Electronic structure of binary and ternary Ti-based shape-memory alloys

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Abstract

The electronic and structural properties for TiMe (Me = Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) alloys are studied using the full-potential linearized augmented plane wave (FLAPW) method. The alteration of electronic structure with disorder and alloying with a third element is analyzed. The calculated emission, absorption X-ray and electron energy-loss spectra are found to be in good agreement with experiments. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

In the last few decades, the Ti-based alloys have been subjects of intensive experimental and theoretical investigations. This interest is connected with martensitic phase transformation that accompanied by the shape memory effect (SME) widely used in aerospace industry, for electronics, mechanical engineering and in medicine also. Most of Ti-based alloys crystallize in B2 structure at higher temperature that transforms martensitically to monoclinic phase (TiNi) or orthorhombic one (TiPd, TiPt) upon cooling. Martensitic transformation (MT) in the nearly equi-atomic alloys are significantly affected by the addition of the third element with respect to the MT temperatures and crystal structure [1]. The mechanism of MT in Ti-based alloys is related to the peculiarities of their electronic structure (ES) [2,3]. In this paper we focus on the comparative study of electron structure for series of Ti-based binary and ternary alloys. The variation of the electronic structure with disordering and the influence of the third elements on the TiNi electron properties are discussed.

2. Calculational details

The electronic structure for three series B2 TiMe (Me = Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) were calculated using FLAPW method [4] within generalized gradient approximation (GGA) for the exchange-correlation potential. The wave function within muffin-tin spheres were expanded in spherical-harmonics up to $l = 10$. Non-spherical contributions to charge density and potential within spheres were considered up to $l_{max} = 4$. In the interstitial region plane waves with reciprocal lattice vectors up to $|G| = 14$ were included. The band structure was calculated at 165 and 506 **k**-points for ordered and disordered cubic phase in the irreducible part of the Brillouin zone (IP BZ). The KKR-CPA method [5] was used for studying the evolution of ES with the variation of composition and disordering. The increase of lattice parameters with alloying was taken into account [1].

3. Results and discussion

The total densities of states (DOS) for two series ordered and disordered TiMe alloys are given in Fig. 1. For alloys with isoelectronic metals DOS are very identical. The DOS curves for B2 transition metal (TM) alloys have two humped structures with a dip between them. With increase of the

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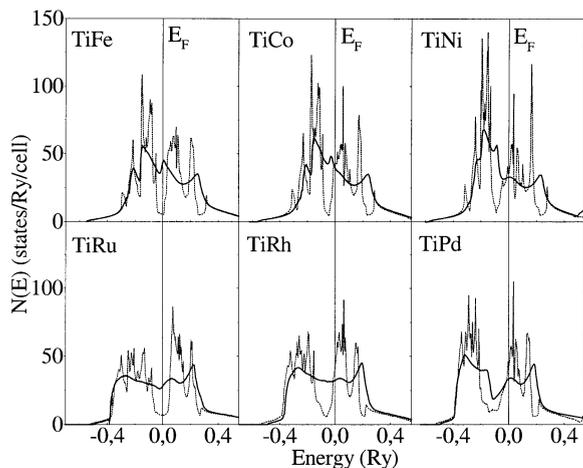
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Fig. 1. Total DOS for ordered (dashed line) and disordered (solid line) B2 TiMe alloys. The energy is given relative to the Fermi level.

