EFFECT OF HEATING RATE AND GRAIN SIZE ON THE MELTING BEHAVIOR OF THE ALLOY Nb–47 MASS% Ti IN PULSE-HEATING EXPERIMENTS

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Abstract — The effect of heating rate and grain size on the melting behavior of Nb–47 mass% Ti is measured and modeled. The experimental method uses rapid resistive self-heating of wire specimens at rates between \(10^2\) and \(10^4\) K/s and simultaneous measurement of radiance temperature and normal spectral emissivity as functions of time until specimen collapse, typically between 0.4 and 0.9 fraction melted. During heating, a sharp drop in emissivity is observed at a temperature that is independent of heating rate and grain size. This drop is due to surface and grain boundary melting at the alloy solidus temperature even though there is very little deflection (limited melting) of the temperature–time curve from the imposed heating rate. Above the solidus temperature, the emissivity remains nearly constant with increasing temperature and the temperature vs time curve gradually reaches a sloped plateau over which the major fraction of the specimen melts. As the heating rate and/or grain size is increased, the onset temperature of the sloped plateau approaches the alloy liquidus temperature and the slope of the plateau approaches zero. This interpretation of the shapes of the temperature–time curves is supported by a model that includes diffusion in the solid coupled with a heat balance during the melting process. There is no evidence of loss of local equilibrium at the melt front during melting in these experiments.

Keywords: Alloy; High temperature; Diffusion; Melting

1. INTRODUCTION

We investigate the extent to which diffusion limitations in the solid affect the melting behavior of alloys. Specifically we examine the effects of heating rate and grain size on the shape of the temperature vs time curve during pulse melting of Nb–47 mass% Ti. Both of these factors strongly affect the extent of solid diffusion. The experimental method employed here is based on rapid resistive self-heating of wire specimens into their melting range at rates between \(10^2\) and \(10^4\) K/s. Heating at these rates permits the partially molten wire sample to survive up to melted fractions between 0.4 and 0.9 before collapsing. The technique is particularly suitable for measurement of thermophysical properties and melting behavior of refractory metals [1].

With this technique, the radiance temperature is measured during heating at two wavelengths with high-speed pyrometers. Simultaneously, the normal spectral emissivity is measured with a high-speed laser polarimeter. During melting, changes in emissivity due to either surface smoothing or due to intrinsic differences between solid and liquid are therefore directly measured. Frequently the emissivity drops \(\sim 5\%\) at the start of melting for elements. Therefore, it is only with corrections due to changing emissivity that reliable true temperature vs time curves can be obtained during melting. Using this technique for pure metals, an arrest or plateau, corresponding to melting, is obtained that is isothermal to within \(\sim 1\) K [2] at temperatures that agree with accepted melting points to within several kelvin. Thus despite the rapid heating, the assumption of equilibrium during melting is in practice realized with this technique for pure metals.

However, during heating of an alloy, equilibrium conditions at a melting interface require the liquid and solid concentrations to differ according to the phase diagram liquidus and solidus. If diffusion of solute is sufficiently fast to ensure that no concentration gradients exist in the liquid and solid phases at each instant during the melting process, the fraction of solid during melting as a function of temperature is given simply by the phase diagram and the lever rule. Thus, as is well known, a temperature vs time curve during slow melting exhibits an abrupt decrease in slope at the solidus temperature, a smooth curve up to the liquidus temperature, followed by an abrupt increase in slope above the
liquidus. This is the basis of traditional thermal analysis techniques such as DTA.

For increased rates of melting, this full equilibrium is usually quite difficult to achieve for substitutional metallic solid solution phases; i.e. a concentration profile will exist in the solid. In this case the shape of measured temperature vs time curves will depend on heating rate. Under the assumption of local equilibrium at the interface, several authors have described the diffusion of solute in the solid phase that necessarily accompanies melting. Verhoeven and Gibson [3] describe how a planar interface, which is melting directionally at constant speed, is at the liquidus temperature due to the concentration profile in the solid. Wan et al. [4] have modeled and measured the concentration profiles in the liquid and solid during isothermal melting as a method to measure liquid diffusion coefficients. In Section 2, we present an analysis of diffusion during melting using local interfacial equilibrium that is relevant for the interpretation of the results obtained using this pulse melting technique.

