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Structural, electronic and elastic properties of TaRu high temperature shape memory alloys

C.L. Tan [a,b,*], J.X. Jiang [a], X. An [c], H.J. Ge [a], B. Zhao [a]

[a] School of Applied Science, Harbin University of Science and Technology, Harbin 150080, China
[b] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[c] Province Key Laboratory of Senior Education for Electronic Engineering, Heilongjiang University, Harbin 150080, China

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ABSTRACT

The structural, electronic and elastic properties of TaRu alloy have been studied by the plane-wave pseudopotential method within the generalized gradient approximation. The crystal structure of the β′ phase is obtained for the first time. Our calculations show that the hybridization between Ta d and Ru d states is responsible for the phase stability of TaRu. The total density of states at the Fermi level of the β′ phase is lower that that of the β phase. In addition, it is found that the β to β′ martensitic transformation is closely related to the elastic properties.

1. Introduction

Shape memory alloys (SMAs) have attracted much attention due to their shape memory effect and superplasticity, which are displayed during martensitic transformations [1]. Many kinds of alloys exhibit shape memory effect. The most well-known and commercially developed material is TiNi SMA [2]. It has been widely used in the fields of engineering and medicine. The operating temperatures of SMAs depend on their martensitic transformation temperatures. However, the martensitic transformation temperature of TiNi and other commercially Cu-based SMAs are below 150 °C, so they are not suitable for potential high-temperature SMAs applications such as automotive engine, gas turbine and nuclear reactor environments [3,4]. Therefore, there is a technological need to develop high-temperature SMAs. Nowadays, TaRu alloys demonstrate both martensitic transformation temperatures above 1000 °C and shape memory effect, which makes them a very promising option for high-temperature SMAs [5]. The phase transformations in this compound have been investigated [6–8]. Above 1100 °C, the crystal structure is the ordered cubic CsCl-type ($Pm\bar{3}m$), called the β phase. Below 1100 °C, the crystal transforms to a tetragonal structure, called the β′ phase. This β to β′ phase transformation is demonstrated to be responsible for the shape memory effects [5]. In addition, some researches including microstructure, shape memory effect and mechanical behavior have been conducted in recent years [9,10]. However, to our knowledge, the crystal structure of the β′ phase is still unclear. Moreover, it is well known that many properties such as the phase stability and the transformation behavior of SMAs are closely related to their electronic structure and elastic properties [11–13]. But, the theoretical studies of electronic and elastic properties of TaRu have not been reported yet. It is highly desirable to perform such calculations. Thus in this study, we investigate the structural, electronic and elastic properties of TaRu by the first-principles method. The crystal structure of TaRu β′ phase is obtained for the first time. Furthermore, the mechanism of phase stability, and transformation behavior are researched based on the electronic structure and elastic properties, respectively.

2. Calculation method

The calculations presented in this study are performed with the CASTEP code [14], based on density functional theory, using Vanderbilt-type ultrasoft pseudopotentials [15] and a plane-wave expansion of the wave functions. We use the generalized gradient approximation (GGA) to describe the exchange and correlation potential. The structure is optimized with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method, and convergence is assumed when the forces on atoms are less than 0.03 eV/Å. The plane-wave cutoff energy of 550 eV is employed. The calculations are done using a (14, 14, 14) Monk horst-Pack grid. The lattice parameters of the β phase are taken from Ref. [6]. In every case, the geometrical optimization is always made, based upon which the electronic structure and elastic constants are then calculated. For cubic crystals there are only three independent elastic constants C_{11}, C_{12} and C_{44}. Due to the importance of $C'((C_{11} - C_{12})/2)$ in the martensitic transformation, we give C' as well.

* Corresponding author at: School of Applied Science, Harbin University of Science and Technology, Harbin 150080, China. Tel.: +86 451 86390728; fax: +86 451 86390728.
E-mail address: changlongtan@yahoo.com.cn (C.L. Tan).

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Table 1
Comparison of the calculated and experimental lattice parameters of TaRu β and β′ phases.

