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Predictions from the equation of state of cerium yield interesting insights into experimental results

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Abstract. There has been much interest in the past in understanding the dynamic properties of phase changing materials. In this paper we begin to explore the dynamic properties of the complex material of cerium. Cerium metal is a good candidate material to explore capabilities in determining a dynamic phase diagram on account of its low dynamic phase boundaries, namely, the γ–α, and α-liquid phase boundaries. Here we present a combination of experimental results with calculated results to try to understand the dynamic behavior of the material. Using the front surface impact technique, we performed a series of experiments which displayed a rarefaction shock upon release. These experiments show that the reversion shock stresses occur at different magnitudes, allowing us to plot out the γ–α phase boundary. Applying a multiphase equation of state a broader understanding of the experimental results will be discussed.

1. INTRODUCTION

Cerium is a complex material with an interesting phase diagram. Cerium exhibits anomalous melting at low pressure yet the dynamic melt boundary is somewhat uncertain at this time. There exists seven known allotropic phases of cerium. The γ–α phase transition at room temperature shows an isomorphic volume collapse of 17%.[1, 2] This behavior has been shown to be an electronic transition[3]. It could be the only material that exhibits a solid-solid critical point where the isomorphic volume collapse decreases to 0%. It exhibits a complicated f-electron behavior. The material as it approaches the low pressure solid-solid phase boundary the material exhibits a negative derivative of the bulk modulus with respect to pressure.

In studying cerium we hope to validate a multi-phase equation of state with experimental evidence. It has been known that cerium as a result of the low pressure phase transition dynamically shows a two wave character indicative of the $\gamma \rightarrow \alpha$ phase transition[4]. One of the co-authors here presented the framework for a multi-phase equation of state that characterized the region between the γ and the α phases[5,6] based on some early thermodynamic work of Aptekar and Ponyatovskiy[7,8]. So in this paper we will show how using the model combined with experiments yield interesting insights into this very interesting metal of cerium.

2. MODEL

The model is constructed based on the common Helmholtz free energy formation. The energy is written as a sum of three terms

$$F(V,T) = F_C(V) + F_H(V, T) + F_{AE}(V, T) - S_{tr}T \qquad (1)$$

Where F_C is the "cold" energy given by a modified Vinet, et. Al. equation of state[9,10]; F_H is the quasi-harmonic phonon free energy described by the Debye approximation; F_{AE} is the joint contribution to the free energy from the anharmonic lattice vibrations and the thermally excited electrons; and S_{tr} is an entropy component which allows for entropy changes during phase transitions. On account of the character of the low pressure phase transition of the $\gamma-\alpha$ phase boundary, namely the material getting softer as one approaches the phase boundary, the Aptekar-Ponyatovsky model was included. This model can be considered as a binary alloy model for the $\gamma-\alpha$ phases and the Gibbs potential energy is written in the form

$$G_{\gamma\alpha} = G_\alpha X_\alpha + G_\gamma X_\gamma + G_{mix} X_\alpha X_\gamma + TS_{conf} \quad (2)$$

Here $G\alpha$ and $G\gamma$ are the thermodynamic potentials for the pure α and the γ phases; G_{mix} is a thermodynamic mixing potential; S_{conf} is the configurational entropy of the system; and T is temperature. The G_{mix} term is a function selected such that it is only dependent upon T and is given by the following

$$G_{mix}(T) = G^0_{mix}[1 + \theta_1/T + (\theta_2/T)^2] \quad (3)$$

Where G^0_{mix}, θ_1, and θ_2 are adjustable parameters which are selected that the critical point is obtained. For a more thorough description of the model and the variables used we refer the reader to the paper by Elkin, et. al. [5,6].

3. EXPERIMENTAL SETUP

We conducted a series of front-surface impact experiments. The experimental configuration consisted of a high-purity cerium sample backed by foam impacting an aluminum coated window. The windows were either lithium fluoride or z-cut sapphire. Particle velocity profiles were obtained at the cerium/window interface using the standard push-pull velocity interferometer system for any reflector (VISAR) system with a time resolution of approximately 1 ns. The wave profile data combined with measured projectile velocity and the known shock response of the window materials provided the stress history at the interface.