We note the extensive literature on premelting of pure metals. Experiments and theory on the formation of “quasiliquid layers” of atomic dimensions on sample surfaces below the equilibrium melting temperature have been summarized by Dash [5]. Observation of surface premelting requires the use of samples that have large surface area to volume ratios for calorimetric studies or requires the use of surface structure sensitive experimental techniques such as proton backscattering. Surface premelting is not detected with the technique employed in this paper as proven by the accuracy of melting point determinations with this method for pure metals. However, we do anticipate the initiation of melting at, or slightly above, the solidus temperature at the grain triple junctions and grain boundaries [6], as well as the sample surface.

The alloy studied here, Nb–47 mass% Ti, was chosen due to its commercial availability in wire form, its particularly simple phase diagram and its relatively high melting range, which is most suitable for the pyrometric technique. The most recent thermodynamic assessment of the binary Nb–Ti phase diagram [7] optimizes available solidus data and is consistent with accepted heats of fusion and melting temperatures at the grain triple junctions and grain boundaries. The phase diagram is shown in Fig. 1. The calculated diagram is consistent with accepted heats of fusion and melting temperatures at the liquidus. This is the basis of traditional thermal analysis techniques such as DTA.

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\[ 4 \pi \int_0^{R(t)} \frac{dc_L(r, t)}{dt} r^2 dr + 4 \pi r^2 \frac{dr}{dt} C_S(r, t) = \frac{4}{3} \pi (R^3 - r_i^3) \frac{dC_i}{dt} - 4 \pi r^2 \frac{dr}{dt} C_L(t) = 0. \]  

(4)

Using equation (1) to permit integration of the first term, and the definition of fraction liquid, equation (4) becomes the flux condition, equation (2).

Conservation of heat requires that the net power represented by the implicit assumption that the net power losses are held constant, a fact that is very nearly true during melting of the specimens studied.

Thus equation (5) represents the implicit assumption that the net power heating the specimen (resistive heating minus radiative losses) is held constant, a fact that is very nearly true during melting of the specimens studied.

The dimensionless Fourier number, \( \hat{F} \), can be characterized by the size of the dimensionless equations, and thus the melting process for the other grain sizes \( R \) as it can be determined from these results with suitably rescaled values of \( \hat{T} \). Indeed the importance of solid diffusion can be characterized by the size of the dimensionless Fourier number, \( F_0 \).

\[ F_0 = \frac{D_b t_m}{R^2} = \frac{D_b \left( \frac{L}{c_p} + (T_L - T_S) \right)}{T R^2}. \]  

(9)

For subsequent discussion, the instantaneous melting velocity is easily obtained from the geometry as \( \left( \frac{1}{3} \right) (R^3 - r_i^3) \frac{d(r_i^3)}{dt} \) (equation (7)).

Calculations were performed for a variety of heating rates for the fixed value of \( R \). We note that for fixed materials parameters, one can substitute dimensionless length \( \hat{r}' = r/R \) and time \( \hat{t}' = t/t_m \) into equations (1), (2) and (5) to show that the dimensionless equations, and thus the melting curves, depend on \( \hat{T} \) and \( R \) only through the product \( T R^2 \). Thus there is no need to recompute the melting process for the other grain sizes \( R \) as it can be determined from these results with suitably rescaled values of \( \hat{T} \). Indeed the importance of solid diffusion can be characterized by the size of the dimensionless Fourier number, \( F_0 \).

\[ t_m = \frac{(L/c_p) f_L + (T_L - T_S)}{T}. \]  

(8)

Figure 2 shows the predicted \( T(t) \) curves for various heating rates with time normalized by the total melting time, \( t_m \). The behavior for melting with full equilibrium (lever law) is also included. For the equilibrium and slow heating rates, a significant break of slope is observed at the solidus. As the heating rate increases, this break essentially disappears and the temperature continues to climb before curving to a relatively linear section (called a quasi-plateau here) at a higher temperature. At the highest heating rates the quasiplateau approaches the liquidus temperature. Thus at high heating rate, very little of the grain melts at temperatures near the solidus and there is practically no change in slope of the heating curve. The majority of the grain (and the entire sample) melts at much higher temperatures near the liquidus temperature where a large decrease in slope of the melting curve is predicted. In other words, the fraction liquid as a function of temperature differs considerably from the lever rule.