number of the valence electrons in all series of alloys the Fermi level (E_F) moves from the dip towards the "anti-bonding" Ti states. This leads to a large increase of $N(E_F)$ and the stability of B2 phase decreases in the considered alloys. The values of $N(E_F)$ are given in Table 1. The DOS structure is lowered with increase of the charge of the isoelectronic metals and its low energy part becomes parabolic. The structure of the high-energy peak (mainly Ti-peak) does not change strongly in TiMe alloys. The change in the valence band of alloys is reflected in the structure of X-ray K-emission spectra (Fig. 2). The K-spectra of TiRu and TiOs are different from those in the TiFe–TiCo–TiNi series and show the broad double peak that agrees well with experiment [6]. The contributions to $N(E_F)$, and partial charges within the MT spheres behaves differently in the series of the alloys and even in the series with isoelectronic metals but some trends may be indicated. For example, the non-monotone change of the Me de_g-contribution to $N(E_F)$ with increasing charge of metal is observed in all series of alloys. The Ti-contribution is
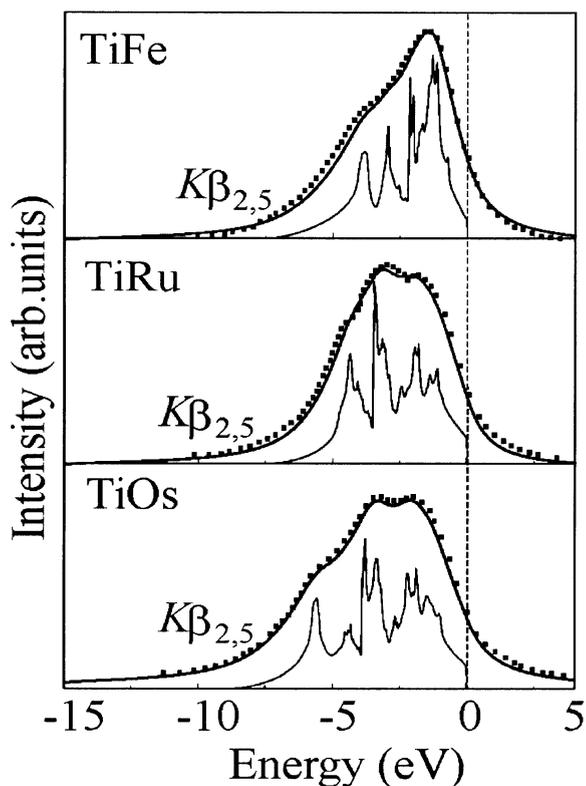

Fig. 2. Ti $K\beta_{25}$–emission spectrum in TiFe–TiRu–TiOs series: the theoretical broadened and unbroadened spectra are shown by solid lines, the experimental ones [6] are given by dotted lines.

virtually twice as high as the corresponding one of Pd in TiPd whereas a small excess of Ti$N(E_F)$ over Ni occurs in TiNi. It is supposed [7] that the Ti d-states could be respon-sible for the phase stability in B2 TiMe alloys because E_F is dominated by the Ti d-states. Unfortunately the inspection of the region from the dip up to E_F shows that it is formed mainly by Me d-states which are here as an admixture to Ti-states. The estimation of the charge in this region for all alloys shows that there is no strong tendency in the charge

Table 1
Volume in a.u.^{3} and DOS at the Fermi level (el./cell/Ry) for TiMe alloys.

| TiMe	TiFe	TiCo	TiNi	TiRu	TiRh	TiPd	TiOs	TiIr	TiPt
V	177.87	180.76	184.98	193.36	206.14	217.08	195.26	205.94	219.47
TiMe-tot	5.35	39.91	35.38	6.79	42.02	43.56	4.30	48.10	36.66
Ti-tot	2.13	11.51	16.77	3.09	18.78	24.62	2.10	19.68	21.21
Ti-d	1.89	10.81	15.97	2.69	18.04	23.96	1.79	18.84	20.53
Ti-de_g	1.71	4.27	9.10	2.33	6.89	12.38	1.64	6.78	10.39
Ti-dt_{2g}	0.18	6.54	6.87	0.36	11.15	11.58	0.15	12.06	10.14
Me-tot	2.01	23.63	12.40	2.19	17.96	10.74	1.16	23.53	10.17
Me-d	1.63	21.24	10.24	1.58	15.32	8.18	0.66	20.18	7.95
Me-de_g	0.94	19.77	8.70	0.92	14.03	6.68	0.33	18.96	7.00
Me-dt_2	0.69	1.47	1.54	0.66	1.29	1.50	0.33	1.22	0.95
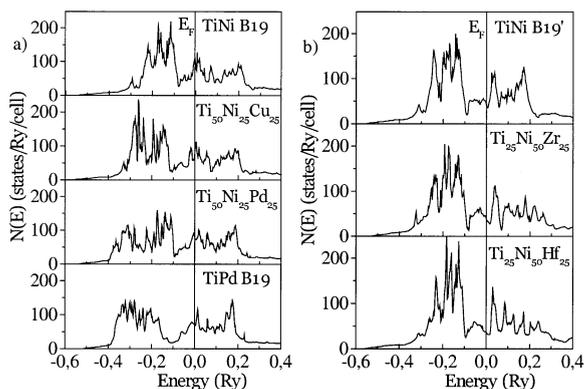
Fig. 3. Total DOS of ternary TiNi-based alloys in orthorhombic B19- and monoclinic $B19'$-phases.

