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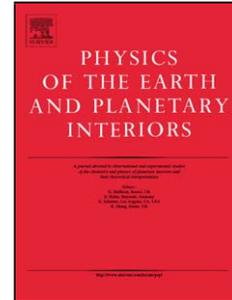
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Microscopic evidence of a flat melting curve of tantalum

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New data on the high-pressure melting curve of Ta up to 48 GPa are reported. Evidence of melting from changes in sample texture was found in five different experiments using scanning electron microscopy. The obtained melting temperatures are in excellent agreement with earlier measurements using x-ray diffraction or the laser-speckled method but are in contrast with several theoretical calculations. The results are also compared with shock-wave data. These findings are of geophysical relevance because they confirm the validity of earlier experimental techniques that resulted in low melting slopes of the transition metals measured in the diamond-anvil cell, including iron.

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1. Introduction

A longstanding problem in the study of materials at high pressure is the determination of their melting curves and phase diagrams. In particular, the melting of the late transition metal iron at high pressures has wide scientific implications, including geophysical and geochemical modeling of the Earth's interior. This fact has triggered a substantial effort to determine the melting curve of Fe (for a review see: Boehler, R. et al., 2007) and other transition metals including Mo, Ta, and W (Belonoshko et al., 2008; Cazorla et al., 2008; Dai et al., 2009; Errandonea et al., 2001; Errandonea et al., 2003; Foata-Prestavoine et al., 2007; Hixon et al., 1989; Liu et al., 2008; Moriarty et al., 2002; Santamaría-Pérez et al., 2009; Taioli et al., 2007; Zhang et al., 2009). However, despite important advances in experimental and theoretical methods, considerable controversy exists about the pressure dependence of the melting temperatures (T_M) of Mo, Ta, and W. The melting curves determined from diamond-anvil cell (DAC) experiments performed up to 120 GPa (Errandonea et al., 2001; Errandonea et al., 2003; Foata-Prestavoine et al., 2007; Santamaría-Pérez et al., 2009) are much flatter than those obtained from shock-wave experiments carried out at higher pressures (Hixon et al., 1989; Dai et al., 2009; Zhang et al., 2009). Substantial variations are also found among calculations (Moriarty et al., 2002; Cazorla et al., 2008), but the majority of them disagree with the DAC results. Therefore, it is clear that further studies are needed to accurately determine the melting temperatures of transition metals. In this letter, we report new experimental data on the melting curve of Ta up to 48 GPa. Melting was determined by observing changes in the Ta surface as the temperature increases. Additional evidence of melting is provided by

scanning electron microscopy measurements. The new melting temperatures confirm previous DAC experiments.

2. Experimental details

Measurements were carried out in a Boehler-Almax DAC (Boehler and De Hantsetters, 2004; Boehler et al., 2006) with 360- μm diameter culets. The gasket was made from a 250 μm thick rhenium disk, pre-indented to a 40 μm thickness and laser-drilled to a diameter of 130 μm . Samples were prepared by extracting small pieces from freshly polished tantalum (Goodfellow, 99.9% purity) and squeezing them between two diamond flats to a thickness of 9-12 μm and about 60 μm in diameter, resulting in mirror-like surfaces and providing an area large enough to allow multiple heating cycles in different positions. The samples were placed on 3- μm thick single-crystal Al_2O_3 plates to thermally insulate them from one diamond anvil. High-purity argon (Ar) gas (99.999%) was used as pressure-transmitting medium and to insulate the sample from the opposite diamond. Ar was loaded at room temperature using a 0.3 GPa gas apparatus. Pressures were measured before and after heating by the ruby fluorescence method from unheated ruby chips placed around 5 μm away from the sample.