Figures 3(a) and (b) show predicted concentration profiles along the radial direction within the grain for two different heating rates. The profiles show the Ti-poor region in front of the advancing melt interface and how it is more spread out for the lower heating rate. As the interface advances (i.e. as more material melts), the concentration of Ti in the solid at the liquid–solid interface decreases toward 0.356 as the liquid concentration decreases toward 0.47. These are the solid and liquid concentrations appropriate at the liquidus temperature of the alloy. The decrease toward 0.356 occurs more rapidly (at shorter distance melted) for the higher heating rate. Simultaneously, the temperature rises to the liquidus temperature more rapidly (again at shorter distance melted) for the higher heating rate. This is why, at high melting rate (or large grain size) and
under the assumption of local equilibrium, the majority of the solid specimens will melt near the liquidus temperature.

3. EXPERIMENTS

3.1. Measurement method

The electrical current pulse used to heat and melt the alloy wire was provided by a bank of batteries. The normal spectral emissivity $\varepsilon$ (hereafter called emissivity) of the specimen was measured with a high-speed laser polarimeter at 633 nm, the wavelength of the helium–neon laser of the polarimeter [9]. The radiance temperature of the specimen was measured at two bracketing wavelengths $\lambda$, 624 and 651 nm, with two high-speed solid-state pyrometers [10, 11]. A set of six (two pyrometry and four polarimetry) experimental quantities was recorded simultaneously with a high-speed digital data acquisition system having 16-bit resolution at rates, depending on the heating rate, in the range 0.5–4 kHz. The true temperature of the specimen, $T$, at each recorded time was then determined from the radiance temperature at 651 nm and the emissivity $\varepsilon$ at the wavelength $\lambda = 633$ nm† using Wien’s law

$$\frac{1}{T} = \frac{1}{T_{\text{rad}}} + \frac{\lambda}{c_2 \ln \varepsilon}$$

where $c_2 = 1.4388 \times 10^{-2}$ mK is Planck’s second constant. Details regarding the pulse heating system [12, 13] and the computer-controlled solid-state switch for the control of the current through the specimen [14] are described elsewhere. All temperatures reported in this paper are traceable to the International Temperature Scale of 1990 [15]. The estimated uncertainties (2σ deviation level) in radiance temperatures measured using this pyrometry system have been determined previously to not exceed 7 K [11, 16]. The uncertainties (2σ) of emissivities obtained with the polarimetry system were found to be less than 2%, or 5 K at the temperatures of interest [9]. The uncertainty in the true temperature obtained by combining these factors is 10 K (2σ).

3.2. Specimens

The Nb–47 mass% Ti specimens were nominally 1.6 mm in diameter and 73 mm in length, and were cut from a single coil of wire. As reported by the manufacturer, the material contains the following major impurities (p.p.m. by mass): 1200 Ta, 600 O, and 100 each Hf, Si, and Zr, with total remaining

†A small correction was made for the difference in wavelength between the polarimeter and pyrometer. The emissivity values at 651 nm used for temperature conversion in equation (10) were taken to be 0.004 (1%) higher than the measured emissivities at 633 nm. The size of this correction was obtained using the radiance temperatures measured at the two wavelengths (which differ by only ~2 K). This correction corresponds to a temperature change of less than 1 K.
500 p.p.m. of other elements. The specimens were prepared with #600 abrasive paper to provide a reproducible starting surface for both pyrometric and polarimetric measurements.

Prior to each melting experiment, specimens were heat treated to convert the deformation structure of the as-received drawn wire to an equiaxed grain structure. Using the solid state switch to control the current input, one of three pretreatments was used for each specimen: (a) pulse heating to $0.1930 \text{ K}$ followed by natural cooling ($0.200 \text{ K/s}$) or (b, c) heating to $0.2090 \text{ K}$ and holding for 3 or 20 s, again followed by natural cooling. These treatments produced structures with mean grain diameters ($2R$) of 40, 100 and 167 $\mu\text{m}$, respectively, as measured by a standard metallographic linear intercept method.

