Redox reaction between tantalum and silica induced by shock loading

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Intense shock waves produce very remarkable effects in solid materials during the short time interval of shock loading [1, 2]. Phase changes due to the electronic or the displacive mechanism without involvement of extensive atomic diffusion, among other things, are most easily induced under shock compression. In the latter cases, they are sometimes retained even after the release of shock pressures [3, 4], leading to the synthesis of new materials, as in the case of diamond. However, the atomic diffusion itself is also known to be extremely enhanced under high pressures and temperatures due to shock-loading, resulting in various kinds of chemical reactions [5, 6]. In some cases diffusion coefficients as high as a few hundred $cm^2 sec^{-1}$ have been reported, leading to ultrafast crystal growth and chemical reaction rates. However, there still remains a great deal of controversy in the understanding of the fundamental mechanism governing the fast diffusion and enhanced chemical reactivity under shock loading, which implies primary importance for the application of shock-wave technique to materials science.

Recently, during the course of shock experiments to confirm the existence (or non-existence) of a denser phase of SiO_2 than the rutile-type stishovite [7], we encountered extensive recognizable chemical reactions taking place along the specimen–container boundary. Quite unexpectedly, we had evidence that the tantalum metal, which was used as a container material to increase the efficiency of pressure generation, was ultimately oxidized to Ta_2O_5 under shock compression, whereas SiO_2 was reduced to silicon. In this letter we describe the results of X-ray powder diffraction analysis and transmission electron microscopic (TEM) observation.

Natural single crystal quartz was used for the shock-loading experiments. Disk-shaped specimens, 0.4 to 1.0 mm thick and 5 to 8 mm in diameter were encased in various kinds of specimen containers, as shown in Fig. 1a to c. Tantalum metal was used for shock pressures higher than 67 GPa because of its high shock impedance (Fig. 1b). The highest shock loading pressures in the present experiments were achieved using pressure enhancement due to Mach configuration in the composite cylinder made of tantalum and stainless steel (Fig. 1c) [8]. In this specimen container, Mach disk was proved to occur in the central part of the tantalum cylinder, thereby achieving pressure enhancement by a factor of more than 1.5.

Shock-loading was achieved by the impact of a flyer plate accelerated to a velocity up to $2.3 km sec^{-1}$ by a 25 mm propellant gun [9]. The velocity of the flyer
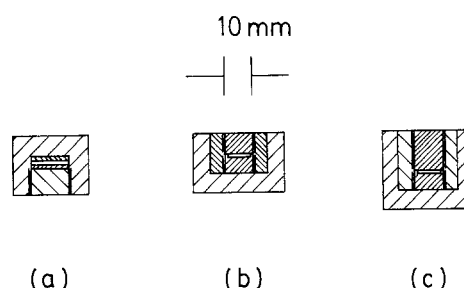

Figure 1 Various shock-recovery fixtures made of (a) stainless steel (b) tantalum and (c) composite of tantalum and stainless steel. Coarsely and finely hatched areas indicate stainless steel and tantalum, respectively.

plate was determined by measuring its flight time between two coils placed ahead of the gun muzzle, with the aid of a small magnet embedded in a plastic projectile which supported the flyer plate. Pressure achieved in the specimen container was estimated from the measured flyer velocity on the basis of impedance match concept [9]. In the case of a composite cylinder, the pressure value at the central mach disk was calculated by assuming the steady state where the propagation velocity of the Mach disk was assumed to be equilibrated with the shock velocity in the outer cylinder made of stainless steel [8].

Experimental results of X-ray diffraction analysis and TEM observation for shock recovered materials are summarized in Table I, together with the experimental conditions. X-ray powder diffraction pattern of shock-loaded materials from above 67 GPa revealed remarkable crystalline peaks in addition to a weak amorphous halo due to diaplectic glass formed in the shock process [10], as shown in Fig. 2. Most diffraction lines were successfully identified to be due to β–Ta_2O_5, suggesting complete oxidation of tantalum metal in contact with the quartz disk. No appreciable reaction was observed when the stainless steel container was used.

