Shock compression of V_2H and V_2D to 135 GPa and anomalous decompression behavior

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Shock-compression measurements of V_2H and V_2D were performed at up to 135 GPa using a 25-mm propellant gun and a 20-mm two-stage light-gas gun. The shock velocity U and particle velocity u obtained by the impedance match solution can be represented by a linear relation, $U=5.51+1.10u$. The compression curve determined is found to lie close to that of vanadium metal without any indication of anomaly, showing that V—H bonds are as incompressible as V—V bonds even in this pressure range. Anomalous free-surface behavior detected as a two-step extinction of the inclined mirror trace above about 110 GPa suggests decomposition in the decompression process.

I. INTRODUCTION

The metal-hydrogen (M-H) system has attracted considerable interest in both basic and applied research. One of the characteristic features is that a large amount of hydrogen can be absorbed in transition metals, showing a wide solid solution range. In M-H systems, H atoms enter interstitially into the metal lattice (d-band metals in most cases), forming covalent bonds with the surrounding M atoms. Spectroscopic investigation as well as band calculations have now established the formation of bonding states between H $1s$ and metal d states as one of the general features of M-H systems.[1] The extremely fast diffusion of H atoms owing to their light mass also characterizes the M-H systems.[2]

There have been a number of high-pressure experiments performed on M-H systems, most of them intending to synthesize novel metal hydrides which do not form under ordinary conditions, and study thermodynamical properties such as pressure-temperature-composition relations at high hydrogen pressures.[3,4] However, application of high pressure can also provide important information on the nature of the atomic and electronic states of hydrogen in metals. Recent compressibility measurements[5] by means of x-ray diffraction using a diamond-anvil cell showed similar pressure-volume relations for V_2H and vanadium up to 60 GPa, the maximum pressure studied, and the result was explained qualitatively in terms of formation of covalent bonds between H and M atoms, comparable in strength to those between M atoms. Phase-stability relations in the pressure-temperature diagram between α and β_1 or β_2 phases in V_2H and V_2D have also been studied and interpreted in terms of volume change due to site changes of H(D) atoms in the α phase.[6]

The aim of the present study is to investigate the compression behavior of V_2H and V_2D under dynamic pressures higher than 100 GPa. Reduction of lattice spacings to such a large extent is expected to induce a transition of H atoms from localized states to delocalized states owing to the increased tunneling probability between neighboring interstitial sites. The V-H system is believed to be a good candidate for its realization because the density distribution of H(D) atoms in V_2H (Ref. 7) and V_2D (Ref. 8) at normal pressure is reported to be rather extended in space by neutron-diffraction experiments. The work is also intended to explore new phenomena which might show up under extreme shock conditions, as is actually observed in anomalous decompression processes.

II. EXPERIMENTAL

Specimens of V_2H and V_2D were prepared by hydriding pure vanadium metal. A vanadium-metal plate of 99.99% purity was purchased from Teledyne Wah Chang Albany Corp., Albany, Oregon. Specimen pieces approximately $(14—20)\times10\times3$ mm^3 in size were cut out from the vanadium plate, and polished chemically by immersion in 20—30 wt.% nitric acid. The specimens were heated in a vacuum of 10^{-5} Torr to 980°C, where they were kept for 20 h. Hydrogen gas of 740 Torr was then introduced into the reaction tube and the temperature was decreased to about 270°C at a cooling rate of 2°C/min. The specimens were further annealed at this temperature for about 20 h, followed by air cooling to room temperature. The amount of absorbed hydrogen was estimated by measuring the pressure drop, and also checked by measuring the increase in weight of the specimen. The hydrogen- (or deuterium-) to-metal ratio thus determined was 0.50 ± 0.01, warranting stoichiometry. The specimens were polished on both parallel surfaces and mounted on a copper or tungsten driver plate 1 mm thick.

Impact experiments were carried out using a 25-mm-bore propellant gun[9] and a 20-mm-bore two-stage light-gas gun[10] for the projectile velocity range up to 4 km/s. The condition of the symmetrical impact was fulfilled by choosing the same material, copper or tungsten, for both the flyer plate and the target plate. The thickness of the flyer plate was 2 mm for copper and 1 mm for tungsten. The velocity of the projectile, bearing a small magnet, was determined with a precision of 0.1% by measuring the

time of flight between two coils placed ahead of gun muzzle.

