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Article · May 2006

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The Temperature of the hcp – bcc Phase Transition in Titanium

Jessada Chureemart and Udomsilp Pinsook*

Molecular dynamic studies were carried out in order to calculate the Helmholtz free energy of hcp and bcc titanium at a wide range of temperatures. The stable phase of titanium can be determined by examining the Helmholtz free energy at a given temperature, *i.e.* the phase that gives the lowest free energy will be stable. We found that at lower than 906K the hcp titanium is stable. At higher than 906K the bcc titanium is stable. Thus 906K marks the phase transition from the hcp to the bcc structure and is the transition temperature. This finding is in agreement with previous experiments.

Key words: Helmholtz free energy and transition temperature

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อุณหภูมิของการเปลี่ยนสถานะแบบ hcp – bcc ในไททาเนียม

เจษฎา จุรีมาศ และ อุดมศิลป์ ปิ่นสุข (2549)

วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย **31(1)**

       ผู้วิจัยใช้พลศาสตร์โมเลกุลคำนวณองค์ประกอบของพลังงานอิสระเฮล์มโฮล์ตซ์ของ ไททาเนียมแบบ hcp และ bcc ในช่วงกว้างๆ ของอุณหภูมิช่วงหนึ่ง สถานะที่เสถียรของ ไททาเนียมระบุได้จากการตรวจสอบพลังงานอิสระเฮล์มโฮล์ตซ์ที่อุณหภูมินั้นๆ โดยสถานะที่ มีพลังงานอิสระต่ำที่สุดจะเสถียรที่สุด ผู้วิจัยพบว่า เมื่ออุณหภูมิต่ำกว่า 906 เคลวิน ไททาเนียม แบบ hcp เสถียร ที่อุณหภูมิสูงกว่า 906 เคลวิน ไททาเนียมแบบ bcc เสถียร ดังนั้น อุณหภูมิ 906 เคลวิน บ่งบอกถึงการเปลี่ยนสถานะจากโครงสร้างแบบ hcp ไปเป็น bcc และเรียก อุณหภูมินี้ว่า อุณหภูมิการเปลี่ยนสถานะ ผลการวิจัยนี้สอดคล้องกับค่าที่วัดได้จากการทดลอง

คำสำคัญ พลังงานอิสระเฮล์มโฮล์ตซ์ อุณหภูมิการเปลี่ยนสถานะ

INTRODUCTION

Titanium (Ti) is a transition metal with a number of remarkable properties. For example, it is strong and corrosion resistant, it is lighter than iron and biocompatible. Ti is used in some heavy-duty machines such as jet turbines. There are a number of medical applications such as the construction of artificial joints and bones. In order to understand all its physical properties and know how to control these properties for specific usage, one needs to know the accurate interatomic potential. There are various potentials representing Ti atoms but we chose a Finnis-Sinclair type potential[1] as it is a many-body potential suitable for metals. In this work we performed molecular dynamic (MD) simulations to calculate the transition temperature of the hcp - bcc phase transition in Ti. The hcp - bcc phase transition was observed in experiments and the transition temperature was measured. Our calculations served as a test for verifying the potential's result. In the future the transition mechanism could be studied at the microscopic level. This is of great interest because the transition mechanism provides some fundamental knowledge on the mechanism of the so-called shape memory effect found in some TiNi alloys.[2]

METHOD

We used a Finnis-Sinclair type potential[1] fitted to some experimental data such as inhomogeneous elastic constants. This was predicted to give correct information on the collective excitations. Furthermore, some information on defect formations would be accounted for. This makes the potential suitable for the study of phase transitions and melting. The Finnis-Sinclair type potential is a many-body potential suitable for metals where the binding part comes from the presence of free electrons. The forms of the potential originated from quantum mechanics. It is well-tested and adaptable for investigating the properties of some technologically important alloys such as TiNi alloys[2] which are shape memory materials.
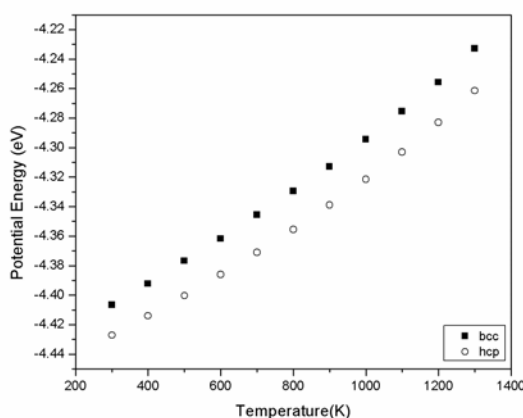

Figure 1. The potential energy of the hcp (open circles) and the bcc (filled squares) phases as a function of temperature.

