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Crystalline nucleation in undercooled liquid nickel

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ABSTRACT

We investigate crystalline nucleation in undercooled liquid Ni by means of x-ray absorption temperature scans in powder samples dispersed in Al_2O_3. We show that the crystallization process is initially dominated by a heterogeneous nucleation process that induces a purity/size selection effect. The nucleation rate displayed by the residual mass fraction of about 30% (determined down to 364 K below the melting point) is in agreement with empirical data from previous single droplet experiments extrapolated to the deeper undercooling range presently achieved. We investigate the possibility that this ultimate nucleation process is actually homogeneous by computing the rate in the framework of the classical nucleation theory. We adopted a recently implemented kinetic Monte Carlo simulation approach using extrapolated values for the self-diffusion coefficient and empirical or simulated models for the excess free energy. The comparison between measured and calculated rates indicates that the homogeneous nucleation scenario is likely.

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1. Introduction

Elemental nickel is a representative 3*d* transition metal exhibiting a close packed liquid phase above the melting temperature $T_m = 1728$ K at ambient pressure. Ni, similarly to other elemental or complex liquids, can be appreciably undercooled below T_m into a metastable liquid state. Following Frank's suggestions [1] that the possible icosahedral short range order developing in the undercooled liquid state is responsible for the large degree of undercooling and the successive views on the polytetrahedral structures in liquids [2], several modern experiments were performed to unravel the relevant structure details [3,4]. These experiments, performed using neutron scattering on electromagnetically levitated samples [3] down to 1435 K or X-ray absorption spectroscopy [4] down to 1493 K, agree that a certain degree of icosahedral short range order develops upon undercooling. Large-scale molecular dynamics (MD) simulations, recently performed [5] to model iron melts, were able to provide an atomistic insight into the nucleation process.

A major issue regards the characteristics of the crystalline nucleation process limiting the lower accessible temperature. The phenomenon is currently understood in the framework of the classical nucleation theory (CNT) [6]. For volume nucleation phenomena the temperature dependent physical quantity of interest is the nucleation rate per unit mass $J(T)$. Any sample of mass m subject to isothermal or cooling processes under thermodynamic equilibrium will have a survival probability in the molten state at time t equal to

$$P_\ell(t) = \exp\left(-\int_0^t mJ\left(T\left(t'\right)\right)dt'\right). \quad (1)$$

In the ideal case of homogeneous nucleation $J(T) = J_h(T)$ while in the presence of heterogeneous nucleation effects $J(T) \gg J_h(T)$ and the probability $P_\ell(t)$ will be correspondingly reduced as well as the accessible undercooling T range. Early estimates of the nucleation rate based on the maximum observed undercooling temperature have been superseded by modern approaches based on the inversion of the information on the inhomogeneous Poisson process embodied in Eq. (1) on a set of repeated thermal cycles on the same sample. Early treatments [7–9] based on a model dependent inversion were successively improved adopting model independent approaches [10–14]. In these approaches it is possible to retrieve experimental information on $J(T)$ that is subsequently analyzed to asses the nature of the dominant processes. In a set of

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recent papers [13,15] undercooled liquid Ni samples embedded in a molten glass matrix were subject to repeated thermal cycles in a differential scanning calorimeter (DSC) obtaining $J(T)$ in the 1418–1443 K range. The data interpretation was supported by umbrella sampling Monte Carlo simulations to obtain the excess free energy of a nucleus of size n, $\Delta G(n,T)$, embedded in the surrounding undercooled liquid for the adopted model interaction. The results provide a strong evidence that the samples were actually subject to homogeneous nucleation and, in spite the simulations displayed evident departures from the spherical nucleus shape, the $\Delta G(n^*,T)$ barrier height (where n^* is the critical nucleus size) was found to follow the temperature dependence predicted by the CNT.

In this paper we extend our previous work [4] and focus on the information related to the nucleation rate that can be obtained from x-ray absorption temperature scans [16] based on a previously assessed methodology [17]. The idea behind this approach is that by using a phase sensitive bulk probe, such as the x-ray absorption coefficient at a selected energy in the element absorption edge region, it is possible to measure the sample liquid (and solid) fractions as a function of temperature (and time) during repeated thermal cycles probing (and averaging) simultaneously about 10^7 droplets. It will be shown that the highest purity fraction of our sample displays a nucleation rate in agreement with previous data extending the undercooling range down to ≈370 K. In order to investigate the nature of the nucleation process the experimental rates are compared with calculated rates for various models, within the coarse grained CNT scenario, using a recently developed kinetic Monte Carlo (KMC) simulation scheme [18]. The paper is organized as follows: in Sec. 2 we discuss and clarify how the nucleation rate in the 1350–1470 K range was obtained in comparison with previous experiments. In Sec. 3 the newly implemented kinetic Monte Carlo simulation approach [18] was used to compute the Ni nucleation rate within the CNT assumptions or adopting the published $\Delta G(n,T)$ functions. The results are discussed in Sec. 4 and conclusions are drawn in Sec. 5.