The redox reaction was confirmed by detailed observation under TEM. A typical TEM image of shock recovered products is shown in Fig. 3. From the interface boundary with the tantalum container, dark-coloured fine particles are found to be distributed to a depth of about 800 nm into the pale-coloured matrix, their size decreasing with increasing distance from the surface. Judging from the difference between the absorption due to tantalum and silicon, we may consider that tantalum-rich particles are dispersed in the silica matrix. The chemical composition determined by analytical TEM clearly lends support for this interpretation, as shown in Fig. 3. The pale-coloured matrix contains only silicon, while that part where

TABLE I Experimental results of shock-loading on the SiO_2–Ta system

Shot no.	Shot assembly*	V_{imp} (km sec^{-1})	P (GPa)	Reaction products
86–152	a[†]	1.142	$29 < P < 40$	a-SiO_2
81–118	a	2.332	59	a-SiO_2
85–225	b	1.8	67	β-Ta_2O_5, Si, a-SiO_2
81–144	b	2.072	80	β-Ta_2O_5, Si, a-SiO_2
81–119	c	1.905	110[‡]	β-Ta_2O_5, Si, a-SiO_2
81–112	c	2.083	130[‡]	β-Ta_2O_5, Si, a-SiO_2

*Shot assembly is shown in Fig. 1.
[†]SiO_2 specimen was sandwiched between tantalum plates.
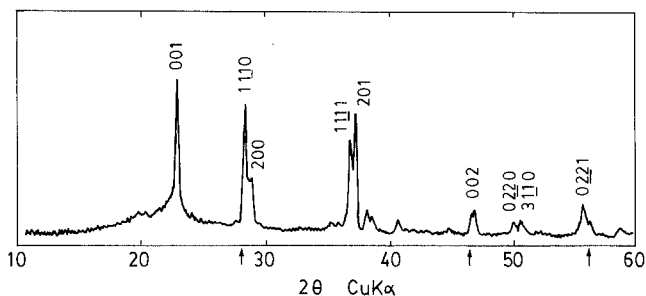[‡]Pressure value is estimated on the basis of simulation experiment [8].

Figure 2 X-ray diffraction pattern of the quartz specimen shocked to 80 GPa using a tantalum container (Fig. 1b). Reflections from β-Ta_2O_5 are indexed with the orthorhombic indices. Diffraction angles expected for silicon are indicated by arrows. Note the weak halo around the 2θ angle of 15 to 25° for Cu$K\alpha$ radiation and also a few unindexed lines.

small dark-coloured particles are precipitated is found to consist of both silicon and tantalum, although quantitative analysis including oxygen could not be made in the present study.

Crystalline particles were completely spherical in shape, as shown in Fig. 4. Close examination of small crystalline particles under high resolution TEM revealed at least two kinds of particles, i.e. tantalum oxide (β–Ta_2O_5) and silicon, as shown in Fig. 5a and b, respectively. The measured distances between the black and white stripes which cross each other orthogonally in Fig. 5a compare favourably with d-spacings of 0.315 and 0.388 nm for (1 1 1 0) and (0 0 1) of β-Ta_2O_5, respectively. Characteristic features of the (1 1 0) plane of silicon are clearly seen in Fig. 5b and the separation of the observed stripes in the [0 0 1] direction is found to be consistent with the $(a/2)$ value of 0.271 nm.

Experimental results clearly demonstrated that a redox reaction, $5SiO_2 + 4Ta = 2Ta_2O_5 + 5Si$, occurs near the interface boundary between the quartz specimen and the tantalum container during intense shock loading. We estimate that the above reaction will only be possible above about 4300° C at atmospheric pressure, by extrapolating the thermodynamic equilibrium relations to the very high temperature

region, using heat of formation and entropy data for the following reactions: $Si + O_2 = SiO_2$, and $4Ta + 5O_2 = 2Ta_2O_5$ [11]. Because the shock and post-shock temperatures are estimated to be 3300 and 2400° C for the lowest shock pressures where the above reaction was observed [12], the reaction cannot be realized at least in the shock released state.

The observed texture of the redox reaction products under TEM strongly suggests that fine particles of tantalum are injected into the quartz specimen because of some jetting mechanism from the container wall and thereby subjected to complete oxidation to Ta_2O_5. The spherical shape of the particles further suggests melting or vaporization behaviour due to a jetting mechanism. Presumably a high-velocity jet of tantalum particles may induce the local decomposition reaction of SiO_2 to $Si + 2O$ and tantalum particles may subsequently be oxidized to Ta_2O_5 in a highly reactive oxygen atmosphere. A similar redox reaction has been observed when a high-velocity projectile of aluminium was injected into quartz sand [13]. Complete reduction of SiO_2 to silicon and oxidation of aluminium to Al_2O_3 were observed in this case, although this redox reaction can be achieved under thermodynamic equilibrium conditions.

