First-Principles Study on Thermodynamic Properties of Ti_2AlC and Ti_2SC

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First-principles calculations of the thermodynamic properties of Ti_2AlC and Ti_2SC 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, $M_{n+1}\text{AX}_n$ (MAX) phases

1. Introduction

Ti_2AlC and Ti_2SC are two members of the so-called $M_{n+1}\text{AX}_n$ (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 $M_{n+1}\text{X}_n$ and A 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_2AlC and Ti_2SC 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_2SC is much stronger than that in other MAX phases.^{4,5)} This means that the ‘soft’ M-A bond is strengthened in Ti_2SC , which is an extraordinary example in MAX phases studied so far. It is believed that the unusual mechanical and physical properties of Ti_2SC , 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_2SC will have strong influence on the physical and chemical properties. In our previous report, the effects of strong M-A bonding on the elastic properties in Ti_2SC 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_2AlC and Ti_2SC 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_2AlC and Ti_2SC using the quasi-harmonic approximation within density functional theory (DFT). The effects of the different M-A bonding in Ti_2AlC and Ti_2SC on their thermodynamic properties were analyzed. Because of the structural similarity between Ti_2AlC and Ti_2SC , 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 $R_{\text{mt}}K_{\text{max}}$, which controls the size of the basis set for the wave function, was set to 7.0, where R_{mt} is the minimum spheres radii and K_{max} is the maximal value of the reciprocal lattice vector used in the plane wave expansion. Integrations in the reciprocal space were performed by using the tetrahedron method with a k mesh of 54 k -points in the irreducible wedge of Brillouin zone (BZ). The total energy is converged to within 0.1 mRy/unit cell during the self-consistency cycle. To investigate the thermodynamic properties of Ti_2AlC and Ti_2SC , 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

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Fig. 1 Temperature dependence of the bulk modulus for Ti_2SC and Ti_2AlC at $P = 0$ GPa.

140 GPa for Ti_2SC and Ti_2AlC respectively, consistent with the previous reports.^{4,14} 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_2SC and Ti_2AlC drops by 6.8% and 8.4%, respectively, from 0 to 1000 K. As is seen, the bulk modulus of Ti_2SC is higher than that of Ti_2AlC in the whole temperature range. Considering the fact that the unit cell volume of Ti_2SC is about 8.3% smaller than that of Ti_2AlC and the Ti-S bonding is stronger than Ti-Al bonding, it is not surprising that Ti_2SC possesses a higher bulk modulus. Because the bulk modulus is proportional to the hardness, it is expected that Ti_2SC will possess a higher hardness. In fact, the Vickers hardness of Ti_2SC is experimentally measured to be 8 GPa, which is a very high value for MAX phases in bulk form.⁶

Figure 2 shows the normalized volume-pressure diagram for Ti_2SC and Ti_2AlC at various temperatures. It is seen that the unit cell volume decreases smoothly and no abrupt change occurs with increasing pressure for both Ti_2SC and Ti_2AlC , 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_2SC and Ti_2AlC .^{15,16} It can be seen that on compression, the reduction in volume for Ti_2SC is smaller than Ti_2AlC , which is due to the higher bulk modulus of Ti_2SC . An experimental work on the compression behavior of Ti_2SC and Ti_2AlC has been recently reported.¹⁵ However, the results showed that the volume-pressure curve is almost identical to each other. It is somewhat surprising because Ti_2SC is much stiffer than Ti_2AlC . We think that this may be due to the low quality of the as-prepared Ti_2SC samples. As is known, the mechanical properties of MAX phases are strongly dependent on the presence of porosity and impurity in the sintered samples.^{17,18} It is also observed that the relative volume V/V_0 decreases slightly at a given pressure for both Ti_2SC and Ti_2AlC with increasing temperature, which indicates a weak temperature dependence for their compressibility.

Figure 3 shows the temperature dependence of the volume thermal expansion coefficient α of Ti_2SC and Ti_2AlC . It can

Fig. 2 Normalized volume-pressure diagram for Ti_2SC and Ti_2AlC at different temperatures.