2. X-ray absorption temperature scans

2.1. Experimental details

The experiment, described in a previous paper [4], was performed at the BM29 beamline [19,20] of the European Synchrotron Radiation Facility using an energy scanning monochromator equipped with a Si(311) flat crystal pair. The rectangular beam size was defined by the primary slit vertical aperture 0.3 mm and the horizontal aperture of the secondary slits prior to the first ion chamber set to a size of 2.0 mm. Samples suitable for X-ray absorption measurements in transmission mode were prepared from a mixture of sub-micron size Ni powder (99.9% purity) and alumina (Al_2O_3) powder in a 1:20 mass ratio suspended in ethyl alcohol, subject to ultrasonic mixing and filtered through a poly-carbonate membrane. The homogeneous mixture of the two powders was pressed in 13 mm diameter and about 100 μm thick pellets suitable for the successive thermal treatments. The overall Ni surface density was optimized for an absorption contrast at the edge of about 1.0–1.5 while the amount of alumina was determined by the compromise to limit the background absorption and simultaneously achieve a sufficient dispersion of the Ni powder. The sample slices were inserted into a folded graphite foil (with a negligible x-ray absorption) acting as a resistive heater and providing a uniform temperature field. This crucible was placed in the center of a high-vacuum $P \approx 10^{-3}$ Pa cylindrical Pyrex glass vessel with suitable x-ray windows. Alumina was not found to react with Ni at the temperatures involved in the experiment in a similar way to the Pd case [21]. In the first thermal cycles a sintering of the alumina grains occurs leading to a slight shrinking of the sample pellets but successively the samples become mechanically stable and can be subject to repeated cycles maintaining the same average Ni surface density relevant to the x-ray transmission measurement. The sample temperature was measured with a high-temperature pyrometer pointing on the outer side of the crucible and calibrated using the graphite emissivity and the Ni melting signature at T_m. The maximum absolute uncertainty in the temperature measurement in the range of interest is ±15 K. The sample phase was assessed using both x-ray diffraction measurements, collected with an area detector, and x-ray absorption spectroscopy at the Ni K-edge. The sample absorption coefficient, apart from a smooth irrelevant background associated with the windows, crucible, Al_2O_3 absorption and ion chamber setting, is related to $\alpha = \ln(I_0/I_1)$ where I_0 and I_1 are the electron currents in the upstream and downstream ion chambers. Preliminary XAS spectra were collected to verify the contrast between solid (prior to melting) and undercooled liquid phases at $T_u \simeq 1493$ K as shown in Fig. 1 and the point of highest contrast identified in the edge region at $E^* = 8.3382$ keV.

2.2. Temperature scans

By setting the monochromator energy to E^* it is possible to measure the sample absorption while cycling the temperature in the desired range. Examples of these temperature scans are reported in Fig. 2. The sample switches from the low absorption solid phase level to the higher liquid phase absorption level (at this selected energy), following the phase transitions occurring in the scan. The sharp rise of absorption at T_m in the heating ramps marks sample melting and the small temperature interval in which this transition occurs $\Delta T \approx 10$ K is due to the temperature spread across the sample area probed by the x-ray beam at T_m. An even better temperature homogeneity (estimated within $\Delta T \approx 2$–3 K) occurs in the cooling ramps and at lower temperatures. In the cooling ramps the evident hysteresis indicates that Ni droplets crystallize only in the temperature range between 1450 K and 1370 K

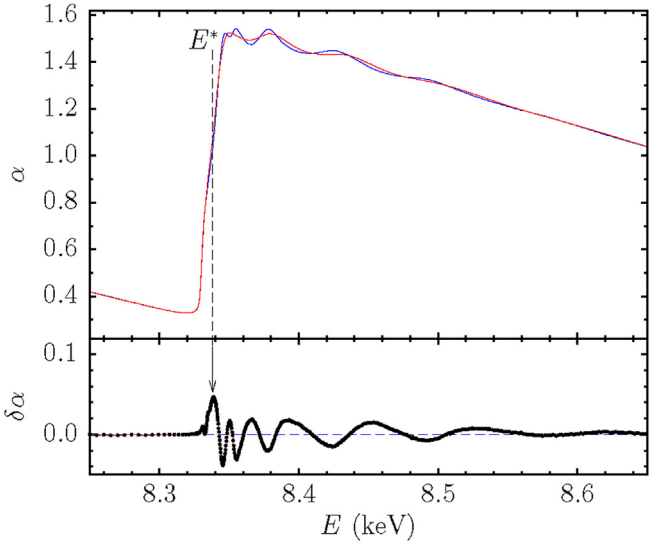

Fig. 1. Ni K-edge x-ray absorption spectra of the liquid (red) and solid (blue) phases at $T_u \simeq 1493$ K. The difference spectrum $\delta\alpha = \alpha_\ell - \alpha_s$ is reported in the lower panel on a magnified scale. The vertical arrow marks the energy E^* corresponding to the maximum contrast. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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