First-Principles Study on Thermodynamic Properties of Ti$_2$AlC and Ti$_2$SC

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First-principles calculations of the thermodynamic properties of Ti$_2$AlC and Ti$_2$SC were carried out. The temperature dependence of bulk modulus, the pressure dependence of normalized volume $V/V_0$, thermal expansion coefficient, specific heats, and Debye temperature were successfully obtained through the quasi-harmonic Debye model in the temperature range from 0 to 1000 K and the pressure range from 0 to 50 GPa. The calculated results were compared with available experimental data. The effects of the bonding strength of Ti-S and Ti-Al on the thermodynamic properties were discussed. [doi:10.2320/matertrans.MAW200903]

(Received April 20, 2009; Accepted June 30, 2009; Published August 19, 2009)

Keywords: first-principles, thermodynamic properties, quasi-harmonic model, $M_{n+1}AX_n$ (MAX) phases

1. Introduction

Ti$_2$AlC and Ti$_2$SC are two members of the so-called $M_{n+1}AX_n$ (MAX) phases, where $n = 1, 2$ or $3$, $M$ is an early transition metal, $A$ is an A-group element, and $X$ is either C or N. MAX phases exhibit unique properties combining the merits of metals and ceramics, such as high thermal and electrical conductivity, high strength and modulus, damage tolerance and thermal shock resistance, and more importantly being machinable.$^{1-3}$ These significant properties make them promising materials for high temperature applications. The structure of MAX phases is characterized by alternating $M-A$ and $A-X$ layers along $c$-direction. Accordingly, the bonding character of MAX phases also shows layered structure feature, consisting of stacks of “hard” $M-X$ bond and relatively “soft” $M-A$ bond along $c$-direction.$^{1-3}$ Ti$_2$AlC and Ti$_2$SC exhibit the typical layered crystal structure for MAX phases. The main difference between them is the different $A$ layer in the layered structure. In the previous studies, it was found that the $M-A$ bonding (Ti-S bonding) in Ti$_2$SC is much stronger than that in other MAX phases.$^{4,5}$ This means that the ‘soft’ $M-A$ bond is strengthened in Ti$_2$SC, which is an extraordinary example in MAX phases studied so far. It is believed that the unusual mechanical and physical properties of Ti$_2$SC, such as the highest room temperature Vickers hardness and thermal conductivity for any MAX phases known to date, are related to the structural anomaly in it.$^{4,6}$

The strengthening of $M-A$ bonding in Ti$_2$SC will have strong influence on the physical and chemical properties. In our previous report, the effects of strong $M-A$ bond on the elastic properties in Ti$_2$SC have been revealed.$^4$ The thermodynamic properties are the basis of solid state science and industrial applications since they can extend our knowledge on the specific behavior of materials under high pressure and high temperature environments. Some thermodynamic properties of Ti$_2$AlC and Ti$_2$SC have been studied experimentally.$^7-9$ However, theoretical investigations are of great benefit to give a global and deep understanding of their thermodynamic properties. In the present work, we carried out a comparative study on the thermodynamic properties of Ti$_2$AlC and Ti$_2$SC using the quasi-harmonic approximation within density functional theory (DFT). The effects of the different $M-A$ bonding in Ti$_2$AlC and Ti$_2$SC on their thermodynamic properties were analyzed. Because of the structural similarity between Ti$_2$AlC and Ti$_2$SC, the effects of different $M-A$ bonding can be well addressed.

