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Near-Critical-Point Thermodynamics from Shock Experiments with Porous Ni Samples[1]

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Results of experiments on the expansion of shock-compressed nickel samples into helium are presented. An isentrope with an initial pressure of 170 GPa was studied. The radiance temperature of the nickel sample and the velocity of the shock wave, generated in helium, were measured by a fast multichannel optical pyrometer; other parameters, such as the particle velocity, the pressure on the He-Ni interface, and the temperature of He were calculated using He Hugoniot (chemical plasma model). To increase the shock entropy up to a near-critical value and to intensify the process of heat-mass transfer, porous samples were used. Final states with pressures below 1.5 GPa, determined by the initial He pressure, were generated. The isobaric overheat of nickel by hot shocked helium provided an information about the nickel liquid spinodal. The change in slope of an isentrope in the pressure-particle velocity plane allowed an estimate of the point of its entrance in the two-phase region. Estimates of the critical temperature and pressure were made from peculiarities of *P-T* path, using various models of the nickel liquid spinodal to represent experimental data.

KEY WORDS: critical point; isentropic expansion; nickel; optical pyrometry; porous sample; shock wave; spinodal.

1. INTRODUCTION

The method of shock loading and isentropic expansion of matter allows one to exceed limitations of common static methods and Hugoniot measurements, and provides the opportunity to investigate thermodynamics of the liquid-vapor phase transition in the near-critical point region. In particular, this method has been used to investigate the location of the coexistence

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curve and critical point in the *P-T* phase diagram of lead and tin [1–4]. In these experiments release isentropes were traced for several initial Hugoniot states, generated by one-dimensional explosive shock generators. A sequence of final pressures was defined by variation of the shock compressibility of the barrier gas. Helium was used as the barrier gas, and a variation of its initial pressure from zero to more than 100 bar was enough to trace isentropes over a wide range of parameters.

Measurement of light emission from a specimen gives us the velocity of a shock wave in helium, and, using a helium Hugoniot, we can calculate the particle velocity and the final pressure of the expanded metal. Because of high ionization energy, helium remains transparent in a shocked state, which makes it possible to measure emission from a metal surface and to calculate its radiance temperature. So, the isentrope can be traced in both pressure-particle velocity and pressure-temperature planes.

Results [1–4] were obtained previously for Pb and Sn, metals with relatively low values of the critical entropy, using the existing explosive launchers with well-defined performance (launch velocity $W < 6.8\ \mathrm{km \cdot s^{-1}}$). Investigation of metals with high critical parameters requires a striker, accelerated up to velocities of more than $10\ \mathrm{km \cdot s^{-1}}$. Design of such launchers is a serious technical problem, not solved up to now. To achieve the required near-critical entropy with usual launching systems, the use of a porous specimen was proposed. Another problem was also solved, if the striker velocity were very high, the temperature of shock-compressed helium would be sufficient to cause noticeable ionization and, thus, loss of transparency. It would make it impossible to register the light emission from a sample-gas interface.

2. EXPERIMENTAL TECHNIQUE

The experimental assembly, used in experiments with porous nickel samples, was similar to that used in experiments with lead and tin [4]. Porous samples, 20 mm in diameter, were compacted from nickel powder in a hydraulic press. The thickness of the samples was chosen to be about 0.2 to 0.3 mm to avoid an overtaking of the shock wave by the release wave, travelling from the back surface of the striker. Samples with a mean porosity $m = \rho_0/\rho = 1.91$ ($\rho_0 =$ normal density of nickel, $\rho =$ sample density) are firm enough, if glued to the bottom, to follow the bottom bulge under helium pressure.

The experimental assembly is shown in Fig. 1. The sample was loaded by impact of a steel striker, accelerated by a two-stage explosive launching system. The hugoniot pressure generated in the samples was 170 GPa. Thermal emission from the assembly was traced by a fast multichannel

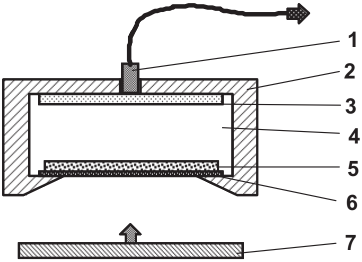

Fig. 1. Experimental assembly. 1, optical fiber with aperture; 2, pressurized case; 3, glass window; 4, helium under pressure; 5, porous nickel sample; 6, steel bottom of assembly; 7, steel striker.

