High Melting Points of Tantalum in a Laser-Heated Diamond Anvil Cell

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In situ x-ray diffraction has been used to characterize the structural modifications of tantalum samples under intense laser irradiation, up to 135 GPa in a diamond anvil cell. Melting data points are obtained that do not confirm the previously reported anomalously low melting curve. Two effects are identified that might alter the melting determination of refractory metals such as Ta under high static pressures. First, a strong chemical reactivity of Ta with the pressure transmitting media and with carbon diffusing out from the surface of the anvils is observed. Second, pyrometry measurements can be distorted when the pressure medium melts. The strong divergence between *ab initio* calculations, shock measurements and static determination is resolved here and hence many theoretical interpretations are ruled out. Finally, the body-centered cubic phase is stable over the pressure-temperature range investigated.

A fundamental issue in materials physics is to know how and when a metal melts at high pressure. Large-scale first-principles molecular dynamics calculations [1–3] are now approaching the microscopic processes at the basis of this phase transition. There is also an urgent need for data and models for melting of metals, in geophysics and space physics (the planetary core being constituted by an iron-rich metallic alloy [4,5]) and in technology (refractory metals being used in shock devices) domains. Ideally, experimental determinations of the melting curves of metals should be used to validate theoretical approaches before predictions can be made in a domain where experiments are the most challenging—the multi-Mbar range. However, there seems to be a consistent pattern of disagreement between the determinations of high pressure melting by two experimental techniques, the static laser-heated diamond anvil cell (LHDAC) and the dynamic shock wave compression. Tantalum is the most striking example of such contradictory data, with melting points obtained by different approaches differing by a few thousands of K around 100 GPa (see Fig. 1). A "high" melting point (e.g., $\simeq 9700 \pm 1000$ K at 300 GPa [6]) has been measured by shock compression and a "low" melting curve has been obtained with the LHDAC ($\simeq 3730$ K at 100 GPa [7,8]). Several interesting hypotheses have been proposed to explain this discrepancy. Intermediate phases, rather than a liquid phase, could have been observed in LHDAC: the formation of an icosahedral short-range ordered phase [9] and a shear-induced plastic phase [3] have been predicted for Ta. Some theoretical models suggest that the shock compression mechanism could allow superheating of the solid above thermodynamic melting temperature [10]. Recent calculations of the melting curve of Ta using *ab initio* techniques confirmed the high shock melting point within 1000 K [11,12]. Certainly, it is not excluded

that the density functional theory may be in error for predicting the melting curves but the amount of discrepancy with the LHDAC data in the case of Ta is surprisingly large [11]. Also, the low Clapeyron slope of the LHDAC melting curve contrasts with predictions of classical melting criteria such as the Lindemann criterium [13]. Further high pressure melting experiments have thus been asked for.

We revisit here the LHDAC determination of the melting curve of Ta up to 120 GPa using x-ray diffraction (XRD) as the primary technique, which allows collecting different
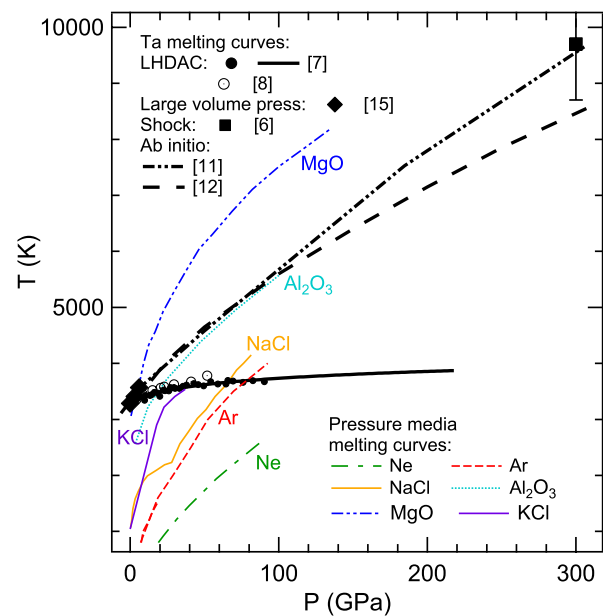
FIG. 1 (color online). Previously reported melting curves or points of Ta [7,8,11,12,27,28] and of pressure media used in this study [18,24,29–31].

important information. The structural evolution of Ta can
be followed during heating. The measured volume of Ta
provides a check of pyrometry temperature measurements.
Chemical reactions in the sample, if any, can be observed
within a few percent detection limit. Finally, fast XRD
measurements provide a bulk signature of melting, as
recently proved for lead [14]. In the first part of this report,
we describe the experimental difficulties in the measure-
ment of the melting curve of tantalum caused by physical
and chemical properties of tantalum (highly reactive and
refractory). They could have biased the previous measure-
ments of its melting curve [7,8]. In the second part, we
show a new trend in the LHDAC melting line of Ta.