Ta samples were laser heated from one side using a fiber laser (IGP Laser GmbH, ytterbium-glass, TEM₀₀-mode CW, 110 W, $\lambda = 1070$ nm). This laser is highly stable providing excellent temperature stability. Its high power allows heating with a defocused beam minimizing radial temperature gradients. In our case, the laser beam was defocused to create a uniform hotspot in an area with a 15–20 μm diameter on the sample surface. Temperatures were measured at the center of the hotspot from areas of 2 μm diameter by fitting Planck's radiation function to the spectra in the spectral range of 500–900 nm

assuming wavelength-independent emissivity (Boehler et al., 1990). Radial temperature gradients in the center of the hotspot were within 100 K in a 10- μm diameter area.

Melting temperatures were measured by heating every sample at a constant load, by increasing the temperature in steps of about 100 K starting at temperatures 500 K lower than the melting temperature reported in previous DAC experiments (Errandonea et al., 2001; Errandonea et al., 2003). After each heating cycle, lasting no more than 10 seconds, the sample surface was examined and photographed, while samples were still under pressure, using a microscope with a 20x objective. These runs were performed at five different samples at pressures of 13, 17, 23, 42, and 48 GPa. Once melting was visually detected by the appearance of round textural features, the sample was recovered and examined with an SEM (Scanning Electron Microscope, LEO 1530). After melting, the Ta samples did not show any visual sign of chemical reaction. In order to avoid sample oxidation after recovery, samples were stored in a vacuum desiccator until the SEM experiments were performed. When compared with unheated samples, no differences in the image contrasts were observed in any of the SEM photographs taken at sample parts heated at different temperatures. In addition, differences in chemical composition (e.g. oxide or carbide formation) of individual samples before and after heating were too small (if any) to be detected with SEM. Both facts point towards the absence of chemical changes in Ta after laser heating.

3. Results and discussion

Five different experiments were made from 13 to 48 GPa in order to cover the pressure range where experimental DAC values and theoretical calculations start to disagree. Figure 1 shows three images of one of the Ta samples compressed at 13 GPa.

The first one was taken after compression at 13 GPa before laser-heating (left), the second one after heating up to 3300 ± 100 K (center, the location of the hot spot is shown), and the third one after heating to 3600 ± 100 K (right, the location of the hot spot is shown). There are no obvious changes in the Ta sample before and after heating up to 3300 ± 100 K with the exception of small cracks next to the heated area. This fact can be interpreted as due to the arising of melting precursors below the melting temperature (Woodruff, D.P, 1973). After heating to 3600 ± 100 K the formation of a crater in a region with raised topography is obvious. We interpret these textures as being due to melting of Ta. This melting temperature is 2000 K higher than the melting temperature of Ar, our pressure-transmitting medium (Boehler, et al., 2001).

In Figure 2 we show SEM images of the Ta sample shown in Fig. 1 (13 GPa). The left image is typical for that of an unheated sample. The middle SEM image was collected in the area of the sample heated to 3300 ± 100 K (13 GPa) showing several microdendrites about 200 nm in size. Microdendrites can be attributed to recrystallization of the Ta surface that could take place a few hundred degrees below bulk melting (Rühm et al., 2003). This recrystallization may occur by short-range diffusion driven by the difference in the internal energy of strained and unstrained grains of Ta. Strain free grains grow when approaching the melting temperature.

In the right image, collected in the area heated up to 3600 ± 100 K at 13 GPa, the effects of melting in the Ta surface can be clearly seen: the surface is completely restructured showing prominent polygonal microstructures, which are most likely the result of quenching from the melt. In pure materials (like our Ta samples), microstructures are formed during solidification. The growth of the solidification

microstructures generally proceeds along so-called “easy growth” directions (Glicksman, M.E., et al., 2004). This process provides an explanation to the morphological changes observed on the surface of our Ta samples when heated to the melting temperature. Similar results than those described above were found for different Ta samples studied at five different pressures. The detected microstructures are typical of a laser-melted surface in metals (Kac et al., 2004). These observed changes of the Ta surface cannot be produced by solid-state processes or by changes in viscosity.