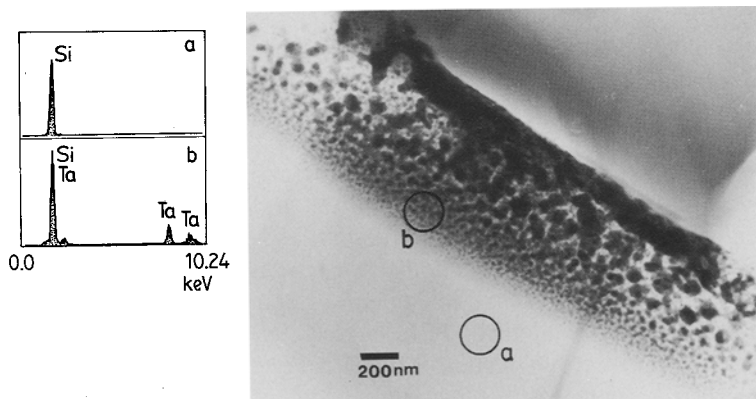The present findings show the marked significance

Figure 3 TEM showing the redox reaction between tantalum and silica at the interface boundary of the specimen shocked to 80 GPa (no. 81–144). Energy-dispersive X-ray analysis at regions circled, a and b, are shown in the inserts.
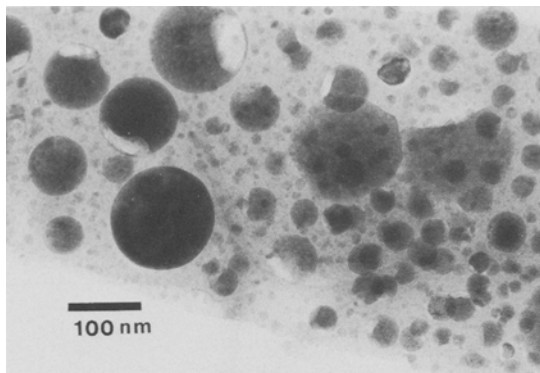
Figure 4 TEM of spherical particles of Ta_2O_5 dispersed in the amorphous SiO_2 matrix.

of enhanced reactivity in shocked solids, when one considers the potential application of shock processing of inorganic substances.

Acknowledgements

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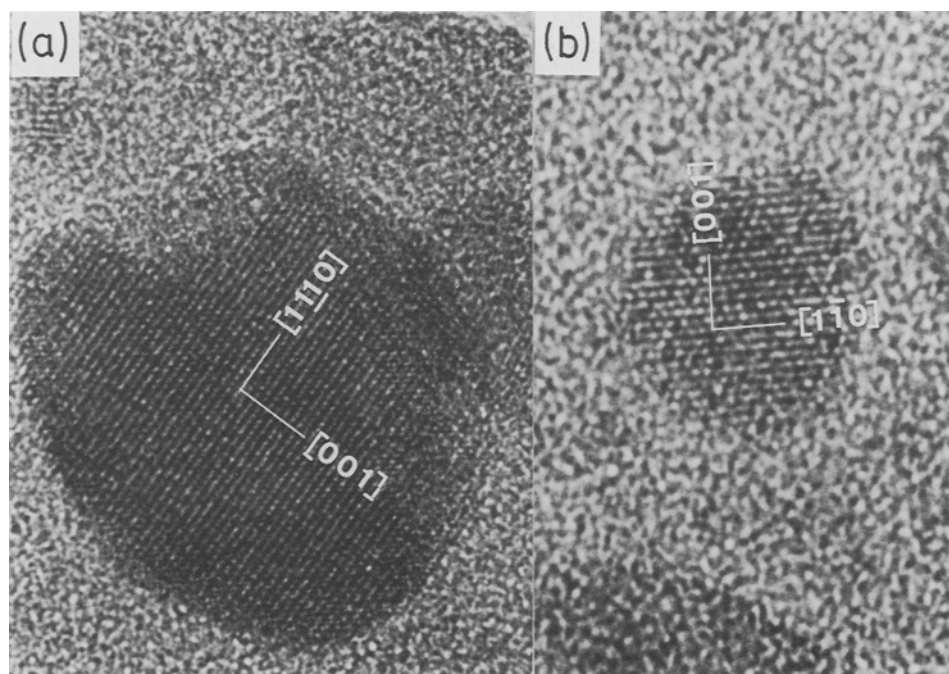
Figure 5 High resolution electron micrographs of (a) β-Ta_2O_5 and (b) silicon.