Fourteen experimental runs have been carried out on the
ID27 beam line of the European Synchrotron Radiation
Facility [15]. Membrane diamond anvil cells equipped
with 300 μm to 75 μm culets diamonds and rhenium
gaskets were used with an automated pressure driver. The
sample assembly was formed by a tantalum foil (thickness
$\simeq 5$ μm) or flattened tantalum grains and a pressure me-
dium (prepressed disks of dry NaCl, KCl, MgO, Al_2O_3, or
gas-loaded neon or argon), which insulated the sample
from the diamonds. For neon and argon loadings, the
diamond anvils were coated with Al_2O_3. Samples were
heated on both sides by two YAG lasers providing a
maximum total power of 200 W. The temperature was
measured at the center of the hot spot by analyzing the
pyrometric signal emitted by a 2×2 μm^2 area [15,16].
The x-ray beam was focused on a 2×3 μm^2 area. X-ray
induced fluorescence of the diamond or pressure medium
was used to align the x-ray beam with the hot spot. During
a heating series (gradual increase of the laser's power), one
XRD spectrum and one pyrometric signal were recorded
every 4 seconds. The pressure was estimated using the Ta
lattice parameter measured by XRD before, after, and
during heating and a recently published high pressure-
high temperature equation of state of Ta [17]. The local
increase of pressure in the laser-heated sample reached
$\simeq 18$ GPa at maximum. At ambient temperature, pressure
has also been calculated using the pressure medium equa-
tion of state [18–20].

X-ray diagnostic allows following, in real time, the
transformations in the laser-heated sample. These trans-
formations include chemical reaction with its environment:
pressure medium, gasket, and diamond anvils. We have
observed a chemical reaction between tantalum and dia-
mond anvils, resulting in the formation of TaC [21,22] (see
Fig. 2). This reaction is not a surprise, since carbidation of
Ta by elemental C is an industrial process around 2000 K
[21] at ambient pressure, and has a negative reaction
volume. It is thus favored by a pressure increase. The Ta-
C reaction was the fastest and the most intense with MgO
and Al_2O_3 pressure media. This could be due to the grain
boundaries in these relatively hard solids which allow
diffusion of chemical species. In some heating series,
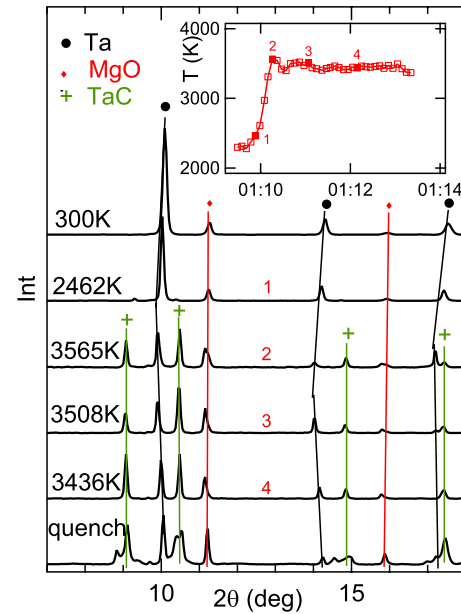
FIG. 2 (color online).   Reactivity of Ta with diamond anvils.
Monochromatic ($\lambda = 0.3738$ Å) XRD spectra of a Ta sample in
a MgO pressure medium recorded during one heating series at
$\simeq 90$ GPa. The MAR-CCD bidimensionnal spectra have been
circularly integrated. The diffraction peaks of TaC appear around
3600 K. Inset: temperature measured by pyrometry as a function
of time (and laser's power). The numbered filled squares corre-
spond to the numbered XRD spectra. After the reaction between
Ta and diamond, the temperature cannot be increased.

more than 50% of Ta was transformed into TaC within a
few minutes, resulting in a pressure drop of several GPa in
the transformed zone. In these cases, the heating tempera-
ture reached a plateau (see Fig. 2) well below the expected
melting temperature of Ta (above 50 GPa, 2900 to 4200 K
depending on the loading). This plateau is misleading, as it
is usually considered a signature of solid-liquid equilib-
rium (see Refs. [14,23]). Carbidation of the tantalum sam-
ple could be diminished, but not completely prevented, by
the use of NaCl, KCl, argon or neon pressure media and a
careful thermal insulation of the sample from the diamond
anvils, helped by the use of an Al_2O_3 coating. It is inter-
esting to notice that a carbide is stable for all transition
metals for which unusually low melting slopes have been
measured in LHDAC (Mo, Ta, W, Cr, Ti, V, Y [23]). We
have considered that carbidation of tantalum did not per-
turb the measurements when the large majority of the
sample remained unreacted after a heating series.