The VISAR optical windows were well-characterized, high-purity Hemlux grade z-cut sapphire samples obtained from Crystal Systems. Sapphire and LiF window materials were chosen as optical windows for this work because of the well-characterized optical and shock wave properties. All windows were polished on both sides and were flat and parallel to 0.0002." The nominal thicknesses of the windows were 19 mm. The nominal density of the lithium fluoride was 2.638 g/cc and the sapphire was 3.985 g/cc.

The cerium used for these experiments were nominally 1 mm or less. The specimens were prepared from starting materials having a nominal purity of 99.99 % with respect to metals. The major non-metal impurity was oxygen at the 1000 ppm level. The processing steps allowed for a final grain size of approximately 50 microns. The samples were lapped flat to the desired thickness and mounted into the projectile.

4. RESULTS AND DISCUSSION

A total of 4 front surface impact shots were performed on cerium for this work. In Fig. 1, we show a two of front surface impact shots were we observe a rarefactions shock wave upon release. For illustration purposes these are representative curves for the experiments performed. The wave profiles illustrate several features that we would like to point out: the initial shock at t_0, a steady state, an isentropic release, and a rarefaction shock. The lower pressure shot shows a partial elastic release of the material as well.

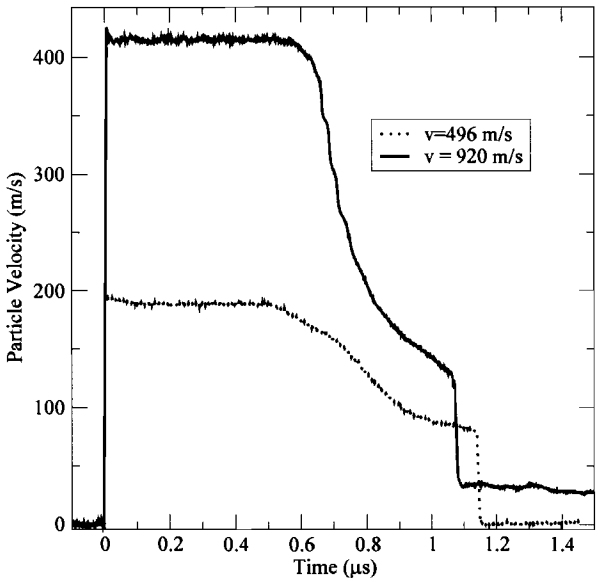

Figure 1. VISAR traces for two representative experiments using the front-surface impact technique at velocities of 498 m/s and 921 m/s.

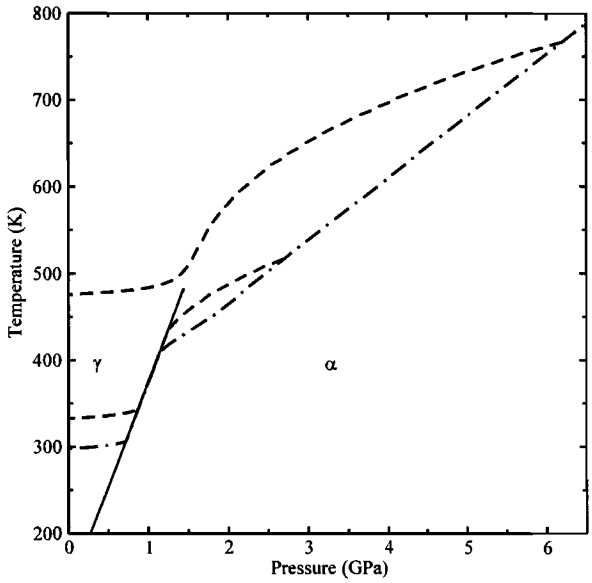

Figure 2. Calculated release isentropes for each of the experiments shown in Fig. 1.

