Superconducting phase prepared from Ta₃Si under high pressure

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Abstract. High-pressure behaviour of Ta₃Si intermetallic compound was investigated by shock compression and static compression methods. Superconducting phase with \( T_C = 9.3 \) K was found in the sample shocked to 50-61 GPa, however most of the shock recovered sample indicated the starting stable phase with the Ti₃P-type structure. The new superconducting phase was not obtained from static compression up to 15 GPa and 800 °C. Bulk modulus of Ta₃Si with the Ti₃P-type structure was determined to be \( K_0 = 246(4) \) GPa. The present results suggest that a rapid phase transformation occurred during shock compression, but most of the high-pressure phase was reverted to the stable phase in the decompression process.

1. Introduction

Tantalum and niobium belong to the same atomic group and those atomic sizes are very similar to each other, but there were some differences in the Ta-Si and the Nb-Si system. Ta₃Si with the tetragonal Ti₃P-type structure is stable at low temperature, but Nb₃Si with the Ti₃P-type phase is a high temperature phase stable at higher than 1790 °C. Although some metastable phases with the bcc or the fcc type structure were reported for the Nb-Si system [1,2], any high-pressure phase of Ta₃Si has not reported yet.

In Nb-Si system, metastable Nb₃Si phase with the cubic Cr₃Si-type structure is known to have a high superconducting transition temperature \( T_C \). Synthesis of this phase has been tried by various methods, such as high-pressure synthesis and liquid quenching [3]. Olinger et. al. [4] discussed the tetragonal Ti₃P-type and the cubic Cr₃Si-type structure are resemble and its volume difference is only 2.8 \%, so that the Cr₃Si-type structure could be rapidly transformed from the Ti₃P-type structure by small displacement without diffusion. On the base of this discussion, some shock compression experiments have been performed [3, 5-7].

In Ta-Si system, Ta₃Si with the Cr₃Si-type structure was also expected to have a superconducting transition and its expecting \( T_C \) was 8.7 K [8]. In fact, Pan et al. [9] reported a superconducting modification of Ta₃Si from the stable Ti₃P-type structure by the explosive compression (> 200 GPa, \( T_C = 8.6 \) K), but its crystal structure has not been identified yet.

The aim of the present study is to synthesis the superconducting phase Ta₃Si and to obtain information on the phase from both shock and static high-pressure experiments.
2. Experimental

Starting material was prepared by arc melting method from a mixture of high purity tantalum and silicon in 3:1 atomic composition. Ingots of the starting material were melted several times for enough reaction. X-ray powder diffraction (XRD) measurement shows that the starting material consists of the tetragonal Ti$_3$P-type Ta$_3$Si ($P 42/n, Z = 8$) with small amount of Ta(Si) solid solution and Ta$_2$Si.

Produced ingots were cut into disk shape (1.0 mm thick and 10 mm in diameter) for shock experiments and powdered for static compression experiments using an agate mortar.

Shock-recovery experiments of Ta$_3$Si disks encased in Cu containers were carried out by the impact of a 3-mm-thick stainless steel flyer plate using a 25 mm bore single-stage propellant gun [10]. The Cu containers were 5-mm-thick at the shock front and further more, 2-mm-thick SUS304 plates were stuck on the front of the Cu containers as a protector. The velocity of the flyer was determined by measuring flight time between two coils placed in front of the gun muzzle, with the aid of a small magnet embedded in the plastic projectile [11]. Pressure achieved in the specimen container was estimated from the measured flyer velocity by the impedance match method [12], and pressure in the specimen was considered to achieve equilibrium to that of the container.

Static compression experiments on powdered Ta$_3$Si were conducted to the pressure up to 15 GPa and to the temperature up to 800 °C using large volume press apparatuses with DIA-6 type and KAWAI type devices [13]. Experimental methods and pressure-transmitting media were same as described in the previous report [13]. Experimental conditions for static compression experiments are summarized in Table 1.

Recovered samples were analyzed by X-ray powder diffraction (XRD) method and transmission electron microscopy (TEM). Magnetic properties of these samples were measured by superconducting quantum interference device (SQUID).

Energy dispersive type X-ray observation of Ta$_3$Si under pressure were also carried out using a cubic-anvil type high-pressure apparatus, the MAX80 system at PF-AR-NE5C in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK) [14]. Powdered Ta$_3$Si and NaCl (works as a pressure marker) [15], were encased separately in a Teflon capsule together with a 4:1 methanol/ethanol mixture (works as a hydrostatic pressure-transmitting medium). The capsule was inserted in a cube-shaped boron-epoxy solid pressure medium [14]. Cell parameters were calculated from observed $d$-values by the least-squares calculation.