distribution especially in TiNi–TiPd–TiPt. The present results suggest a more complicated picture near E_F and the influence of Me may be very important for understanding the chemical bond and MT in the Ti-based alloys.

It is known that TiPd and TiPt undergo MT into the B19 orthorhombic phase whereas TiNi transforms in monoclinic $B19'$ phase [1]. The electronic structure changes insignificantly during MT in these alloys [8]. The higher localization of Pd and Pt-states in comparison with Ni occurs in both B2- and B19-phases of TiPd and TiPt. This results in weakening d–d hybridization with Ti-states. We think that the difference in the Me–Me bonding in the TiNi, TiPd and TiPt series could have an influence on MT in these systems. The situation for TiNi is very interesting because there are a number of crystal structures describing the $B19'$-phase. Our calculations showed that Kudoh structure [9] has a lower $N(E_F)$ among other structures and the lowest ground state energy. It is possible to find the crystal structure of $B19'$-phase on the basis of a minimization of the total energy but it needs to be optimized for a large number of parameters. This remains a very expensive computational task. The
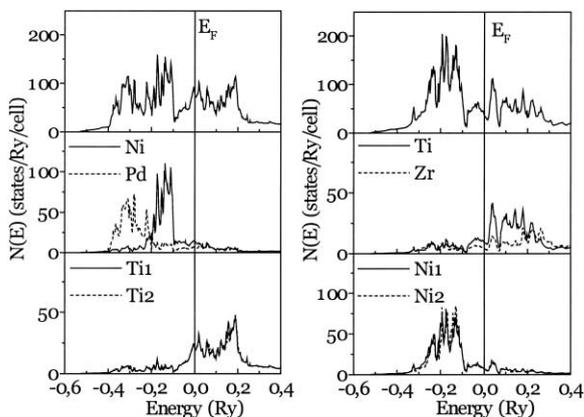

Fig. 4. Total and local DOS of ternary $Ti_{50}Ni_{25}Pd_{25}$ and $Ti_{25}Ni_{50}Zr_{25}$ alloys.
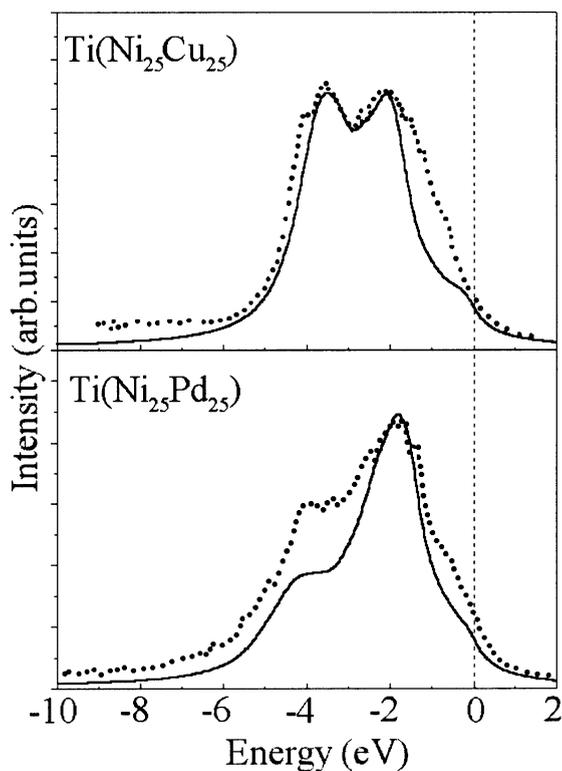

Fig. 5. The calculated X-ray photoelectron spectra for ternary TiNi-based alloys (solid line) and experimental XPS from [10] (dotted line).