2. Computational Details

The zero-temperature energy calculations were performed using the full-potential linearized augmented plane-wave method (FLAPW) plus local orbital as implemented in WIEN2K code.$^{10}$ The effects of the approximation to the exchange-correlation energy were treated by the generalized gradient approximation (GGA-PBE96).$^{11}$ The muffin-tin sphere radii ($R_i$) of Ti, S, Al and C have been chosen as 2.0, 2.1, 2.5, and 1.8 a.u., respectively. The convergence parameter $R_{mt}$ was converged to within 0.1 mRy/unit cell during the self-consistency cycle. To investigate the thermodynamic properties of Ti$_2$AlC and Ti$_2$SC, we applied the quasi-harmonic Debye model. Through this model, one could calculate the thermodynamic parameters including the bulk modulus, thermal expansion coefficient, specific heats, and Debye temperature etc. of any temperatures and pressures from the calculated $E-V$ data at $T = 0$ K and $P = 0$ GPa. The detailed description of quasi-harmonic Debye model can be found in the literatures.$^{12,13}$

3. Results and Discussion

Figure 1 shows the temperature dependence of the bulk modulus $B$ at $P = 0$ GPa. At 0 K, the bulk modulus is 183 and...
140 GPa for Ti$_2$SC and Ti$_2$AlC respectively, consistent with the previous reports.\textsuperscript{5,14} The bulk modulus is nearly a constant when $T < 100$ K, however, it decreases linearly with increasing temperature $T$ when $T > 100$ K. The bulk modulus of Ti$_2$SC and Ti$_2$AlC drops by 6.8% and 8.4%, respectively, from 0 to 1000 K. As is seen, the bulk modulus of Ti$_2$SC is higher than that of Ti$_2$AlC in the whole temperature range. Considering the fact that the unit cell volume of Ti$_2$SC is about 8.3% smaller than that of Ti$_2$AlC and the Ti-S bonding is stronger than Ti-Al bonding, it is not surprising that Ti$_2$SC possesses a higher bulk modulus. Because the bulk modulus is proportional to the hardness, it is expected that Ti$_2$SC will possess a higher hardness. In fact, the Vickers hardness of Ti$_2$SC is experimentally measured to be 8 GPa, which is a very high value for MAX phases in bulk form.\textsuperscript{6}

Figure 2 shows the normalized volume-pressure diagram for Ti$_2$SC and Ti$_2$AlC at various temperatures. It is seen that the unit cell volume decreases smoothly and no abrupt change occurs with increasing pressure for both Ti$_2$SC and Ti$_2$AlC, indicating that the crystal structure of them is stable up to a pressure of 50 GPa. This is consistent with the experimental studies on the compression behavior of Ti$_2$SC and Ti$_2$AlC.\textsuperscript{15,16} It can be seen that on compression, the reduction in volume for Ti$_2$SC is smaller than Ti$_2$AlC, which is due to the higher bulk modulus of Ti$_2$SC. An experimental work on the compression behavior of Ti$_2$SC and Ti$_2$AlC has been recently reported.\textsuperscript{15} However, the results showed that the volume-pressure curve is almost identical to each other. It is somewhat surprising because Ti$_2$SC is much stiffer than Ti$_2$AlC. We think that this may be due to the low quality of the as-prepared Ti$_2$SC samples. As is known, the mechanical properties of MAX phases are strongly dependent on the presence of porosity and impurity in the sintered samples.\textsuperscript{17,18} It is also observed that the relative volume $V/V_0$ decreases slightly at a given pressure for both Ti$_2$SC and Ti$_2$AlC with increasing temperature, which indicates a weak temperature dependence for their compressibility.

Figure 3 shows the temperature dependence of the volume thermal expansion coefficient $\alpha$ of Ti$_2$SC and Ti$_2$AlC. It can be seen that $\alpha$ increases rapidly with increasing temperature at low temperature region of $T < 300$ K and increases smoothly at high temperatures. The thermal expansion coefficient of Ti$_2$SC is lower than that of Ti$_2$AlC, which is consistent with the fact that Ti$_2$SC possesses a higher bulk modulus and lower volume reduction when compressed. As reported previously, the volume thermal expansion coefficient of Ti$_2$SC and Ti$_2$AlC is experimentally measured to be $2.52 \times 10^{-5}$ K$^{-1}$ and $2.61 \times 10^{-5}$ K$^{-1}$ respectively, larger than the present calculation.\textsuperscript{19,20} It is known that additional expansion can be caused by lattice vacancies.\textsuperscript{21} It has been found that carbon vacancies in VC significantly increase the thermal expansion coefficient.\textsuperscript{22} As is well known, non-metal vacancies were generally found in MAX phases.\textsuperscript{23-25} Therefore, the discrepancy between the calculated and experimental thermal expansion coefficient of Ti$_2$SC and Ti$_2$AlC can be attributed to the vacancies effects.

