# The effect of Fe on the martensitic transformation of TaRu high-temperature shape memory alloys: A first-principles study*

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(Received 13 December 2011; revised manuscript received 15 February 2012)

The effect of Fe on the martensitic transformation of TaRu high-temperature shape memory alloys has been investigated using first-principles calculations. The site preference of Fe in TaRu alloys has been clarified for the first time, and the results show that Fe is predicted to occupy Ru sites. The addition of Fe increases the stability of the $Ta_{50}Ru_{50-x}Fe_x$ β phase, leading to a significant decrease in the β to β′ martensitic transformation temperature. In addition, the mechanism of the Fe alloying effect is explained on the basis of the electronic structure.

**Keywords:** shape memory alloys, TaRu, martensitic transformation, electronic structure

**PACS:** 71.20.Lp, 81.30.Kf **DOI:** 10.1088/1674-1056/21/5/057105

## 1. Introduction

Shape memory alloys (SMAs) have attracted much attention due to their shape memory effect and superplasticity, which are displayed during martensitic transformations.[1−4] Many kinds of alloys exhibit shape memory effects. The most well-known and commercially developed material is TiNi SMA,[5−8] which 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 commercial Cu-based SMAs are below 150 °C, so they are not suitable for potential high-temperature SMA applications such as automotive engine, gas turbine and nuclear-reactor environments.[7,8] 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 effects, which makes them a very promising option for high-temperature SMAs.[9] The phase transformations in this compound have been investigated.[10−12] Above 1100 °C, the crystal structure is of ordered cubic CsCl-type ($Pm\bar{3}m$), and 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.[9] In addition, some research into the microstructures, shape memory effects and mechanical behaviors have been conducted in recent years.[13,14] However, it was found that TaRu alloys show poor toughness at room temperature, which limits their application.[14] On the other hand, previous studies have indicated that the addition of the third element, Fe, commonly improves the mechanical properties of shape memory alloys, and significantly influences the martensitic transformation behavior of TaRu alloys.[15−17] To our knowledge, theoretical investigations on the addition of Fe in TaRu alloys have not been reported yet.

In this study, we investigate the effect of Fe on the martensitic transformation of TaRu high-temperature shape memory alloys by first-principles methods. The site preference of Fe in TaRu alloys has been clarified for the first time. Furthermore, the mechanism of the phase stability and transformation behavior of $Ta_{50}Ru_{50-x}Fe_x$ alloys are studied on the basis of the electronic structure.

*Project supported by the National Natural Science Foundation of China (Grant No. 50901026) and the China Postdoctoral Science Foundation (Grant Nos. 20100471084 and 201104418).

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## 2. Calculation methods

The calculations presented in this study are performed with the CASTEP code,[18] based on density functional theory, using Vanderbilt-type ultrasoft pseudopotentials[19] 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. A plane-wave cutoff energy of 300 eV is employed, and the calculations are carried out using a (8, 8, 8) Monkhorst–Pack grid. In order to study the site preference of Fe in TaRu, calculations are performed for the $Ta_{50}Ru_{50-x}Fe_x$ and $Ta_{50-x}Ru_{50}Fe_x$ ($x$ = 0, 6.25, 12.5) β phases, respectively. The crystal structures of the $Ta_{50}Ru_{50-x}Fe_x$ β phases are taken as a 2×2×2 CsCl-type TaRu supercell, in which appropriate Ru is replaced by Fe. The supercells for the $Ta_{50-x}Ru_{50}Fe_x$ β phases are similar to these, but with Ta replaced by Fe. The lattice parameters of CsCl-type TaRu are taken from Ref. [9]. In every case, geometrical optimization is performed, based upon which the formation heats, lattice parameters and electronic structures are then calculated.

## 3. Results and discussion

In order to investigate the site preference of Fe, the formation heats for the β phases of the $Ta_{50}Ru_{50-x}Fe_x$ and $Ta_{50-x}Ru_{50}Fe_x$ ($x$ = 0, 6.25, 12.5) alloys are calculated, respectively, and shown in Fig. 1. For the $Ta_{50}Ru_{50-x}Fe_x$ alloys with Fe occupying Ru sites, the formation heats decrease with increasing Fe content. On the other hand, the formation heats of the $Ta_{50-x}Ru_{50}Fe_x$ alloys with Fe occupying Ta sites increase with increasing Fe content. According to the correlation between phase stability and formation heat, the result clearly shows that Fe prefers to occupy the Ru sites.