One possibility that should be considered in our experiments is the formation of TaC during laser heating due to the carbon diffusion from the diamond-anvils, which could affect the determination of the melting curve of Ta. During recent laser-heating X-ray diffraction (XRD) experiments, we observed the formation of tantalum carbide, which could be related to the different heating procedure used. In XRD experiments, a high laser power (80 – 100 W) is used to heat a large portion of the sample for several minutes causing substantial heating of the diamond anvils. This facilitates the transport of carbon from the diamond culet surface into the heated part of the sample. In contrast to XRD experiments, in the present experiments the laser power and heating time are substantially less (20 W). In addition, only a small portion of the sample is heated with one-sided for only a few seconds, thus explaining the absence of chemical reaction. As described above, this conclusion is supported by SEM measurements.

Figure 3 summarizes the present and previous data (Errandonea et al., 2001; Errandonea et al., 2003; Fatteva et al., 1971, Moriarty et al., 2002; Taioli et al., 2007). The solid circles represent the highest temperature for which no evidence of melting was found. The solid squares show the lowest temperatures where evidence of melting was

been found. Compared with previous DAC experiments, where melting was detected by XRD (Errandonea et al., 2003) or the speckle method (Errandonea et al., 2001), the present data show a larger data scatter. In addition, they show a tendency to slightly higher melting temperatures. However, the maximum differences in the melting temperatures among different experiments are within 200 K, i.e. they are slightly larger than uncertainties in the temperature determination. These differences small compared to the discrepancies between DAC experiments and theoretical calculations as shown in Fig. 3. The present experiments confirm that as pressure increases the melting slope of Ta decreases. Molecular dynamics (MD) (Liu et al., 2008), first-principles (FP) (Taioli et al., 2007), and quantum-based (QB) atomistic (Moriarty et al., 2002) calculations give, above 10 GPa, consistently a higher T_M than the DAC experiments.

Another method for attaining melting temperatures above megabar pressures and several thousand of Kelvins is by shock-wave experiments. Using this technique, melting of Ta was detected in the pressure range from 250 to 300 GPa, with a calculated melting temperature of 7000-10000 K (Dai et al., 2009; Shaner et al., 1984). After applying a superheating correction, T_M may be as low as 5000-8000 K (Errandonea, 2005; Errandonea, 2006; Luo et al., 2003). A linear extrapolation of the DAC data to 300 GPa, puts an upper limit of $T_M = 4800K$. Different ideas have been proposed to clarify this apparent discrepancy. It was proposed that the DAC melting temperature corresponds to a solid-solid phase boundary instead of a solid-liquid transition (Belonoshko et al., 2008). However, this interpretation has been contradicted (Cazorla et al., 2008) and x-ray experiments rule out the existence of a high-temperature solid phase in Ta and Mo below 120 GPa (Errandonea et al., 2003; Santamaría-Pérez et al., 2009). More recently, Wu et

al. (2009) attempted to explain the low melting slopes as due to shear-induced anisotropic pre-melting in Ta prior to melting. Within this framework, they concluded that at high-temperature Ta becomes a one-dimensional thermodynamically unstable liquid-glass (detected in DAC experiments) before it melts into a liquid (Errandonea, 2009). This proposed behavior provides a possible explanation for flat melting curves in metals like Ta or Mo. However, it does not explain why in experiments performed under drastically different stress conditions, using soft or stiff pressure media, the same melting temperatures are detected in DAC experiments. In spite of this, melt mechanisms suggested by Wu et al. and Ross et al., which include glass formation or plastic deformation, (Wu et al, 2009; Ross et al., 2007a; Ross et al., 2007b) indicate that melting could be far more complex than assumed up to now. In particular, the presence of a viscoelastic phase could reconcile the discrepancies between the low- and high-pressure melting behaviour of Ta. In such a case, the shock-melting temperature reported for Mo below 200 GPa (Zhang, et al., 2008) would correspond to viscoelastic-liquid transition (Santamaría-Pérez et al., 2009). A definitive picture reconciling all data available on melting of Ta would be only resolved by further DAC experiments extended beyond 100 GPa , shock-wave experiments using time-resolved XRD and further theoretical studies.