We set up MD simulations by putting Ti atoms on lattice sites, *i.e.* the hcp or the bcc lattice. Then the temperature was set by distributing the atomic velocities according to the Maxwell-Boltzmann distribution. Ti atoms evolve in space by numerically integrating Newton's equation of motion. After equilibration, the system's total energy was monitored. The equilibrium values of potential energy of the hcp and the bcc structures are shown in Figure 1. At a given temperature, the equilibrium kinetic energy of both phases is equal. Later when we consider the difference between the energy, the kinetic part of both phases will cancel out and hence be of no interest. From Figure 1, it can be seen that the hcp phase has lower potential energy for all ranges of temperature considered here. By using the energy alone, we can argue that the hcp phase is stable. However, according to our experiments, this is not true. It was found that after heating Ti samples to around 1155K, it transforms from the hcp to the bcc structure.[3] The explanation lies in the

entropy part of Helmholtz free energy. In order to calculate the entropy, the velocity autocorrelation function (VACF) was also evaluated during the MD simulations. The VACF is used for calculating the phonon density of states (DOS) and then the vibrational entropy.[4-6] Typical phonon DOS of both structures are illustrated in Figure 2.
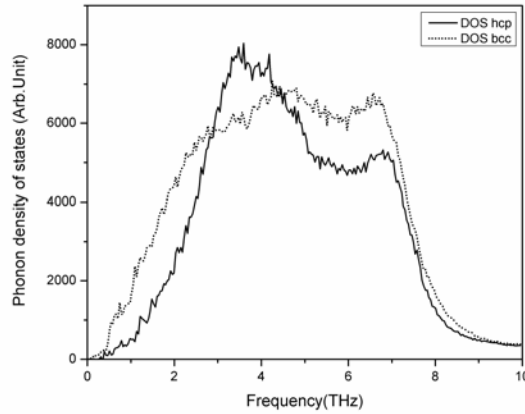

Figure 2. Typical phonon DOS of the hcp (full line) and the bcc (dotted line) structures.

Next we calculated the Helmholtz free energy (F) because this would determine which phase of Ti is stable at a given temperature. According to thermodynamic consideration, the phase with the lowest free energy will be favorable at each temperature.

Our task was to evaluate the components of F which consist of the internal energy (U) and the entropy (S), using $F = U - TS$ at a wide range of temperatures (T) of the hcp and bcc phases. In fact, it is easier to consider

$$\Delta F = F_{bcc} - F_{hcp} = (U_{bcc} - U_{hcp}) - T(S_{bcc} - S_{hcp}) \qquad \dots (1)$$

At a temperature where $\Delta F > 0$, the hcp structure is stable. At a temperature where $\Delta F < 0$, the bcc structure is stable. The temperature where $\Delta F = 0$ or, in the other words $(U_{bcc} - U_{hcp}) = T(S_{bcc} - S_{hcp})$, is called the transition temperature and both phases

coexist. Therefore, if we plot the differences of these components, *i.e.* $(U_{bcc} - U_{hcp})$ and $T(S_{bcc} - S_{hcp})$, as functions of temperature, their interception point will denote the transition temperature.
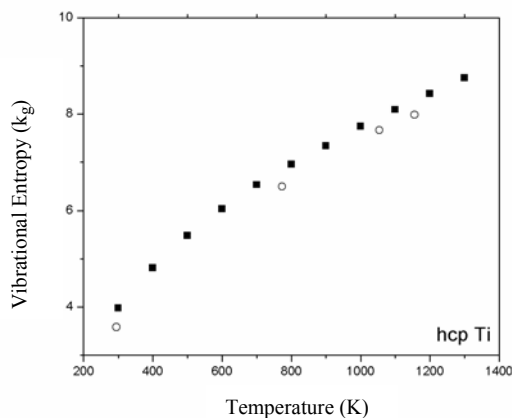

Figure 3. The calculated values of the total vibrational entropy of the hcp Ti (filled squares) compared with those of experiments[3] (open circles).

RESULTS AND DISCUSSION

According to Eq. (1), the information needed for determining the difference of F is U and S. Both functions can be obtained from a series of MD simulations in a wide range of temperatures. We used 300K - 1300K. The potential part of U for both phases has been shown earlier in Figure 1. Next, we evaluated S, after DOS were calculated at each temperature by using the method suggested by Srepusharawoot and Pinsook.[5,6]
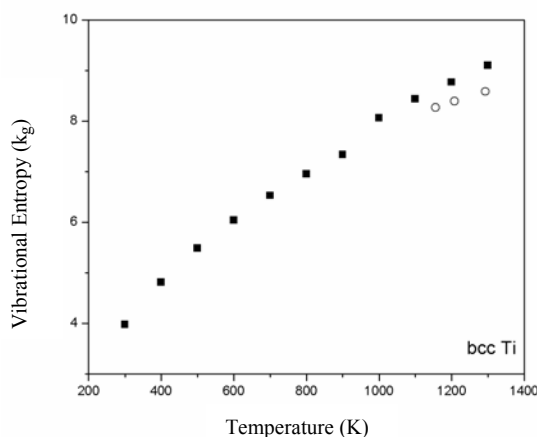

Figure 4. The calculated values of the total vibrational entropy of the bcc Ti (filled squares) compared with those of experiments[3] (open circles).