Shock parameters were optically measured by means of streak photography.[11] A rotating-mirror-type streak camera with a 10-mm/μs writing speed was used. Shock velocity was determined from the specimen thickness and the transit time of the shock wave in the specimen, which was detected by making use of the sudden decrease in reflectivity of small flat mirrors fixed on the surface of the specimens and the driver plate upon arrival of the shock waves. The motion of the free surface of the specimens was also recorded by using an inclined mirror fixed on the specimen surface with a small angle. The precision of our measurements of the shock velocities and the free surface velocities was 1% and 3%, respectively.

The shocked state was computed on the basis of the impedance-match solution as well as the free-surface approximation. The experimental error in determining the pressure and volume was estimated to be 1% in the case of the impedance-match solution.

III. RESULTS

Results from the shock-compression experiments are summarized in Table I. Information on the shock-compressed state can be obtained from the impedance-match solution, in which the pressure and particle velocity are taken to be the same across the specimen—driver-plate boundary upon passage of the shock wave. The relation between shock velocity and particle velocity is shown in Fig. 1. No systematic difference was noted between the data for V_2H and V_2D. All of the data points can be closely represented by a linear relation $U=5.56+1.10u$, and no anomaly was detected in the impact range investigated. Shock velocity as extrapolated to $u=0$ was found to be in close agreement with the value of the bulk sound velocity of V_2H, $C_0=5.51$ km/s, estimated from the bulk modulus as determined from static compression experiments by Fukizawa and Fukai.[5]

The pressure-volume relation obtained from the impedance match solution is shown in Fig. 2. The figure includes the compression data for V_2H obtained from x-ray diffraction studies done under static high pressure using a diamond-anvil cell[5] and also shock-compression data for vanadium reported by McQueen *et al.*[12] The shock-compression curve (Hugoniot) obtained for V_2H and V_2D in the present study was found to lie slightly below the static compression data for V_2H and to come rather close to the shock-compression curve for vanadium.

Owing to the lack of pertinent data for certain thermodynamic properties of V_2H, such as the specific heat, the Debye temperature, the thermal expansion, etc., the conventional reduction method of Hugoniot to the isothermal pressure-volume relation is not applicable. Therefore, we tentatively assume that the temperature increase during the shock compression of V_2H and V_2D is the same as that of vanadium. Fortunately, the volume correction due to temperature increase is rather small in vanadium in the pressure range studied; i.e., it amounts to only 1.1% at 100 GPa, where the shock temperature is estimated to be 1400 °C.[12] It is also to be noted that, since the temperature increase along the Hugoniot curve becomes steeper with increasing pressure, the Hugoniot curve may intersect the phase boundary β_1-β_2 and/or β_2-α.[6] If the Hugoniot temperature calculated for vanadium is applied to the case of V_2H, it is expected to cross the β_1-β_2 boundary at about 80 GPa, but remain in the β_2 phase up to 135 GPa, the maximum pressure studied. Absence of any anomaly in the shock-compression data caused by a possible phase transition β_1-β_2 is consistent with x-ray data under static compression (5 GPa) showing no volume change across the transition β_1-β_2.[6]

The pressure-volume relation V_2H and V_2D obtained by the shock-compression method was fitted by the least-squares method to the Murnaghan-Birch equation of state,

$$P=\tfrac{3}{2}K_0(x^7-x^5)[1-\tfrac{3}{4}(4-K_0')(x^2-1)] ,$$

where $x=(V/V_0)^{-1/3}$, K_0 is the bulk modulus, and K_0' is its pressure derivative (subscript 0 means the value at $P=0$). Our results are summarized in Table II, together

TABLE I. Summary of shock-compression data of V_2H and V_2D.

