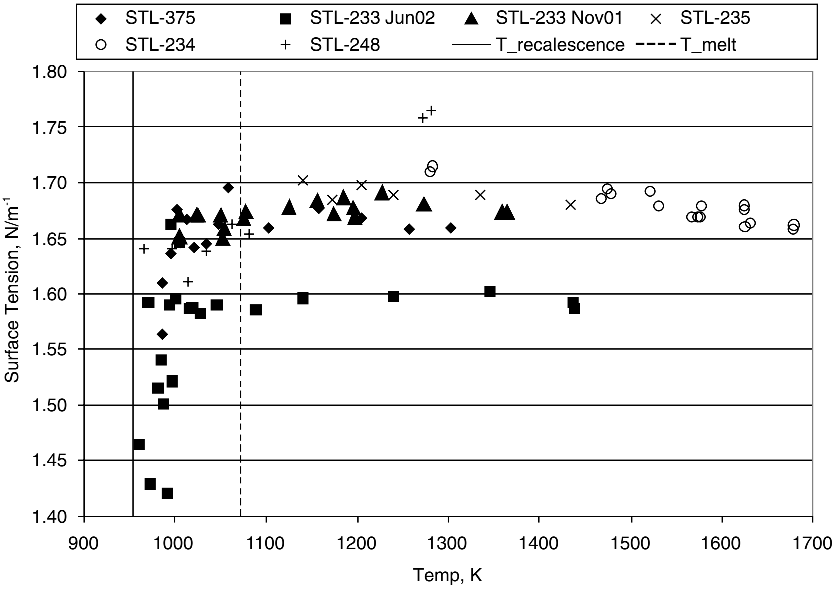

Fig. 2. Surface tension of $Ti_{37}Zr_{42}Ni_{21}$in the stable and undercooled liquid shows a fit within ±1.5% to a single line from 50 K below to 600 K above the solidus temperature (upper band), but a sharp decrease below about 70 K undercooling. The solid squares (lower band) show the same slope and sharp decrease, but with a 5% lower value of surface tension presumably caused by oxygen contamination due to storage in laboratory air.

The lower band (filled squares) represents a single sample, STL-233, of 57 mg mass. This band is extremely self-consistent, showing a scatter of less than ±1% and the same slope as the upper band. What is surprising about this lower band is that these data are from the same sample as the filled triangles in the upper band. The difference between these data sets is storage in lab air for 7 months. The surface tension is changed by over 5%, even though the undercooling behavior and phase selection are not yet affected. This series is presumed to show a strong effect of oxygen on the surface tension of these alloys.

The most interesting feature is the sharp drop in surface tension at about 1000 and 70 K undercooled. After having changed less than 2% in 650 K, the surface tension suddenly falls almost 20% in less than 50 K. The drop is consistent, appearing in all three samples with data in this temperature range.

This behavior is not caused by viscous effects on the oscillation frequency; as discussed above, viscous effects would only cause a 1% drop in surface tension at these temperatures. That leaves us with the possibility that the sudden change in surface tension represents a physical change in the structure of the liquid at these temperatures.

The hypothesis of a physical change in the liquid structure is supported by the X-ray data of Kelton et al. [3], which indicate an increase of icosahedral short-range order in melts of this composition with increasing undercooling. Even more compelling are unpublished results [18] from the same group which indicate a sharp maximum in specific heat at the same temperature. However, any change in viscosity is small at best, and no such change can be inferred from the data in Fig. 1.

4. CONCLUSIONS

Measurements of surface tension and viscosity of $Ti_{37}Zr_{42}Ni_{21}$were made, using five different samples of masses from 30.4 to 113 mg. The surface tension data are very self-consistent, with a slope near zero and a scatter of ±1.5%, and clearly demonstrate the sensitivity of the surface tension in this system to oxygen. The data show a sudden change in surface tension at about 1000 K, which is attributed to a change in local structure in the liquid. This change is correlated with X-ray scattering data and a similar drop in specific heat, but there is no corresponding change in viscosity apparent from the data.

Further theoretical work is required to explain a change that affects X-ray scattering, surface tension, and specific heat, but not viscosity. Measurements of all of these properties and others (such as density and electrical conductivity) are needed in various alloys with and without strong local icosahedral short range order to better understand the changes in deeply undercooled quasicrystal-forming liquids and the role these changes play in phase selection and nucleation of solid crystals and quasicrystals.

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