The total vibrational entropy as a function of temperature is shown in Figure 3 for the hcp Ti and in Figure 4 for the bcc Ti. The experimental results[3] are quoted for comparison. It is seen that the vibrational entropy is proportional to $\ln(T)$ as suggested by the classic solid theory. The results are also in reasonable agreement with experimental findings.
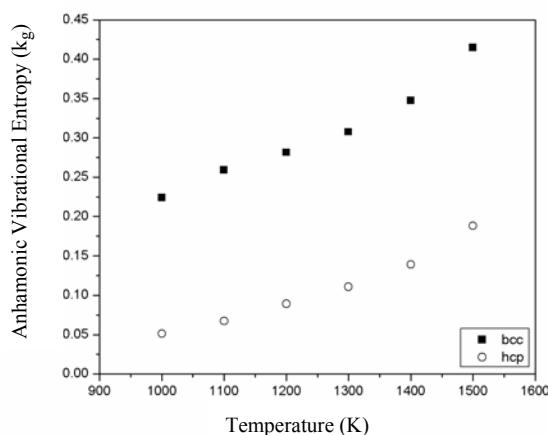

Figure 5. The anharmonic contribution of the hcp (open circles) and the bcc (filled squares) structures.

The vibrational entropy can be divided into two components, harmonic and anharmonic.[7,8] It has been argued for a long time that the mechanism of the hcp - bcc transition is due to excess vibrational entropy.[3] Furthermore, there are a few clues showing that the anharmonic part plays a major role. Thus, in this work, we extracted the anharmonic contribution at each temperature using a method suggested by Lacks and Shukla[9] and displayed in Figure 5. The anharmonic entropy in the bcc phase is

three-to-four times larger than that of the hcp. The anharmonic entropy difference between the two phases is in reasonable agreement with the difference of the total vibrational entropy measured from experiments,[3] *i.e.*

$(S_{bcc} - S_{hcp})_{experiment} = 0.29 k_B$. This finding confirms that the anharmonic entropy is the key element for the hcp - bcc transition in Ti.
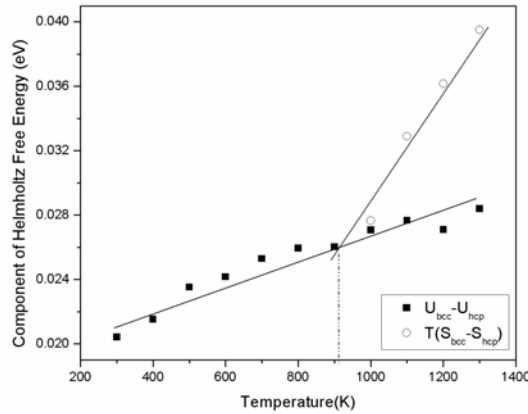

Figure 6. The differences of the components of F, composed of the energy difference (filled squares) and the entropy difference (open circles). The intercept point denotes the transition temperature.

By plotting the differences of the components of F between the two phases versus temperature, as shown in Figure 6, we found an intercept at around 906K. At temperatures lower than this point, the hcp phase has less free energy and is hence stable. At temperatures higher than the intercept point, the bcc has less free energy and Ti transforms from the hcp to the bcc structure. Thus the temperature of the intercepting point is the transition temperature. According to experiments, the transition temperature was 1155K.[3] Some previous calculations showed that the transition temperature was in the range of 1295K - 3350K.[10] Hence our calculations are in closer agreement with the experiments and better than those of some previous works. The limitation of some previous works was that they completely neglected the contribution of the anharmonic entropy, thus the transition temperature was overestimated.

CONCLUSIONS

We have done a series of MD simulations in order to calculate the components of Helmholtz free energy of the hcp and the bcc titanium at a wide range of temperature. The vibrational entropy was examined and the results were consistent with

the experimental results. Then the transition temperature of the hcp – bcc transition was determined by considering the interception of the components of Helmholtz free energy. We found that 906K is the phase transition temperature of titanium from the hcp to the bcc structure. This finding is close to the results of experiments. The possible discrepancy is that electronic entropy has not yet been accounted for. The electronic entropy will change the slope of $T(S_{bcc} - S_{hcp})$ and hence will improve the interception point. This modification will be done in our future works.

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