### Table 1. Experimental conditions for the static compression.

| Press No. | Apparatus | Pressure /GPa | Temperature /°C | Hold time /min |
|-----------|-----------|---------------|-----------------|---------------|
| 1         | DIA-6     | 7.0           | 800             | 30            |
| 2         | DIA-6     | 7.5           | 400             | 60            |
| 3         | DIA-6     | 7.7           | 27              | 60            |
| 4         | KAWAI     | 12            | 800             | 60            |
| 5         | KAWAI     | 15            | 800             | 60            |

3. Results and discussion

3.1. Shock compression

Figure 1 shows typical XRD patterns of arc-melted and shock recovered Ta$_3$Si. The sample shocked to 50 GPa consists mostly of the Ti$_3$P-type phase as shown in Figure 1(b), but its diffraction peaks were broadened by shock compression. Figure 2 shows temperature dependence of susceptibility of the sample shocked to 50 GPa. A small diamagnetic signal was observed at 9.3K, indicating that a superconducting phase was synthesized. Results of XRD and TEM analysis showed the shock-
recovered Ta₃Si was partially amorphousized and the remaining part indicates the starting Ti₃P-type texture. Considering excellent sensitivity of SQUID for the superconductor, quantity of the produced superconducting phase was very small. The superconducting phase of \( T_c \) 9.3 K was also found in the sample shocked to 61 GPa, however its quantity was smaller than that of shocked to 50 GPa. The superconducting phase was not observed in the sample shocked to 45 GPa. The pressure range of generating the superconducting phase was relatively narrow. These results imply that a reverting phase transition reaction could easily occur under decompression process or by the effect of residual temperature, so that it is difficult to quench the superconducting phase.

3.2. Static compression
Figure 3 shows XRD pattern of Ta$_3$Si recovered from the static compression. Both non-heated and heated samples have the starting Ti$_3$P-type structure, however peaks due to impurities, Ta(Si) and Ta$_2$Si, were disappeared in heated sample. These impurities might solve into the lattice of Ti$_3$P-type Ta$_3$Si and the chemical composition of Ta$_3$Si might be changed from the stoichiometric ratio due to the high-pressure annealing. In case of static compression up to pressure of 15 GPa, any new superconducting phase has not been found in pressure-recovered samples.

3.3. In-situ X-ray observation under high-pressure

Tetragonal cell parameters of Ta$_3$Si with the Ti$_3$P-type structure under hydrostatic condition at room temperature are summarised in Table 2. Figure 4 shows energy-dispersive type XRD patterns observed

| Pressure /GPa | a /Å  | c /Å  | V /Å$^3$ | c/a       |
|---------------|-------|-------|----------|-----------|
| 0.0*          | 10.1791(4) | 5.1653(1) | 535.20(3) | 0.5074(4) |
| 0.6           | 10.175(3)  | 5.159(1)  | 535.2(3)  | 0.507(3)  |
| 1.5           | 10.162(4)  | 5.153(2)  | 534.1(4)  | 0.507(4)  |
| 2.4           | 10.146(4)  | 5.148(2)  | 532.1(4)  | 0.507(4)  |
| 3.1           | 10.135(3)  | 5.145(2)  | 529.9(3)  | 0.508(4)  |
| 3.8           | 10.126(4)  | 5.137(2)  | 528.4(4)  | 0.507(5)  |
| 4.7           | 10.119(4)  | 5.136(2)  | 526.7(4)  | 0.508(5)  |
| 5.7           | 10.106(3)  | 5.126(2)  | 525.8(3)  | 0.507(4)  |

*: Data obtained by angular-dispersive X-ray powder diffraction method at ambient condition.

Figure 4. Typical energy-dispersive type XRD patterns of Ta$_3$Si observed under static compression process ($2\theta = 6.50^\circ$); (a) at ambient pressure (b) at 5.7 GPa. Major diffraction lines of the Ti$_3$P-type phase are only indexed in this figure. Asterisks in figures indicate diffractions of Ta(Si) and Ta$_2$Si impurities.

Figure 5. Volume per chemical formula of Ti$_3$P-type Ta$_3$Si as a function of pressure.
at ambient-pressure and at 5.7 GPa. Ta₃Si was kept the Ti₃P-type structure up to the pressure of 5.7 GPa, and the c/a axis ratio maintains the constant value within an observational error. Any indications of the phase transition were not observed in this range of pressure.

Figure 5 shows P-V data of the Ti₃P-type Ta₃Si phase at 27 °C, which observed in the compression process. The bulk modulus of the Ta₃Si was determined to be $K_0 = 246(4)$ GPa by fitting the P-V data to the third-order Birch-Murnaghan equation of state with $K' = 4$ \cite{10}. The present value was larger than that of pure tantalum ($K_0 = 200$ GPa \cite{17}). These results indicate Ta₃Si is hard and difficult to be compressed. Higher pressure should be needed for phase transformation to the Cr₃Si-type structure.

4. Conclusion

High-pressure behaviour of Ta₃Si with the Ti₃P-type structure was investigated by both shock and static compression methods. A superconducting phase was found in shock-recovered sample. The present results suggest the possibility that a phase transition occurred during shock compression process, and that most of the high-pressure phase is reverted to the stable Ti₃P-type phase in the decompression process. Our inference is consistent with a relationship between the Ti₃P-type to the Cr₃Si-type structure, which discussed by Olinger et al. \cite{4}; the Cr₃Si-type structure could be rapidly transformed from the Ti₃P-type structure by small displacement without diffusion.

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