4. Concluding remarks

In summary, we provide extra experimental evidence for a flat melting curve of Ta from optical and scanning electron microscopic analysis of the quenched samples. The reported melting temperatures are in agreement with earlier DAC studies (Errandonea et al., 2001; Errandonea et al., 2003) supporting that near 100 GPa Ta has a flat melting curve.

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Figure captions

Figure 1: Optical evidence of the fusion of Ta. Pressures and temperatures are indicated. The heated areas are highlighted.

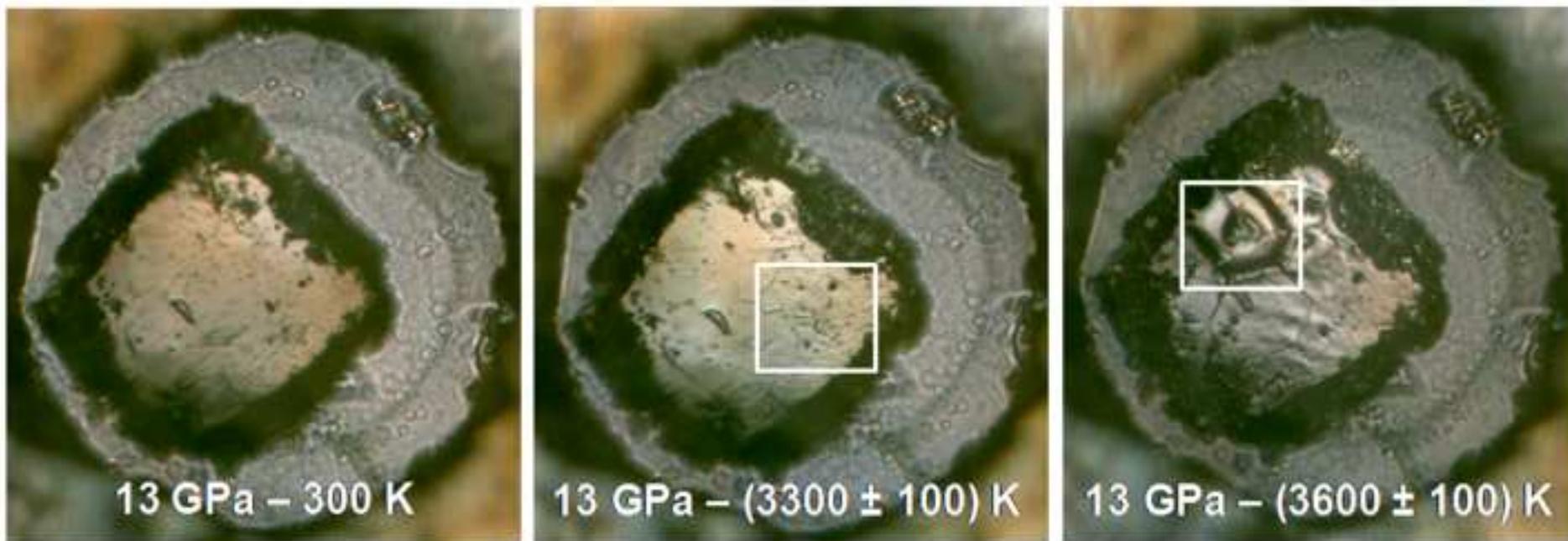
Figure 2: SEM images taken in recovered Ta samples that were pressurized at 13 GPa. Unheated (left, area within the white frame) and heated up to 3300 ± 100 K (center) and 3600 ± 100 K (right).

Figure 3: The melting curve of Ta. Solid squares: lowest temperature where melting is detected. Solid circles: highest temperature where no surface change are found. Empty squares: (Errandonea, et al. 2001). Empty circles: (Errandonea, et al., 2003). Triangles: (Fatteva, et al., 1971). Calculated melting curves are included [FP (Taioli, et al., 2007) and QB (Moriarty et al., 2002)] together with the Lindemann (L) estimates (Errandonea, D., 2005).

Figure 1

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