Phase	Present results (nm)	Experimental results [6] (nm)
β phase		
a	0.3148	0.3190
β′ phase		
a	0.3026	0.3090
c	0.3414	0.3360

3. Results and discussion

To understand the martensitic transformation, it is essential to know the crystal structure of the β phase and β′ phase. The crystal structure of TaRu β phase is generally believed to be the ordered cubic CsCl-type ($Pm\bar{3}m$) with the Ta and Ru atoms occupying the corners and the center of the cube. In reality, this has not been proved owing to the similar X-ray scattering lengths of Ta and Ru. In this study, using symmetry analysis implemented in CASTEP, we find that the optimized structure of the β phase is of $Pm\bar{3}m$ symmetry. This theoretically proves that the symmetry of the β phase is simple cubic CsCl-type ($Pm\bar{3}m$). The calculated and experimental lattice constants of the β phase are listed in Table 1. It can be seen that the calculated lattice constants agree well with the experimental values. Moreover, in order to obtain the crystal structure of the β′ phase, we deform the CsCl-type structure of the β phase by continuously varying the *c*/*a* ratio, but keeping the volume fixed at the equilibrium volume. Fig. 1 shows the relation of energy change to the *c*/*a* ratio. It is clear seen that there are two local minimum of energy at 0.92 and 1.15, respectively. The local minimum at 0.92 is higher in energy than the 1.15 minimum. These indicate that the β phase is unfavorable in energy relative to the tetragonal phase, and undergo slight two continuous tetragonal transformations. The β phase first undergo cubic to tetragonal transformations with $c/a < 1$, and then with $c/a > 1$. Our theoretical results are consistent with the experiment [6]. In addition, our results show that the optimal *c*/*a* for the β′ phase is 1.15, which is very close to the experimental value 1.12 [17]. Furthermore, we perform the geometrical optimization and the similar symmetry analysis to determine crystal structure of the β′ phase. It is found that the β′ phase has P4/mmm space group with atomic positions: Ta (0, 0, 0), Ru (0.5, 0.5, 0.5). The detailed lattice constants of the β′ phase are also listed in Table 1. The calculated volume of the β phase is 31.20 Å^3, while that of the β′ phase is 31.26 Å^3. Thus, the martensitic transformation involves slight change in volume. It is well known that volume conserving martensitic transformation is a necessary and sufficient condition for shape memory alloy effect in systems with cubic austenitic phase [16]. Therefore, our results show why TaRu is a shape memory alloy. In the following, we employ the above crystal parameters of the β′ phase to calculate its electronic structure and elastic constants.

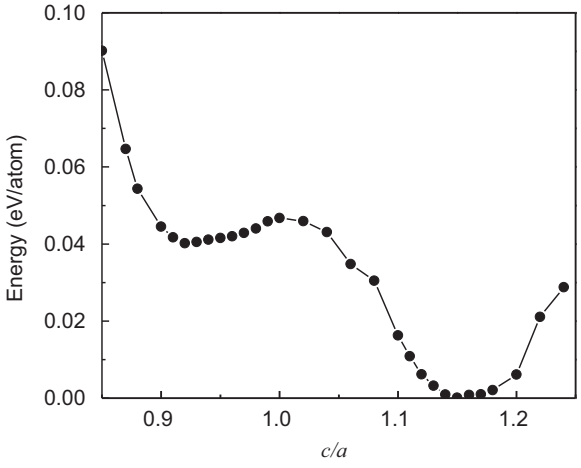

Fig. 1. The total energy of TaRu as a function of *c*/*a* for the equilibrium volume.

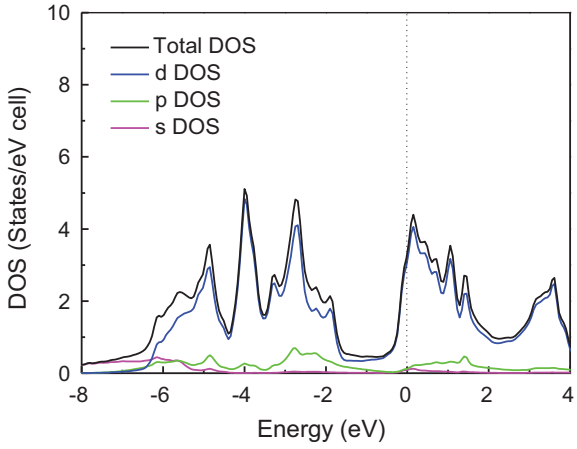

Fig. 2. Total and partial DOS of TaRu β phase.