The heat treatment and pulse heating were conducted in argon (99.999% pure) slightly above atmospheric pressure.

The Ti concentration and its variation within the specimens were checked with a scanning electron microscope by energy dispersive spectroscopy using elemental standards. Three as-received specimens from different parts of the coil were cross sectioned transverse to the wire axis, polished by standard metallographic techniques and analyzed for composition at 100 points along a diameter of each cross section. The compositions were consistent with the maximum $\pm 1$ mass% variation about 47 mass% Ti specified by the manufacturer of the wire. All three specimens exhibited slight Ti enrichment toward the center and surface of the wire, with a minimum at approximately one half the wire radius. The heat treatment of the wires to establish the grain size did not alter these profiles significantly. A variation of 1 mass% in concentration corresponds to a change in solidus temperature of $-6 \text{ K}$ and liquidus temperature of $-7 \text{ K}$ following equation (6).

After heat treatment, specimens were pulse heated into their melting regions at various heating rates until they collapsed prior to complete melting. The current in each experiment was nearly constant over the melting temperature range, decreasing by $\sim 2\%$. The minimum useable heating rate is determined by the limitations of radiative heat loss whereas the maximum useable heating rate is determined by the limitations of the power supply.

### 4. EXPERIMENTAL RESULTS

The results of a typical pulse heating experiment on a Nb–47 mass% Ti sample are presented in Fig. 4(a), where specimen radiance temperature at 651 nm and normal spectral emissivity at 633 nm are plotted as functions of time. The corresponding true temperature vs time plot is shown in Fig. 4(b). In Fig. 4(a), the heating curve can be divided into three regions. The transition from Region I to II is marked by a sharp decrease in the emissivity trace and a small corresponding "kink" in the radiance temperature trace. In Region II the emissivity remains fairly constant and the slope of the radiance temperature decreases slightly. This slight decrease of slope as well as the kink are absent in the true temperature plot [Fig. 4(b)]. A substantial but gradual change in slope occurs at a higher temperature, defining the transition from Region II to III and the beginning of a sloped plateau. It is evident that the emissivity drop is not associated with this plateau. In contrast, for pure metals, the drop in emissivity occurs in conjunction with the beginning of the melting plateau.

The transition from Region I to II was defined by the *kink radiance temperature* as the first data point that deviated from the imposed heating rate during the emissivity drop. The transition from
Region II to III was characterized by another parameter called the plateau onset temperature. As shown in Fig. 4(a), this value was obtained from the intersection of the linear extrapolation of the radiance temperature traces during the rapid heating before the onset and during the slower heating after the onset. Such a construction is often used to determine the initiation of melting, but as we will see below, this interpretation is incorrect here and melting actually begins at the kink temperature. 

Fig. 4. (a) Radiance temperature at 651 nm and normal spectral emissivity at 633 nm of a Nb-47-mass% Ti specimen as a function of time during rapid heating to its melting region. (b) Corresponding true temperature vs time curve. Regions of interest are indicated in (a). The heating rate is 320 K/s and the grain diameter is nominally 40 μm.
Despite its slope, Region III will be referred to as the "plateau" for the remainder of this paper.

The acquired emissivity data are often noisier and are also more sensitive to specimen motion than the radiance temperature data. Increased specimen motion is encountered in the later stages of melting, just prior to specimen collapse in Region III. Therefore, for clarity, much of the data presented below will be reported as radiance temperature at 651 nm. In these cases, conversion of kink and plateau onset radiance temperatures to true temperatures was performed using average emissivities in equation (10) from data just prior to and after the large emissivity drop, respectively. The mean value of the emissivity at 651 nm (averaged over 20 data points for each test and then averaged over all the tests) just prior to the kink is 0.414 with a standard deviation of 0.014. The mean value of the emissivity after its drop is 0.389 with a standard deviation of 0.005. The changes in true temperature due to one standard deviation in these emissivity values are 7 and 3 K, respectively.