We observed that Ta also reacts with argon (around
25 GPa) and with Al_2O_3 and NaCl during melting (see
Fig. 3). If not detected, these reactions could perturb the
melting measurements by a chemical contamination of the
sample. To minimize it, each heating series was performed
on a new unreacted zone, and the purity of the sample was
checked by XRD up to the melting point. Inert neon, argon
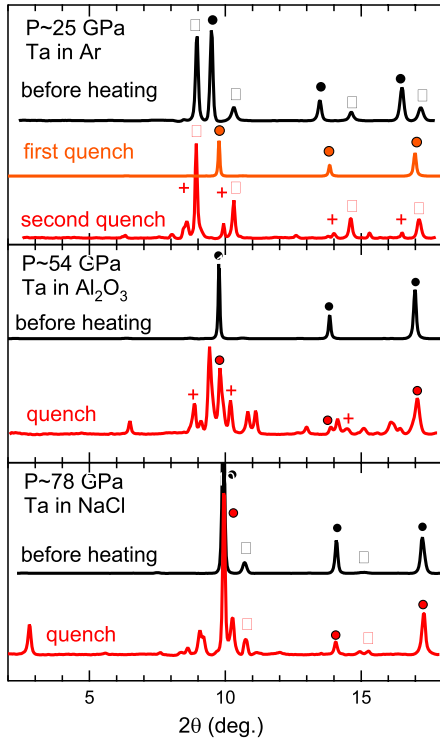
FIG. 3 (color online). Reactivity of Ta with pressure medium. XRD spectra of Ta before or after heating above 4000 K in Ar (a), Al_2O_3 (b) and NaCl (c) pressure media. The circles, squares and plus signs, respectively, identify Ta, pressure medium, and TaC. Our interpretation of these spectra is: tantalum forms a amorphous alloy with Ar and chemically reacts with Al_2O_3 and NaCl (new unassigned peaks).

(above 50 GPa), and KCl were preferentially used as pressure media.

Our objective melting criterion was the observation of the characteristic diffuse ring in the XRD spectrum of the sample and/or the fast recrystallization of the solid sample (see the discussion in Ref. [14]). This criterion was reached in several heating series, but we encountered difficulties in obtaining reliable pyrometric temperatures. Figure 4 shows the evolution of pyrometry temperature T_{pyr} *vs.* time for tantalum heated in argon around 90.5 GPa. T_{pyr} forms a plateau around 3950 K, which happens to be the expected melting temperature of argon at 90.5 GPa (see Fig. 1 and Ref. [18]). We have calculated T_{Ta}, a temperature based on Ta measured volume, Ta equation of state [17] and the assumption of constant pressure during a heating series. T_{pyr} and T_{Ta} are similar at the beginning of the heating series, but T_{Ta} diverges from T_{pyr} above $\simeq 3950$ K and reaches a plateau around 4950 K. Even if T_{Ta} is approximate due to the assumption done and the uncertainty in the assumed equation of state for Ta, this suggests that the sample temperature could be underestimated by pyrometry when the argon pressure medium is molten. This could be ascribed to changes of optical properties of argon (emis-
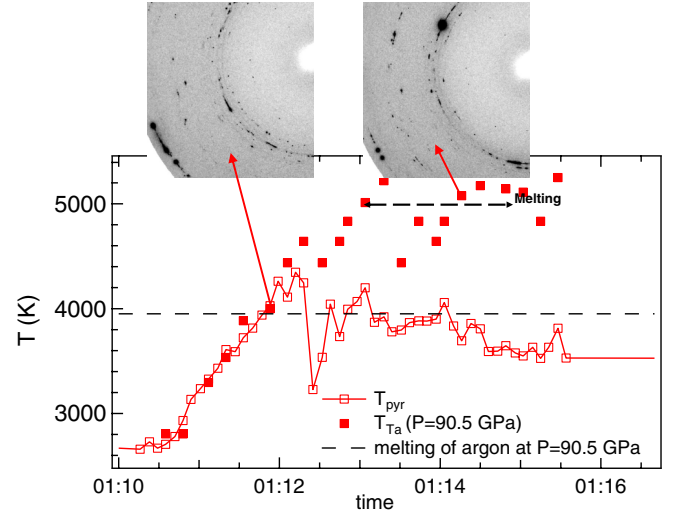
FIG. 4 (color online). Difficulties in pyrometry measurements. Pyrometry temperature (T_{pyr}) and temperature estimated using Ta lattice parameter (T_{Ta}) as a function of time during a heating series in the argon pressure medium at $P = 90.5$ GPa. Fast recrystallization of Ta single crystals has been observed between 01:12:12 and 01:15:28. The XRD signal from a liquid has been recorded between 01:12:58 and 01:15:02, during a plateau of $T_{Ta} \simeq 4950$ K.