The total and partial density of states (DOS) of TaRu β phase and β′ phase are shown in Figs. 2 and 3, respectively. The Fermi level is set at 0 eV and denoted by the dotted line. In the case of β phase, the total DOS resembles that of a bcc metal in that it consists of two sets of peaks separated by a dip about 1.6 eV wide. The Fermi level lies in a rising part of the DOS below the higher energy peaks which are mostly unoccupied. For the β′ phase, the general shape of DOS is similar to that of the β phase. This is understandable considering that the β to β′ phase transformation involves only slight tetragonal deformation. But, compared with the β phase, the peaks of β′ phase is broader, due to the fact that the β′ phase has a lower symmetry. Another important feature in the total DOS of the β′ phase lies in the peak centered at about 0.2 eV above the Fermi level. This peak nearly disappears comparing to the corresponding of the β phase. Moreover, it can be seen that for both phases, the total DOS is mainly due to d partial DOS. There are negligible contributions from the p and s states. Within a rigid band model, the total DOS at the Fermi level is an important indication of the stability of alloys [17]. Higher stability corresponds to lower total DOS value at the Fermi level. Comparing Figs. 2 and 3, it is found that the total DOS at the Fermi level of the β′ phase is lower that that of the β phase. Thus, it can be conclude that the stability of the β′ phase is higher than that of

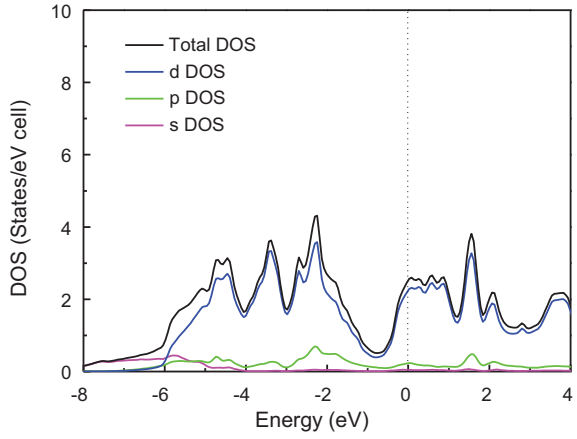

Fig. 3. Total and partial DOS of TaRu β′ phase.

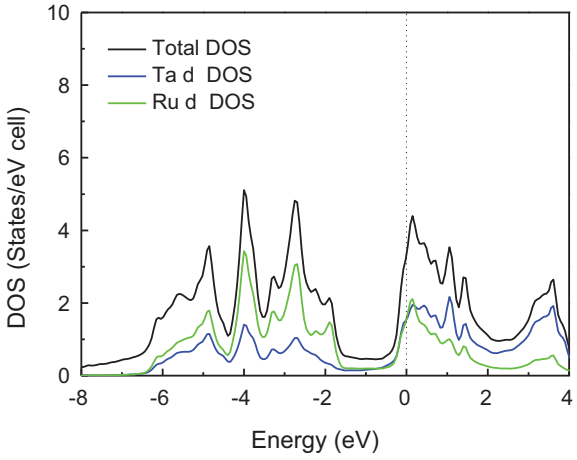

Fig. 4. Total DOS, Ru d DOS and Ta d DOS of TaRu β phase.

the β phase, which is supported by the experiment [5] that the β′ phase is observed at low temperatures.

As discussed above, the total DOS is mainly consisted of d states. In order to further investigate phase stability from the electronic structure, we decompose the total DOS into site and angular momentum contributions. Ta d and Ru d DOS for the β phase and β′ phase are shown in Figs. 4 and 5, respectively. It can be seen that, the total DOS below the Fermi level is mainly dominated by the Ru d states, while the total DOS above the Fermi level is mainly due to the Ta d states. Moreover, there is a significant intensity for Ru site at the lower energies, and Ta site at the higher energies, indicating hybridization between the d orbitals on the Ru and Ta sites. The double peak structure mentioned above is just produced by the hybridization between Ru d and Ta d states. In addition, comparing Figs. 4 and 5, it can be found that Ru d DOS is significantly lowed during the β to β′ phase transformation. This indicates that the hybridization between Ru d and Ta d states of the β phase is weaker than that of the β′ phase. Therefore, it can be conclude that this hybridization is responsible for the phase stability of TaRu.