A summary of the kink and plateau onset radiance temperatures as functions of grain size and heating rate is shown in Fig. 5. Heating rates prior to the kink are given in terms of true temperature, which are 1.2 times the heating rates in radiance temperature for an emissivity value of 0.41. It can be seen that the kink radiance temperature is essentially independent of the heating rate. The lower dashed horizontal line in Fig. 5 represents the average kink radiance temperature of 1959 ± 3 K (unless otherwise noted, ± represents 1σ). In contrast, the plateau onset radiance temperatures show a consistent increasing trend with heating rate. A distinct grain size effect is also apparent. The data approach an asymptotic value (upper dashed horizontal line in Fig. 5) of 2004 ± 2 K obtained by fitting the data for each grain size (solid lines) to a simple function $T = a + bT^{-c}$, where $a$, $b$, and $c$ are fitting parameters. Using the average values of the emissivities before and after the kink, respectively, the average kink temperature and the asymptotic plateau onset temperature convert to true temperatures of 2125 ± 3 K and 2192 ± 2 K, respectively. The combination of these measurement uncertainties with those intrinsic to the experimental technique gives total uncertainties of ±10 K (2σ). The average kink true temperature and asymptotic plateau onset true temperature agree quite well with the solidus and liquidus temperatures of the alloy of 2118 and 2191 K from the phase diagram.

To determine further whether the model of Section 2 applied to the current experiments, we sought to confirm that melting was occurring at the kink despite the absence of a significant slope.

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Fig. 5. Summary of the radiance temperatures for the various specimens corresponding to the kink and plateau onset of Nb–47 mass% Ti specimens plotted against heating rate. The results for the three grain sizes are shown separately. The dashed lines are the mean kink temperature and the asymptotic value of the plateau onset temperature. The solid lines are fits to the data provided to guide the eye. The heating rates are evaluated at a temperature a few degrees below the kink. An approximate true temperature scale is shown on the right using the mean values of the emissivity.

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4Independent but less precise measurements of the liquidus and solidus using levitation melting (without measurement of emissivity) at slower heating rates, where the assumption of full equilibrium is appropriate, confirmed the liquidus and solidus temperatures of Ref. [7].
change in the heating curve. For this purpose, interrupted tests were performed to prepare specimens for examination by optical microscopy and SEM. Specimens were heated to the following temperatures and cooled: (a) just below the kink, (b) just above the kink but below the plateau onset, (c) early on the plateau and (d) later on the plateau. Microscopy of specimen surfaces (Fig. 6) indicates that the surface of (a) still exhibits surface roughness from its preparation with 800 abrasive paper. Thus no melting has occurred. This roughness disappears from the surface of (b), consistent with the measured decrease of the emissivity at the kink. Some shallow grain boundary grooves are also evident. A molten surface could smooth itself in millisecond time scales, thus lowering its emissivity. No other mechanism for surface smoothing, such as surface diffusion, would be expected to have such a sharp temperature dependence. These observations therefore suggest that liquid has formed on the specimen surface and along the grain boundaries at or just above the kink temperature. On the surfaces of (c) and (d) there are, in addition to deeper grain boundary grooves, structures at some triple junctions and grain boundaries that suggest further melting proceeding inward from the grain boundaries. Optical microscopy of cross sectioned specimens shows voids and other microstructure only in the specimens heated to the plateau (c, d). These structures are consistent with melting and resolidification of a large portion of the grains. Because the cooling rate is not very rapid (~200 K/s), some aspects of the microstructure seen in (c, d) are most probably formed during solidification. The metallography supports the conclusion that the kink at the solidus temperature and the associated drop in emissivity are due to the initiation of melting at the surface and grain boundaries.

Figures 7–9 illustrate the effect of heating rate at fixed grain size on the full melting curves. The figures plot the radiance temperature vs normalized time. Zero time for each curve was taken just prior to the kink temperature for each specimen. Normalized time is the ratio of the actual time to the total melting time, \( t_m \) defined in Section 2 (574/T s, with the heating rate, \( T \), in K/s). As the heating rate is increased, the curves shift to higher temperatures, resulting in the increase of the plateau onset temperatures already summarized in Fig. 5. The slopes of the plateaus tend to decrease with increasing heating rate for a fixed grain size.