Figure 2 shows the lattice constants as a function of Fe content for the $Ta_{50}Ru_{50-x}Fe_x$ β phases. It can be seen that the lattice constants decrease almost linearly with increasing Fe content. This trend is attributed to the fact that the atomic size of Fe is smaller than that of Ru. Moreover, the decrease in lattice constants is closely related to the change in the phase stability of the $Ta_{50}Ru_{50-x}Fe_x$ β phases. In addition, we find that the error in the calculated lattice constant compared with the experimental data for the TaRu β phase is less than 1%,[9] demonstrating that the pseudopotentials used here and the geometry are reliable.

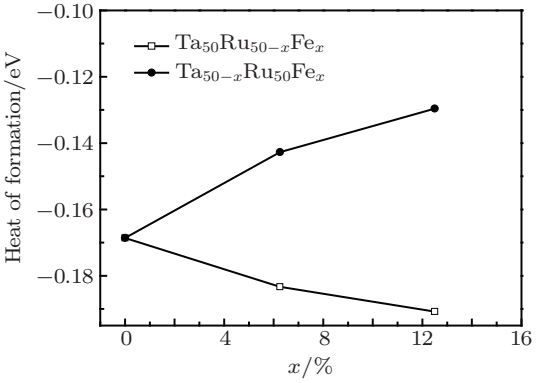



**Fig. 1.** The formation heats of the $Ta_{50}Ru_{50-x}Fe_x$ and $Ta_{50-x}Ru_{50}Fe_x$ ($x$ = 0, 6.25, 12.5) β phases.

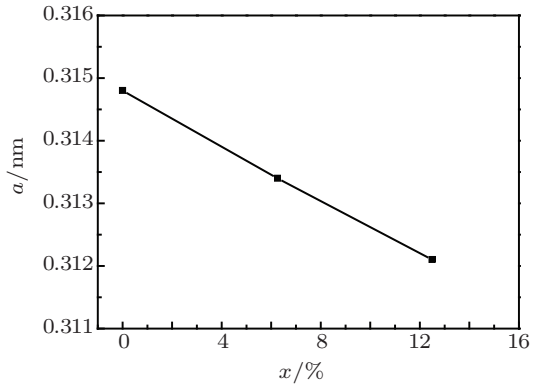



**Fig. 2.** The dependence of lattice constant $a$ on Fe content for the $Ta_{50}Ru_{50-x}Fe_x$ β phases.

To study the effect of Fe content on the phase stability and martensitic transformation behavior, the difference in formation heat between the $Ta_{50}Ru_{50-x}Fe_x$ and TaRu β phases are calculated based on the results of Fig. 1. It is found that the difference in formation heat decreases with increasing Fe content. This suggests that the phase stability of the $Ta_{50}Ru_{50-x}Fe_x$ β phases increase with the increase in Fe content. For the TaRu alloys, a greater stability of the β phase would imply a lower β to β′ martensitic transformation temperature. For the Ni–Mn–Ga shape memory alloys, this is indeed found to be the case.[20] Therefore, our results indicate that the addition of Fe brings a decrease in the β to β′ martensitic transformation temperature, which is in agreement with the experimental data.[17] Both our results and the previous studies demonstrate that the martensitic transformation temperature of TaRu alloys can be adjusted by the addition of Fe, which greatly benefits their application.

The effect of Fe content on phase stability can be deeply understood on the basis of the density of states

(DOS). Figure 3 shows the total and partial DOS of the $Ta_{50}Ru_{50-x}Fe_x$ ($x = 0$, 6.25, 12.5) β phases. For the β phase of TaRu, the total DOS resembles that of a bcc metal, in that it consists of two sets of peaks separated by a dip with a width of 1.6 eV. The Fermi level lies in a rising part of the DOS below the higher energy peaks, which are mostly unoccupied. In the case of the $Ta_{50}Ru_{50-x}Fe_x$ β phase, the general shape of the total DOS is similar to that of TaRu. This is understandable because the shape of the DOS is mainly determined by the crystal structure. In particular, it is found that the dip of total DOS for $Ta_{50}Ru_{50-x}Fe_x$ decreases with increasing Fe content. At 12.5% Fe, the dip lies exactly at the minimum, giving the largest heat formation magnitude, and therefore the largest stabilizing effect for the β phase. This is actually a typical pseudogap effect,[21] and suggests that the β phase becomes more stable with increasing Fe content, in accordance with the heat formation results. Furthermore, the stability effect of the pseudogap can be explained in more details in the partial DOS. Comparing the partial DOS with the atoms, we can find that the change is mainly due to Fe. The dip in partial DOS for Fe is located at the same position of the dip of the total DOS. This contributes to the decreases in the dip in total DOS.