The elastic properties can provide valuable information on structural stability and are closely related to the martensitic transformation. However, the studies of these are limited, most probably due to the difficulties of making the standard type of measurements at very high temperatures. To gain insight into the relationship between the transformation behavior and elastic properties, we calculate the elastic constants of TaRu β and β′ phases. Table 2 lists

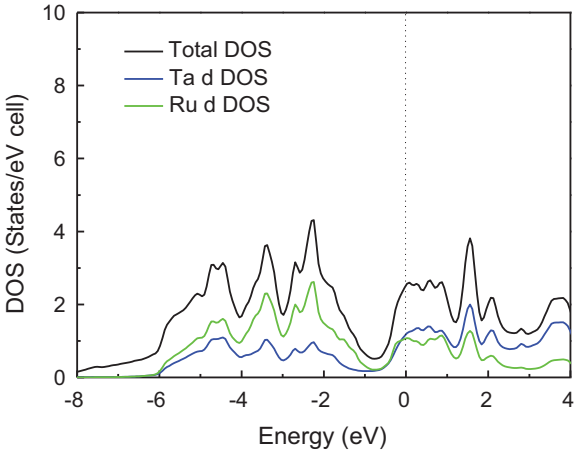

Fig. 5. Total DOS, Ru d DOS and Ta d DOS of TaRu β′ phase.

Table 2
The calculated elastic constants (GPa) of TaRu β and β′ phases.

	C_{11}	C_{12}	C_{44}	C'
β phase	95	347	85	−126
β′ phase	329	219	71	55

the calculated elastic constants of the β and β′ phases. For the β phase, it can be seen that the calculated value of C_{44} is positive. But our calculations yield a negative C'. Although our calculations are valid at 0 K, the knowledge of the limiting values of the elastic constants for vanishing temperature can provide useful information about the behavior of structure transition near the transformation temperature. For a cubic material, it is well known that B, C' and C_{44} must be positive for a structure to remain mechanically stable. However, the calculated value of C' is negative, thus indicating instability of cubic β phase with respect to tetragonal distortions. Since the β phase is, in fact, unstable at 0 K, we can understand this instability. But, we want to investigate this point further. At temperature well above the β to β′ phase transformation, both C' and C_{44} are positive. At absolute zero only C_{44} has a non-negative value. Therefore, C' should go to zero at transformation temperature of β to β′ phase, while C_{44} should still be positive. On the other hand, Table 2 shows that both C' and C_{44} of the β′ phase are positive, implying its mechanical stability. It is also well known that the shear modulus C' characterizes the stability of the lattice under shear deformation and is related with the tetragonal distortion. Thus, our calculations indicate that the softening of C' to zero triggers the β to β′ phase transformation. Very recently, Shapiro et al. [18] measured the phonon dispersion curves on NbRu single crystal. They found that the [1 1 0]-TA_2 phonon branch has an anomalous temperature dependence. Based on our calculations, it can be concluded that an anomalous temperature dependence of the [1 1 0]-TA_2 phonon branch and softening in C' are responsible for the β to β′ phase transformation.

4. Conclusions

In summary, the structural, electronic and elastic properties of TaRu high temperature shape memory alloys have been investigated for both the β and β′ phases by the first-principles method. We theoretically confirm that the β phase is indeed cubic CsCl structure ($Pm\bar{3}m$). Moreover, it is found that the β phase first undergo cubic to tetragonal transformations with $c/a < 1$, and then with $c/a > 1$, which is consistent with the experiment. The crystal structure of the β′ phase is determined to be $P4/mmm$ space group. The calculated lattice constants are in good agreement with the experimental data. The calculated DOS shows that the hybridization between Ta d and Ru d states is responsible for the phase stability of TaRu. The total DOS at the Fermi level of the β′ phase is lower that that of the β phase. In addition, the calculated elastic constants show that the β to β′ phase transformation is closely related to softening in C'.

Acknowledgements

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