Projectile velocity (km/s)	Flyer and driver material	Sample thickness (mm)	Impedance-match solution U_1 (km/s)	u_1 (km/s)	P_1 (GPa)	V_1/V_0	Free-surface approximation $u_{fs}/2$ (km/s)	P_1 (GPa)	V_1/V_0	Remarks $u_{fs}/2$ (km/s) abnormal
					V_2H ($\rho_0=5.713$ g/cm^3)					
1.903	Cu	3.272	6.75	1.04	40.7	0.846	1.18	46	0.83	
2.773	Cu	3.450	7.21	1.54	63.5	0.786	1.65	68	0.77	
3.417	Cu	3.345	7.64	1.91	83.3	0.750	1.99	87	0.74	
3.570	W	3.447	8.30	2.45	116.2	0.704	2.44[a]	116	0.71	3.54[b]
4.005	W	3.245	8.54	2.75	134.2	0.678	c			3.52[b]
					V_2D ($\rho_0=5.770$ g/cm^3)					
2.947	Cu	3.428	7.27	1.64	68.8	0.775	1.78	75	0.76	
3.884	Cu	3.408	7.97	2.17	99.6	0.728	2.16	99	0.73	
3.898	W	3.435	8.47	2.67	130.6	0.685	2.63[a]	129	0.69	3.46[b]

[a]The value for the free-surface velocity of the slower component labeled 2 in Figs. 3 and 4.
[b]The value for the free-surface velocity of the faster component labeled 1 in Figs. 3 and 4.
[c]The slower component could not be measured because of a partial failure of the experiment.

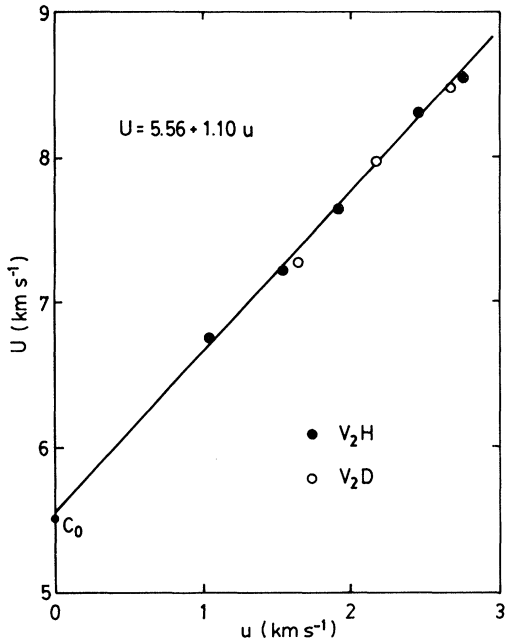

FIG. 1. Shock velocity U vs particle velocity u of V_2H (solid circles) and V_2D (open circles).

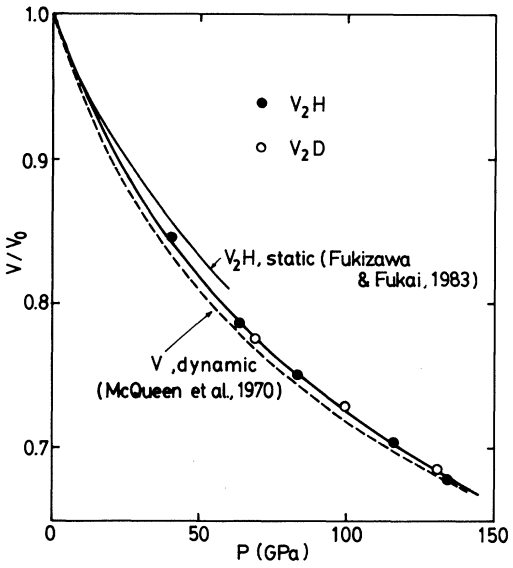

FIG. 2. Shock-compression curve of V_2H and V_2D. The shock-compression curve of vanadium (Ref. 12) and the static compression curve of V_2H (Ref. 5) are shown by a dashed and thin solid line, respectively.

with the static compression data for V_2H and both the static and dynamic compression data for vanadium.