To further study the mechanism of the site preference of Fe, the charge densities in the (110) plane of the $Ta_{50}Ru_{43.75}Fe_{6.25}$ and $Ta_{43.75}Ru_{50}Fe_{6.25}$ β phases are calculated and shown in Fig. 4. In general, high charge accumulation between neighboring atoms indicates a strong hybridization between the orbital of the atoms and thus a strong bonding interaction. From Fig. 4, we can see that when Fe occupies the Ru sites, there is a high charge accumulation in the interatomic areas, indicating a strong bonding interaction. In contrast, the charge accumulation between atoms is much less when Fe occupies the Ta sites, suggesting a weaker bonding interaction, which explains why Fe has a tendency to occupy the Ru sites.

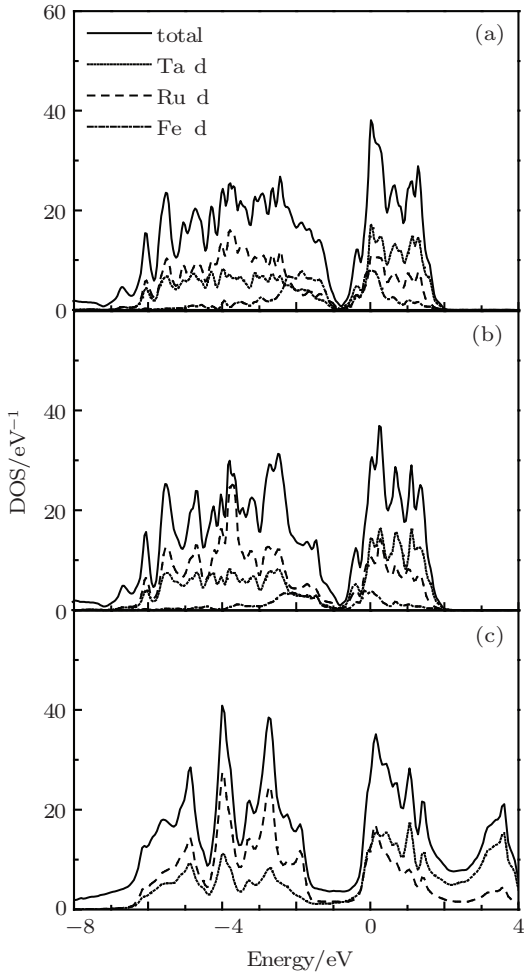



**Fig. 3.** Total and partial DOS of the $Ta_{50}Ru_{50-x}Fe_x$ ($x = 0$, 6.25, 12.5) β phases: (a) $Ta_{50}Ru_{37.5}Fe_{12.5}$, (b) $Ta_{50}Ru_{43.75}Fe_{6.25}$, and (c) $Ta_{50}Ru_{50}$.

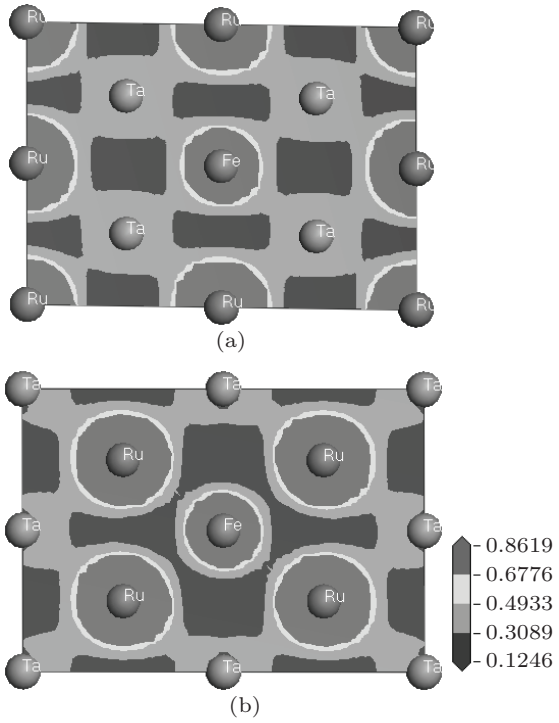



**Fig. 4.** The charge density of the β phases in the (110) plane: (a) $Ta_{50}Ru_{43.75}Fe_{6.25}$, (b) $Ta_{43.75}Ru_{50}Fe_{6.25}$.

## 4. Conclusions

We used first-principles calculations to study the effect of Fe on the martensitic transformation of TaRu high-temperature shape memory alloys. The results show that the electronic states of Fe hybrid with those of Ta more than those of Ru, giving the site preferences of Fe on the Ru sites. Moreover, it is found

that the addition of Fe increases the stability of the $Ta_{50}Ru_{50-x}Fe_x$ β phase, leading to a decrease in the β to β′ martensitic transformation temperature. In addition, the calculated DOS shows that the Fe partial DOS plays an important role on the stability of the $Ta_{50}Ru_{50-x}Fe_x$ β phase.

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