A crude estimate of the temperature when melting would be complete if the specimens did not collapse is obtained by a linear extrapolation of the curves to a dimensionless time of unity. Inspection of all of the melting curves indicates that melting would finish at a radiance temperature in the range of 2007 ± 9 K (2σ), which converts to a true tem-
perature of $2195 \pm 11$ K ($2\sigma$), using the average emissivity value after the kink. Again, this temperature agrees quite well with the liquidus temperature of the alloy, 2191 K from the phase diagram.

Finally, Fig. 10 shows true temperature vs dimensionless time curves for 40 μm grain diameter specimens heated at 470 and 5800 K/s using point by point conversion to true temperature using the measured emissivity. The kinks, occurring at 2118 K (true temperature) for both curves, while visible in plots of radiance temperature, are not visible in the true temperature plot because they are a result only of the changing emissivity (see Fig. 4). This temperature is identical to the solidus temperature of the alloy. The plateau onset temperature is higher, and the plateau slope is lower, for the higher heating rate, trends noted previously. Both curves extrapolate to a true temperature of $\sim 2199$ K at a dimensionless time of unity, consistent with the liquidus temperature of the alloy of 2191 K.

5. DISCUSSION

5.1. Shape of temperature vs time curves

The $T(t)$ curves, computed for different heating rate (or grain size) and shown in Fig. 2, generally resemble those measured. As melting begins at the specimen surface and grain boundaries upon crossing the solidus temperature, the Ti concentration in

Fig. 7. Radiance temperature at 651 nm of Nb–47 mass% Ti specimens as a function of normalized time for the indicated heating rates for the small grain diameter materials (40 μm).

Fig. 8. Radiance temperature at 651 nm of Nb–47 mass% Ti specimens as a function of normalized time for the indicated heating rates for the intermediate grain diameter materials (100 μm).

Fig. 9. Radiance temperature at 651 nm of Nb–47 mass% Ti specimens as a function of normalized time for the indicated heating rates for the large grain diameter materials (167 μm).

Fig. 10. True temperature of two Nb–47 mass% Ti specimens as a function of normalized time for the indicated heating rates for the 40 μm grain diameter material.
the solid at the melting interface decreases rapidly with time with little associated melting [Region II in Fig. 4(a)]. As the Ti concentration in the solid at the melting interface subsequently approaches its minimum possible value (while solid is still present), the temperature approaches the liquidus temperature for the original alloy concentration [Region III in Fig. 4(a)]. Similar to that observed experimentally, the slopes of the calculated $T(t)$ curves at a dimensionless melting time of 0.5, for example, approach zero as the heating rate (or grain size) is increased. The asymptotic value at high heating rate of the experimentally observed plateau onset temperature should, and does, compare favorably with the liquidus temperature from the published phase diagram.

From the model of Section 2 we expect that, for a fixed alloy, the shapes of the experimental temperature vs dimensionless time curves will depend only on the product $\hat{T}R^2$ ($R$ is the grain radius). We therefore plot in Fig. 11 the plateau onset temperatures as a function of $\hat{T}R^2$. The data collapse well to a single curve. The solid line is a fit of the data employing the same functional form as used in Fig. 5 to guide the eye.

While the general trends of the experimental $T(t)$ curves with changing grain size and heating rate agree with those calculated, the calculated curves are more rounded than the measured curves in the region of the plateau onset. Thus it is difficult to define an unambiguous “plateau onset temperature” from the calculated curves for comparison to experiment. Nonetheless, we have defined a theoretical plateau onset temperature by finding the intersection temperature of tangents to the calculated melting curves at dimensionless times of 0.1 and 0.5. The heating rate dependence of this theoretical plateau onset, expressed as radiance temperature and plotted using the $\hat{T}R^2$ relation, is compared to the measured data in Fig. 11. The agreement is seen to be quite good using the materials parameters in Section 2. Even better agreement can be obtained using a diffusion coefficient that is a factor of two smaller than the literature value. Alternately this would correspond to using a grain size larger by a factor of $\sqrt{2}$.