Fig. 3 The volume thermal expansion versus temperature for Ti_2SC and Ti_2AlC at pressure of 0 GPa.

be seen that α 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_2SC is lower than that of Ti_2AlC , which is consistent with the fact that Ti_2SC possesses a higher bulk modulus and lower volume reduction when compressed. As reported previously, the volume thermal expansion coefficient of Ti_2SC and Ti_2AlC is experimentally measured to be $2.52 \times 10^{-5} \text{ K}^{-1}$ and $2.61 \times 10^{-5} \text{ K}^{-1}$ respectively, larger than the present calculation.^{19,20} It is known that additional expansion can be caused by lattice vacancies.²¹ It has been found that carbon vacancies in VC significantly increase the thermal expansion coefficient.²² As is well known, non-metal vacancies were generally found in MAX phases.^{23–25} Therefore, the discrepancy between the calculated and experimental thermal expansion coefficient of Ti_2SC and Ti_2AlC can be attributed to the vacancies effects.

The constant-volume specific heats C_v and constant-pressure specific heats C_p of Ti_2SC and Ti_2AlC are calculated and shown in Fig. 4. The differences in both C_v and C_p of

Fig. 4 The heat capacity versus temperature for Ti₂SC and Ti₂AlC at pressure of 0 GPa.

Ti₂SC and Ti₂AlC 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 Ti₂SC and Ti₂AlC obey the expected T^3 power-law behavior, and they both approach the classical asymptotic limit of $C_v = 3nNk_B = 99.8 \text{ J/mol K}$. The values of C_p for Ti₂SC and Ti₂AlC are slightly larger than the C_v , which can be explained by the relation between C_p and C_v as follows:

$$C_p - C_v = \alpha_V^2(T)BVT \quad (1)$$

where α_V , B , V and T are the volume thermal expansion coefficient, bulk modulus, volume and absolute temperature, respectively. Our calculated values for C_p of Ti₂SC and Ti₂AlC 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 Θ_D at 300 K of Ti₂SC and Ti₂AlC. It is clear that the Debye temperature increases almost linearly with pressure. Figure 5(b) shows the temperature dependence of Θ_D at $P = 0 \text{ GPa}$. It can be seen that Θ_D of Ti₂SC and Ti₂AlC remains unchanged as $T < 100 \text{ K}$ and decreases linearly as $T > 100 \text{ K}$. It is known that Debye temperature Θ_D is related to the maximum thermal vibration frequency of a solid. The variation of Θ_D with pressure and temperature reflects the fact that the thermal vibration frequency of the particles in Ti₂SC and Ti₂AlC changes with pressure and temperature. In the present work, Θ_D of Ti₂SC and Ti₂AlC 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, Θ_D can be used to measure the stiffness of solids.²⁶⁾ Usually, a solid with high modulus and hardness will possess high Debye temperature. For example, Θ_D of diamond is 2240 K, much higher than 402 K of graphite.²⁶⁾ It should be noted that Θ_D of Ti₂SC is the largest measured to date for 211 MAX phases, which is consistent with the fact that Ti₂SC possesses the highest bulk modulus and hardness among 211 MAX phases.

Fig. 5 (a) The pressure dependence of Debye temperature at 300 K; (b) the temperature dependence of Debye temperature at $P = 0 \text{ GPa}$.

4. Conclusion

In conclusion, we have calculated the thermodynamic properties of Ti₂SC and Ti₂AlC using the quasi-harmonic approximation within density functional theory. The bulk modulus of Ti₂SC and Ti₂AlC decreased with temperature. The reduction in volume on compression for Ti₂SC is smaller than Ti₂AlC, which is due to the higher bulk modulus of Ti₂SC. The volume thermal expansion coefficient α of Ti₂SC and Ti₂AlC increases rapidly with increasing temperature at low temperature region of $T < 300 \text{ K}$ and increases smoothly at high temperatures. The calculated values for C_p of Ti₂SC and Ti₂AlC in the range of 0–300 K are well agreement with the experimental values. The Debye temperature Θ_D of Ti₂SC and Ti₂AlC remains unchanged as $T < 100 \text{ K}$ and decreases linearly as $T > 100 \text{ K}$.

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