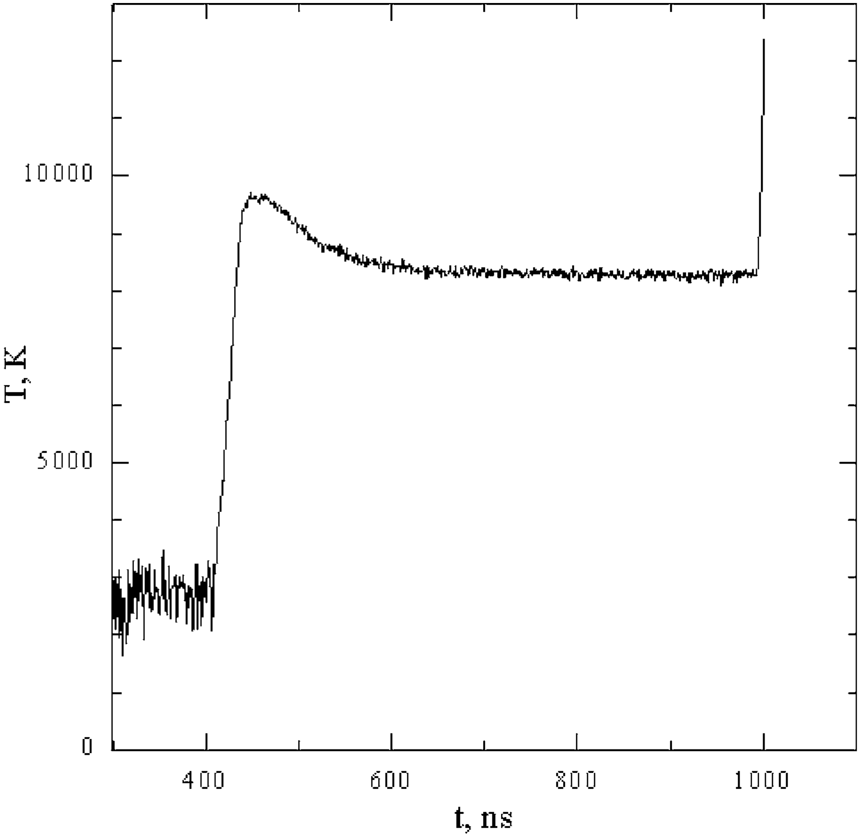

Fig. 2. Typical experimental snapshot. Emission intensity already converted to radiance temperature.

pyrometer with PIN-photodiodes as photoreceivers at several wavelengths. To transmit emission from the assembly, a quartz-polymer optical fiber with an aperture on the assembly end was used. Light was collected from a small area of 2 to 3 mm in diameter. Before each experiment, a pyrometer, connected with a fiber and aperture, was calibrated using a standard tungsten ribbon lamp, so the radiance temperatures at various wavelengths can be computed. The black body emissivity of the sample surface was taken for reasons, which are discussed in Ref. 4.

A typical experimental snapshot is presented in Fig. 2. For calculation of the shock velocity in helium we needed a precise value of the distance between the window and nickel sample surface. At high initial pressures of helium, the bulge of the steel bottom can add significant error in the distance measurement, so the dependence of the bulge on the initial pressure

Table I. Experimental Data on Isentropic Expansion of Porous Nickel. Initial Hugoniot Pressure of 170 GPa. (P_0, initial helium pressure; D and T, measured shock velocity and temperature in He; U_p and P, calculated particle velocity and pressure of shock wave in He that, in continuous flow, are equal to pressure and particle velocity of released Ni; T_{He}, calculated temperature of He; ΔU_p and ΔT, experimental uncertainties of corresponding values.)