Preferential melting near the wire center might have been expected because radiative losses at the surface should lead to a radial temperature gradient. We obtain an upper bound on the temperature difference between the center and surface of the wire by solving the steady state heat flow equation for an infinite cylinder (wire) with a uniform source term within the wire and a radiative loss term on the wire surface. This temperature difference, given by $T^4\sigma\beta R/2k$, is small (~3 K) at the highest temperature, $T = 2200$ K, for specimen radius $R = 0.8$ mm, approximate conductivity $k =$
67 W/m K (Nb at 1900 K), emissivity ε = 0.4, and σ_B being Boltzmann’s constant.

The applicability of the analysis in Section 2 also assumes that the temperature (and the liquid concentration) remains uniform within each grain during melting. A simple estimate of when a uniform temperature assumption is valid requires that \( t_m \gg R^2/\alpha \) where \( \alpha \) is the thermal diffusivity, with typical values of \( 10^{-1} \text{cm}^2/\text{s} \). A similar analysis for liquid solute diffusion would replace \( \alpha \) with \( D_L \), the liquid diffusion coefficient, with typical values of \( 5 \times 10^{-5} \text{cm}^2/\text{s} \). These conditions are met except for liquid solute diffusion at the highest heating rate and largest grain size. A revised model, which includes solute diffusion in the liquid, was formulated. The resultant temperature vs time curve for 5000 K/s and \( R = 25 \mu \text{m} \), for example, is only a few kelvin higher than that shown in Fig. 2, and then only toward the end of melting (\( t/t_m > 0.9 \)) when liquid diffusion distances are greatest. The assumption of a uniform liquid in the model is therefore applicable to the majority of the experimental data.

Using the grain radius produced by the heat treatments as the length scale for the analysis of diffusion seems to provide a reasonable approximation to the measured \( T(t) \) curves. For the data shown, the heat treatments used to establish the different grain sizes were of considerably longer duration than the melting experiments. Thus the grain size does not change significantly during the melting runs. Plateau onset temperatures obtained from slower tests on 40 \( \mu \text{m} \) grain specimens are not included in this publication; microscopy from interrupted tests at these slower heating rates revealed further grain growth during the heatup to melting. It should be noted that the melting solid is constitutionally superheated and therefore the melting interface may develop Mullins–Sekerka type instabilities [17]. Another possibility would involve nucleation of liquid pockets in front of the melting interface. Such effects would require a more complex model of melting involving other length scales.

5.2. Validity of local equilibrium assumption

Our results indicate that the assumption of local equilibrium made in Section 2 seems reasonable for the interpretation of these experiments. Unfortunately, little is known about loss of local equilibrium during melting.

Allen et al. [18] sought evidence for loss of local equilibrium during the melting process, particularly \( T_0 \) (diffusionless) melting in analogy with \( T_0 \) freezing [19]. During the melting of a population of small droplets of a Sn–Bi alloy at rates between 0.1 and 50 K/s, they observed a change of slope in temperature vs time curves at a temperature consistent with a thermodynamic estimate of the \( T_0 \) temperature for the alloy. As the heating rate was increased, the signal associated with the \( T_0 \) temperature increased (larger number of droplets participating) at the expense of the signal associated with melting at the solidus. Allen et al. argued that \( T_0 \) melting occurred at relatively low heating rates because the interdiffusion diffusion coefficient in solid Sn–Bi (4.1 \( \times 10^{-10} \text{cm}^2/\text{s} \)) is one or two orders of magnitude lower than that for most substitutional solid solutions at their solidus (\( 10^{-8}–10^{-9} \text{cm}^2/\text{s} \)). The interdiffusion coefficient for the Nb–Ti alloy extrapolated to the solidus [8] (6.0 \( \times 10^{-8} \text{cm}^2/\text{s} \)) is more than two orders of magnitude higher than that for Sn–Bi. Thus using the argument of Allen et al., we would not expect to observe \( T_0 \) melting in Nb–Ti at heating rates used by Allen et al. Indeed we observed no experimental event for the Nb–Ti alloy, at any heating rate, associated with the \( T_0 \) temperature of 2151 K calculated from the thermodynamic parameters from the phase diagram evaluation [7]. Rettenmayr et al. [20] have recently performed experiments from which they inferred that a significant loss of local equilibrium occurs during the melting of an aluminum alloy at interface speeds as low as 10 \( \mu \text{m/s} \). As argued below, we expect no such effect for the Nb–Ti alloy in the present experiments.