The constant-volume specific heats $C_v$ and constant-pressure specific heats $C_p$ of Ti$_2$SC and Ti$_2$AlC are calculated and shown in Fig. 4. The differences in both $C_v$ and $C_p$ of
$\Theta_D$ and $T_2$ are very slight, which means that the effect of different M-A bonding on the specific heat is negligible. In the low-temperature limit, $C_v$ of $T_2$ and $T_2$ obey the expected $T^3$ power-law behavior, and they both approach the classical asymptotic limit of $C_v = 3n N k_B = 99.8 J/mol K$. The values of $C_p$ for $T_2$ and $T_2$ are slightly larger than the $C_v$, which can be explained by the relation between $C_p$ and $C_v$ as follows:

$$C_p - C_v = \alpha(T) BVT$$  (1)

where $\alpha$, $B$, $V$ and $T$ are the volume thermal expansion coefficient, bulk modulus, volume and absolute temperature, respectively. Our calculated values for $C_p$ of $T_2$ and $T_2$ in the range of 0–300 K are well in agreement with the experimental values.\(^7\)\(^9\)

Figure 5(a) displays the pressure dependence of Debye temperature $\Theta_D$ at 300 K of $T_2$ and $T_2$. It is clear that the Debye temperature increases almost linearly with pressure. Figure 5(b) shows the temperature dependence of $\Theta_D$ at $P = 0$ GPa. It can be seen that $\Theta_D$ of $T_2$ and $T_2$ remains unchanged as $T < 100 K$ and decreases linearly as $T > 100 K$. It is known that Debye temperature $\Theta_D$ is related to the maximum thermal vibration frequency of a solid. The variation of $\Theta_D$ with pressure and temperature reflects the fact that the thermal vibration frequency of the particles in $T_2$ and $T_2$ changes with pressure and temperature. In the present work, $\Theta_D$ of $T_2$ and $T_2$ is calculated to be 762 and 691 K respectively, in good agreement with the experimental value of 765 and 672 K.\(^8\)\(^9\)

Since vibration frequency is proportional to square root of the stiffness within the harmonic approximation, $\Theta_D$ can be used to measure the stiffness of solids.\(^20\) Usually, a solid with high modulus and hardness will possess high Debye temperature. For example, $\Theta_D$ of diamond is 2240 K, much higher than 402 K of graphite.\(^20\) It should be noted that $\Theta_D$ of $T_2$ is the largest measured to date for 211 MAX phases, which is consistent with the fact that $T_2$ possesses the highest bulk modulus and hardness among 211 MAX phases.

4. Conclusion

In conclusion, we have calculated the thermodynamic properties of $T_2$ and $T_2$ using the quasi-harmonic approximation within density functional theory. The bulk modulus of $T_2$ and $T_2$ decreased with temperature. The reduction in volume on compression for $T_2$ is smaller than $T_2$, which is due to the higher bulk modulus of $T_2$. The volume thermal expansion coefficient $c$ of $T_2$ and $T_2$ increases rapidly with increasing temperature at low temperature region of $T < 300 K$ and increases smoothly at high temperatures. The calculated values for $C_p$ of $T_2$ and $T_2$ in the range of 0–300 K are well agreement with the experimental values. The Debye temperature $\Theta_D$ of $T_2$ and $T_2$ remains unchanged as $T < 100 K$ and decreases linearly as $T > 100 K$.

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