P_0 (MPa)	D (km·s^{-1})	U_p (km·s^{-1})	P (GPa)	T_{He} (K)	T (K)	ΔU_p (km·s^{-1})	ΔT (K)
0.0056	16.96	13.78	0.002185	20140	5400	0.4	400
0.051	14.56	11.12	0.0138	18340	5730	0.5	200
0.085	14.46	10.99	0.0226	18310	6680	0.3	230
0.2005	13.25	9.92	0.0441	16000	8900	0.4	280
0.346	11.79	8.78	0.0715	15110	10300	0.45	330
1.01	11.77	8.76	0.174	12750	9150	0.3	300
1.16	11.16	8.70	0.195	12570	9050	0.4	290
1.3557	12.0	8.61	0.223	12300	8900	0.28	300
2.219	11.26	8.38	0.351	11700	8350	0.3	400
2.533	11.2	8.27	0.386	11400	8390	0.25	240
2.724	11.0	8.23	0.41	11300	8050	0.33	200
3.49	11.05	8.22	0.531	11260	8100	0.3	400
3.914	11.13	8.28	0.605	11430	8380	0.3	300
4.809	10.84	8.07	0.705	11220	8740	0.29	220
3.02	11.08	8.24	0.741	11330	8970	0.3	300
4.809	11.49	8.56	0.792	10840	9100	0.4	350
6.77	9.95	7.38	0.836	11330	8790	0.39	300
6.002	10.61	8.16	0.889	11085	9500	0.3	300
5.876	11.04	8.21	0.893	11260	9950	0.3	400
6.771	10.85	8.07	0.994	10890	9100	0.3	300
8.733	9.76	7.22	1.038	10800	8300	0.37	300
10.16	9.91	7.31	1.243	10900	8100	0.29	250
11.75	9.8	7.21	1.402	11300	8000	0.36	200

in the assembly was studied. Parameters of the shock wave in helium were calculated using a plasma equation of state (EOS) [5], although discrepancy between EOS data and the basic expression for a monoatomic ideal gas ($D = 4/3U_p$) was only a few percents.

3. RESULTS AND DISCUSSION

Experimental results are presented in Table I, and in Figs. 3 and 4 together with calculations [7] of the release isentrope, the coexistence curve, and liquid and gas spinodals. As was demonstrated in Ref. 6, a change in the slope of the isentrope in the pressure-particle velocity plane is caused by formation of a shock boiling wave at the point of its entrance in the two-phase region. We can assume that this isentrope crosses the coexistence curve at a pressure of 0.08 to 0.09 GPa.

The process of shock exit on the surface of the sample would be accompanied by various instabilities, leading to intense mixing of Ni and He and heat-mass transfer. Actually, in experiments with compact samples

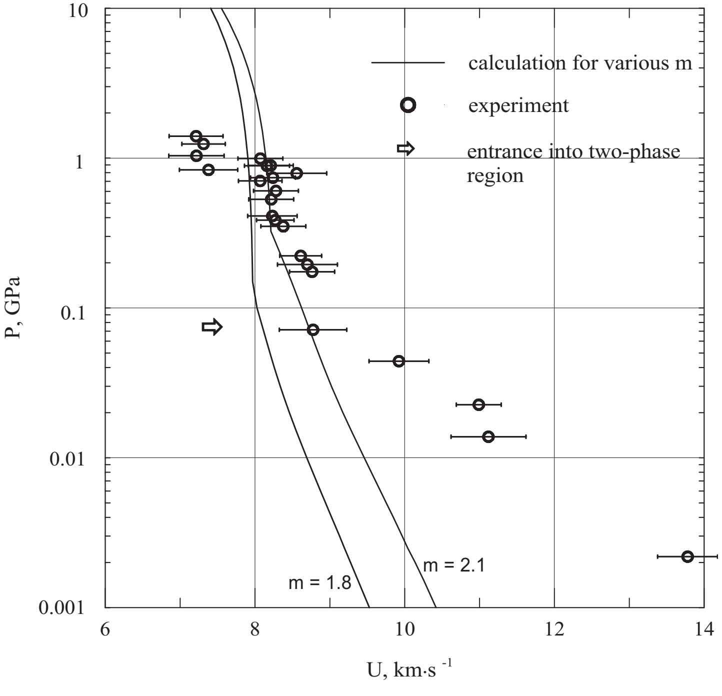

Fig. 3. Pressure-particle velocity graph. Curves-equation of state [7] calculation of release isentropes with various initial porosities *m* of sample.