As shown in Table I, the free-surface velocity measured by the inclined-mirror technique was found to be in reasonable agreement with twice the particle velocity determined from the impedance-match solution, so long as the particle velocity remains under 2.2 km/s. This is illustrated in the pressure—versus—particle-velocity diagram in Fig. 3. However, a striking anomaly was observed in the inclined-mirror trace in the streak photograph when the particle velocity is greater than 2.4 km/s, as demonstrated in Fig. 4. The inclined-mirror trajectory apparently disappeared in two steps: Presumably, this implies that the faster and slower component of the free surface arrive successively at the inclined mirror. The slower component, labeled 2 in Fig. 4, gives a normal value, i.e., twice the particle velocity obtained by the impedance-match solution, as expected from the ordinary free-surface approximation. On the other hand, the faster component, labeled 1 in Fig. 4, shows an abnormally high free-surface velocity, as illustrated by the broken lines in Fig. 3.

IV. DISCUSSION AND CONCLUSION

It is surprising to find that V_2H and V_2D are as incompressible as vanadium up to 135 GPa, where the

TABLE II. Bulk modulus K_0 and its pressure derivative K_0' of $V_2H(V_2D)$ and vanadium determined by fitting the dynamic and static compression data to the Murnaghan-Birch equation of state.

Material	Method (pressure range)	K_0 (GPa)	K_0'	Remarks
$V_2H(V_2D)$	Dynamic	175	3.3	Present work[b]
	(0—135 GPa)	152	4.0[a]	
		(173)	(3.6)	(raw Hugoniot)[c]
		(162)	(4.0)[a]	
	Static, x-ray	173.5	5.3	Fukizawa and Fukai[d]
	(0—60 GPa)	193.5	4.0[a]	
V	Dynamic	155	3.8	McQueen *et al.*[e]
	(0—130 GPa)	149	4.0[a]	
	Static, x-ray	157.4	5.3	Fukizawa and Fukai[d]
	(0—60 GPa)	176.4	4.0[a]	

[a] K_0' was fixed to be 4.
[b] Correction due to temperature increase along shock-compression curve was assumed to be the same in $V_2H(V_2D)$ and vanadium (Ref. 12).
[c] Raw Hugoniot data without temperature correction were used.
[d] Reference 5.
[e] Reference 12.

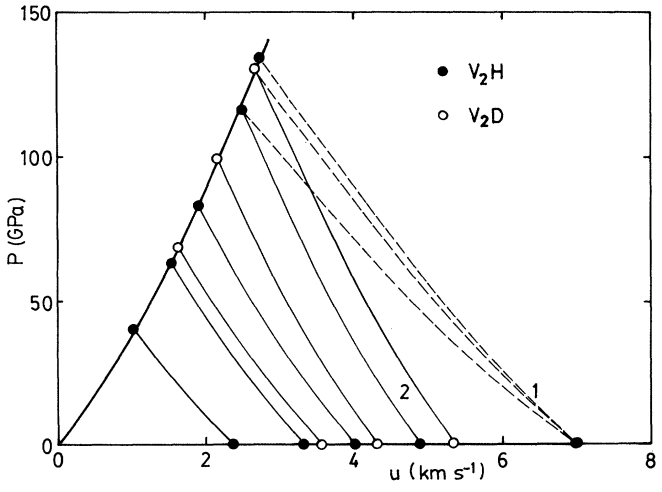

FIG. 3. Decompression behavior of V_2H and V_2D represented in the pressure-particle velocity diagram. The dashed line labeled 1 indicates the faster component with anomalously high free-surface velocity, whereas the thin solid line labeled 2 indicates the slower component with normal free-surface velocity as expected from the impedance-match solution.

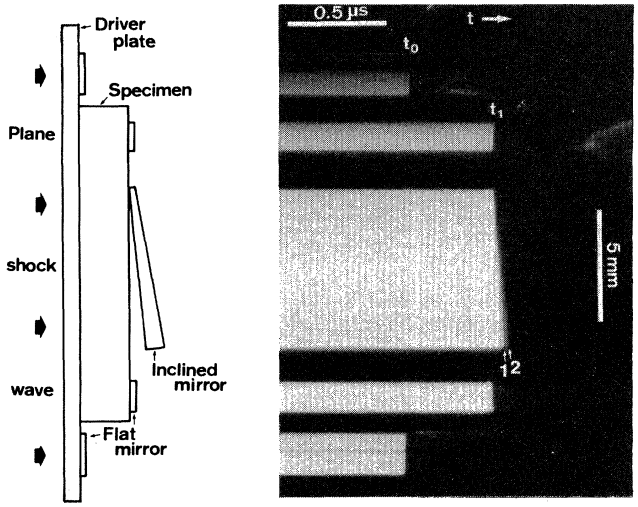

FIG. 4. Streak photograph and experimental setup of V_2D shocked to 130.6 GPa. The arrival time of the shock wave at the rear and front surface of the specimen is shown by t_0 and t_1, respectively. Arrows labeled 1 and 2 indicate the extinction trajectory of the inclined mirror due to the faster and slower free-surface component, respectively.