To gain some insight as to when significant loss of local equilibrium might be expected during melting, we examine the situation for freezing, which has been extensively studied [21, 22]. Loss of local equilibrium is normally associated with interface speeds that approach a characteristic diffusive speed. As the solidification speed is increased, a continuous kinetic change occurs from “local equilibrium” freezing to “\( T_0 \) freezing” where no solute diffusion is required. From theoretical models, this diffusive speed scales with \( D_0/d \), where \( D_0 \) is the diffusion coefficient in the interfacial region, a quantity not directly measurable. The interface thickness, \( d \), is usually taken as \( \sim 10^{-7} \text{cm} \). Experiments have indicated that this speed depends on the alloy system and lies in the range between 6 and 38 m/s for metallic alloys. An attempt to correlate \( D_0 \) with \( D_L \), the liquid diffusion coefficient, and/or \( D_S \), the solid diffusion coefficient, has not been very successful [22], but \( D_I \) is clearly closer to \( D_L \) than to \( D_S \) for solidification.

One hypothesis would then suggest that, on melting, nonequilibrium interface effects would be significant when the melt front velocity is greater than the speed \( D_0/d \). For Nb–Ti, \( D_S = 6 \times 10^{-8} \text{cm}^2/\text{s} \) [8], giving a characteristic speed of \( \sim 0.6 \text{cm/s} \). On the other hand, a recent theoretical investigation using the phase-field method by Ahmad et al. [23] indicates that the critical speed for solute trapping for both melting and solidification is the same and depends only on the value of \( D_I \) and not on the diffusion coefficient of the parent phase. This alternative hypothesis would anticipate that the critical speed for trapping during melting would be the same as for freezing; i.e. in excess of \( 10^2 \text{cm/s} \).
These two estimates, 0.6 and 100 cm/s, are both larger than the melting speeds achieved in the current experiments. An expression for the melting speed is given in Section 2 as \( (1/3)(R^3/r_f^2)(dL/dt) \). Using \( 1/f_m \) as an approximation for \( dL/dt \), one obtains

\[
\frac{1}{3} \frac{R^3}{r_f^2} \frac{T}{[L/c_p + (T_L - T_S)]}
\]

for the melting speed. This expression gives values that agree quite well with the numerical velocity results obtained from our numerical calculations. For the most rapid melting experiment in this study (largest grain radius of 83 \( \mu \)m, highest heating rate of 10\(^4\) K/s), the melting speed \( V \) is 0.05 cm/s at \( f_L = 0 \), and 0.22 cm/s at \( f_L = 0.9 \). These melting speeds are smaller than both estimates required for significant solute trapping during melting. Thus it is reasonable that the local interfacial equilibrium hypothesis is valid for these experiments. Experiments at higher heating rates are planned using a microsecond pulse heating system [24].

6. CONCLUSIONS

1. Through simultaneous measurements of radiance temperature and emissivity, true temperature vs time curves have been obtained for the melting of Nb–47 mass\% Ti alloy at heating rates between \( 10^2 \) and \( 10^4 \) K/s.
2. A significant drop in emissivity occurs as melting starts at the solidus temperature and the specimen surface is smoothed. However, the major portion of the specimen melts on a sloped plateau initiated at a higher temperature, which increases towards the liquidus temperature as the grain size and/or the heating rate are increased.
3. Predictions obtained using a solid diffusion analysis with melting proceeding from the grain boundaries toward the grain centers and local equilibrium at the melt interface are consistent with the measured temperature vs time curves. Specifically, initial melting at the solidus involves only a small volume of material due to the limited solid diffusion. Moreover, the majority of the enthalpy input is absorbed near the liquidus temperature causing the formation of the plateau near this temperature. The analysis properly describes the effect of heating rate and grain size variations.
4. The highest melting speed obtained in these experiments, i.e. for the largest grain size and fastest heating rate, is only \( \sim 0.2 \) cm/s, a speed apparently not rapid enough to cause a loss of local equilibrium at the melt interface in this alloy system.
5. This interpretation of the temperature vs time curves enables a method to measure liquidus and solidus temperatures of refractory alloys.

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