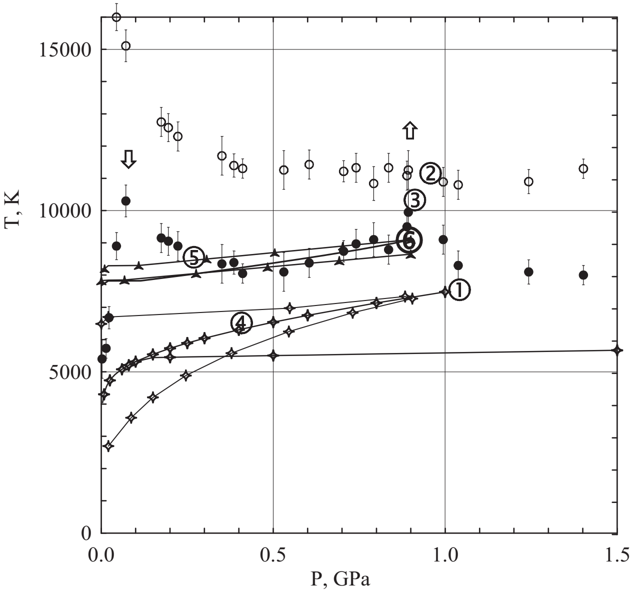

Fig. 4. Pressure-temperature diagram of Ni. (●) temperature of Ni overheat; (○) helium temperature; (—✧—) spinodal, saturation curve and isentrope, calculated by EOS [7]; (—▲—) spinodal [12]; (——) van der Waals spinodal; (⇩) entrance into two-phase region; (⇧) temperature anomaly. Critical point estimates: (①) Bushman et al. (1992) [10]; (②) Fortov et al. (1976) [9]; (③) Young (1971); (④) Hess and Schneidenbach (1996) [11]; (⑤) Martynyuk (1999) [13]; (⑥) this work.

[1–4, 6], we investigated the process of overheating of the sample surface by hot shocked helium and used these data to trace the liquid spinodal of metals.

For the case of porous Ni the process of heat-mass transfer becomes so fast, that it is impossible to measure the initial temperature of the metal surface. Moreover, in some experiments, we obtained a slow cooling of the initially hot surface. So we accepted, that in experiments with porous samples, the measurement of temperature on an isentrope is impossible, and only the temperature of overheat (experimental spinodal temperature) can be measured. This information is significant in order to understand the phase diagram.

If the isentrope passes extremely close to the critical point, it can get into a region of low mechanic and thermodynamic stability [8], where anomalies in compressibility, heat conductance, and sound speed are predicted. At pressures close to critical, the process of heat-mass transfer becomes superefficacious, and temperatures of overheat of the metal surface increase close to helium temperature, the maximum temperature in the system. On *P-T* graphs of both lead and tin [1–4], this temperature anomaly was found and used to estimate the critical pressure. On the nickel *P-T* diagram (Fig. 4), one can see this anomaly at a pressure of about 0.9 GPa. We suppose that this is the pressure of the critical point. This value does not contradict existing theoretical predictions [9–13].

For estimation of the critical temperature, the van-der-Waals model and Skripov model [11] of the liquid spinodal were applied. Experimental points of Ni overheat were approximated by both models. Only points with pressures higher than the point of isentrope entrance into the two-phase region were used, because on the lower part of the experimental spinodal, unusual processes such as shock rarefaction [6] take place. As seen in Fig. 4, all constructed spinodals are located within experimental uncertainties. The best value of the critical temperature is $T_c = 9100$ K. It should be pointed out that both models used are the most simple models for the liquid spinodal. A lot of other models can be used for such calculations [14].

Now we can estimate parameters of the critical point of nickel: $P_c = 0.9 \pm 0.1$ GPa and $T_c = 9100 \pm 150$ K. The accuracy of T_c definition depends on the spinodal model used. Unfortunately, using this method, it's impossible to estimate the critical density. To find Vc it's nessesary to trace an isentrope over a wide pressure range—from Hugoniot to the critical pressure, and calculate Riemann's integrals. The accuracy of such a large range of investigation would not be sufficient.

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