volume is reduced to two-thirds of its original value. Although the statement that V—H bonds are as incompressible as V—V bonds is concise and expedient for its explanation, it must be recognized that the actual situation is not so simple. Recent electronic band calculations on transition metals[13] have shown that, although the cohesion of *d*-band metals comes mainly from *d* electrons, the compressibility is determined by conduction electrons of *s,p* character. Thus, discussions of compression behavior in terms of *M—M* bonds should not be taken too literally. Moreover, at large concentrations of hydrogen, as in V_2H and V_2D, the electronic structure as a whole should be modified to a large extent by electrons contributed by H(D) atoms. Therefore, it is only from band calculations on metal hydrides at different pressures that we may learn the physics of the compression behavior observed here. Such calculations have been performed by Terakura[14] on V-H, Fe-H, and Pd-H systems, and have shown that all of these hydrides are nearly as incompressible as host metals.

Absence of any anomaly in the compression curve (Fig. 2) indicates that a transition to delocalized states has not taken place below 135 GPa. Formation of a proton band by application of high pressures is left for future experiments.

Regarding the origin of the anomalous behavior observed as two-step extinction of the inclined-mirror trace, we believe that it is due to some process induced in decompression. The compression behavior deduced from the impedance-match solution is considered to be quite normal. It is worth noticing that such anomaly apparently takes place when the shock pressure exceeds a certain threshold value. We propose that the observed anomaly is due to the decomposition reaction of vanadium hydride (or deuteride) into vanadium plus hydrogen (or deuterium) in the decompression stage. The faster component with an anomalously high velocity may be due to hydrogen, selectively accelerated from the shocked surface upon rarefaction, and reduces the reflectivity of the inclined mirror upon impact, while the slower component is most probably due to vanadium which ultimately destroys the inclined mirror. Similar selective acceleration of hydrogen was reported in the detonation product of high explosives, which was confirmed by *in situ* spectroscopy.[15] Furthermore, an anomalously high free-surface velocity in decompression has similarly been found by Lange and Ahrens[16] in hydrated minerals (serpentine and brucite) and carbonate (calcite), where dehydration or devolatilization was definitely confirmed in previous reports.[17,18] More direct evidence either for emission of decomposed hydrogen from the shock-decompressed surface or for shock-decomposed products is highly desirable to substantiate the interpretation in terms of decomposition reaction in the metal-hydrogen system, since this new phenomenon might bear important implications in shock-induced chemistry.[19]

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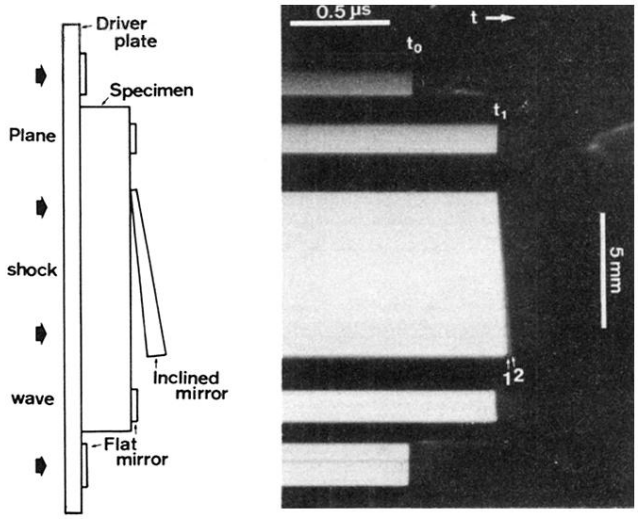

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