sivity, absorption) on melting. Movements of the sample in molten argon and changes in spatial temperature distribution could also render T_{pyr} smaller than the XRD sample temperature. T_{Ta} was thus calculated, when possible, and used to cross-check T_{pyr}; when they diverged by more than 500 K, the estimated uncertainty of T_{pyr}, the melting point was dismissed. With the NaCl pressure medium, a dramatic increase of thermal emission associated to the melting of NaCl [24] prevented pyrometry measurements at very high T; in that case, only T_{Ta} was estimated.

Figure 5 shows the *P-T* paths followed in this study and the conditions under which melting of tantalum has been observed. The only solid phase observed for tantalum was body-centered cubic. It can be seen in Fig. 5(a) that tantalum has been heated up to 1400 K above the published LHDAC melting curve [7,8] without recording any x-ray evidence of melting. The melting points obtained with the conditions described in the previous paragraphs [Fig. 5(b)] are largely above the melting points previously measured in LHDAC [7,8]. In contrast, they are compatible with the *ab initio* predicted melting curves [11,12], though a bit lower. We thus believe that the tantalum melting curve has been underestimated in previous LHDAC studies [7,8]. In Ref. [8], the melting was detected by the disappearance of the XRD lines of the solid sample, which can be also caused by its solid state recrystallization [14,25]. In Ref. [7], melting was optically detected and no *in situ* or *ex situ* characterization of the sample was performed; undetected chemical reactions or errors of pyrometry could have biased the measurements.
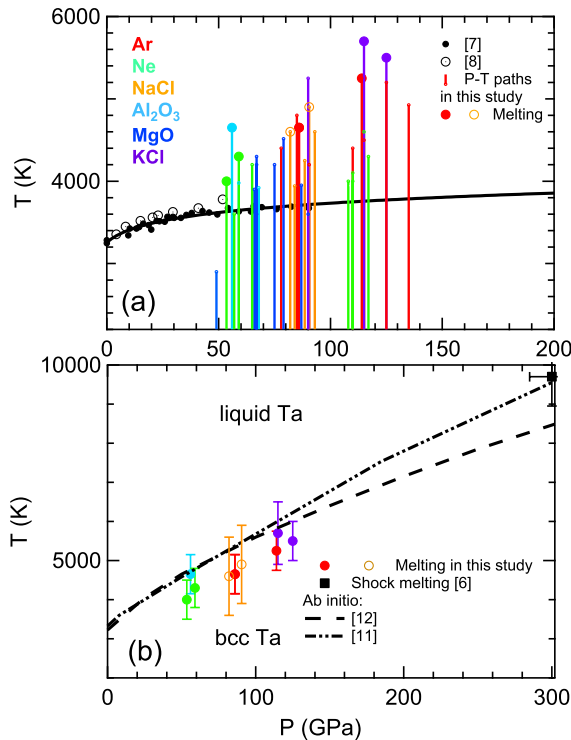
FIG. 5 (color online).   (a) Approximate *P-T* paths in the current study, compared to the LHDAC melting curves previously published. The colors of the vertical lines correspond to different pressure media. The circles indicate XRD evidence of melting (closed circles: T_{pyr}, open circles: T_{Ta}, for NaCl pressure medium). (b) Ta phase diagram.

This work shows that the convergence of the information given by visual observations, pyrometry and *in situ* x-ray diffraction is essential to constrain high pressure melting curves. In particular, the x-ray diagnostic provides the detection of chemical reactions and improves pressure-temperature metrology. A similar approach should be used for the measurement of the iron melting curve [4,5,26].

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