Using the cerium multi-phase equation of state we calculated the release isentropes for each of the experiments performed using the measured stress state as a starting point. Great care was taken when developing this muli-phase equation of state for cerium, in order to replicate the measured bulk sound speed response of cerium through γ–α phase transition. Using the Rankine-Hugoniot jump conditions and the model we determined the temperature. In Fig. 2, we show the calculated release states for the two experiments shown in Fig. 1. Following the calculated release isentrope we determine the transition pressure to be the point where the minimum in the calculated bulk sound speed as a function of pressure occurs. The calculated temperature and pressure state where the

minimum occurs is presented in Table 1 for all of the experiments performed using the front-surface impact technique. In Table 1 and Fig. 2, three of the four experiments have temperatures and pressures which fall above the solid-solid critical point in temperature. Experiment 56-08-11 was an experiment that used sapphire as a window material and the measured velocity at the transition was very low. This could account for measured reversion stress being lower than the reported room temperature phase transition stress upon shocking cerium using a transmission kind of geometry(known impactor material hitting a cerium sample glued to a window material)[4]. All of the front surface impact shots performed below the melt transition in cerium show a rarefaction shock. Only one of the experiments falls into the region where we expect to observe a volume expansion or the first order phase transitions of $\alpha \rightarrow \gamma$. The difference in shock velocity and sound speed variation in the material whether the material undergoes a first order or a second order phase transition provides for the generation of a rarefaction shock wave to be observed. This observation slightly contradicts the lore in the shock wave community that a volume expansion is necessary for the development of a rarefaction wave.

Table 1. Calculated transition pressure and measured transition pressure for all of the experiments performed.

Experiment	Measured Impact Stress (GPa)	Measured reversion stress (GPa)	Calculated reversion stress (GPa)	Calculated reversion temperature (K)
56-06-25	2.7	1.15	1.22	428
69ss-06-15	6.2	1.78	1.57	523
69ss-09-04	8.1	1.86	1.89	617
56-08-11	5.8	0.719	1.51	505

Examining the values of the measured versus predicted from the model reversion stresses, we see a remarkable agreement from the model and the experiment. On account of this agreement, we plot in Fig. 3 a predicted phase diagram using the temperatures found from the calculations and the measured reversion stresses reported above. Future work to actually measure temperature on the phase boundary line using a transmission shot should be considered to better pin down the phase transition temperature. One could conceive of using a well controlled heated cell over a finite temperature range experiment which would allow one to measure the transition stress combined with the pyrometry. Although for these low temperatures it is known that making such temperature methods is very difficult. Thus for the time being we will have to accept that a well characterized multi-phase equation of state as the way to infer what the temperatures may be across phase boundaries.

5. CONCLUSIONS

It has been long assumed that a volume expansion is necessary for the formation of a rarefaction wave. In the particular case of cerium where the change in volume across the phase boundary disappears yet there is a marked minimum in the sound speed as a function of pressure, rarefaction shocks appear. Using the experimentally determined stresses and marching down the isentropic release calculating sound speed shows a minimum. The stress state and temperature can be determined from the equation of state and for three of the four experiments shows an excellent agreement with the experimental reversion stress state. The fourth experiment which used a sapphire window has a lower reversion stress state than the measured phase transition stress starting from room temperature which implies that this data point needs to be revisited.

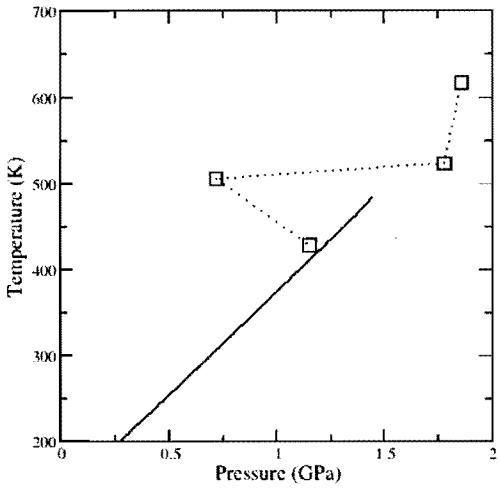

Figure 3. Plot of the reversion stresses versus calculated temperature. The solid black line is the phase line between α and γ phases. The dashed lines and the symbols represent the measured reversion stress with the reversion temperature.

Acknowledgments

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