calculation of the hypothetical B19-TiNi structure (Fig. 3a) shows that E_F falls exactly in the sharp DOS peak in comparison with TiPd and TiPt where it lies in the vicinity of the local minimum of the high-energy peak. The value of $N(E_F) = 23.87$ el./Ry/atom exceeds not only that obtained for B19'-TiNi (11.52 el./Ry/atom) but also that for B2-TiNi (17.69 el./Ry/atom). Thus the monoclinic distortion of the lattice leads to the stable $B19'$-TiNi phase (Fig. 3b). The addition of an adequate amount of Cu or Pd on Ni-site can stabilize the B19 structure for ternary alloy Fig. 3a and E_F shifts away the sharp peak. Replacing Ti by Zr or Hf changes ES insignificantly in comparison with binary $B19'$-TiNi (Fig. 3b). For ternary alloys we used lattice parameters from [1]. The optimization of atomic positions was performed for B19-phase. For $Ti_{50}Ni_{25}Pd_{25}$ the new position (only z) of Ti atom was found to be 0.2131 whereas old one was 0.2105, for Ni atom they are 0.6822 (0.6925) and for Pd atom −0.3146 (0.3075). The change of the electron characteristics were insignificant. Fig. 4 shows local DOS (LDOS) for some calculated ternary alloys. There is no noticeable difference in LDOS for Ti and Ni atoms, which can occupy the two inequivalent positions in the ternary structure. At the same time LDOS of Ni and Pd in $Ti_{50}Ni_{25}Pd_{25}$ or Ni and Cu in $Ti_{50}Ni_{25}Cu_{25}$ are significantly different. The difference between LDOS of Ti and Zr(Hf) in
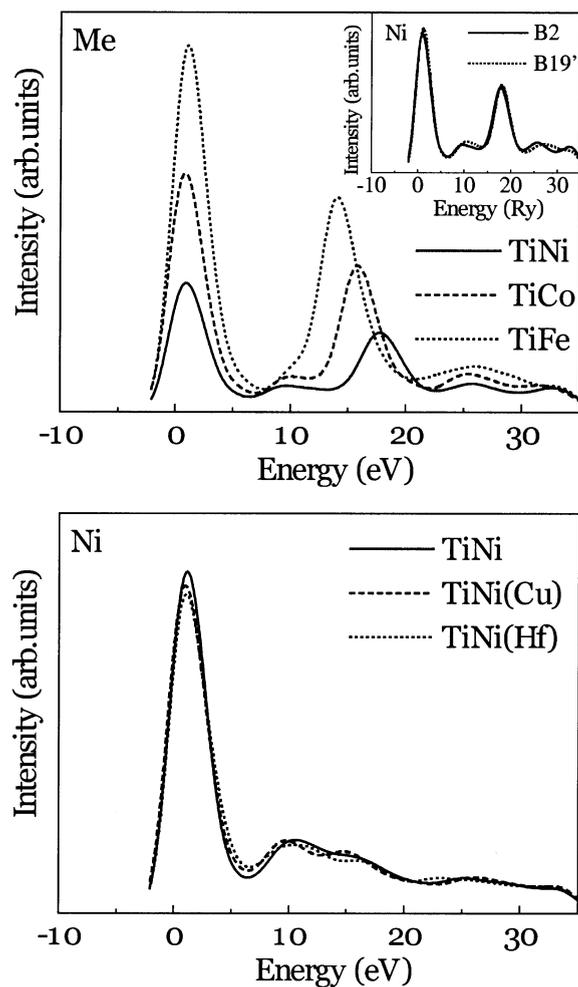
Fig. 6. Me L_{23} EELS edges in TiFe–TiCo–TiNi series (top panel), the insert shows the change of Ni L_{23} spectrum during B2-B19$'$ phase transition in TiNi. Ni L_3 EELS edges in the ternary alloys are given on the bottom panel.

$Ni_{50}Ti_{25}Zr(Hf)_{25}$ can be ascribed to an essential decrease of Zr(Hf)-states comparing with Ti-ones. In general introducing Pd or Cu (20–25 at.%) in TiNi changes ES and the value of $N(E_F)$ significantly in comparison with B19$'$-TiNi. The obtained characteristics are close to those in B19-TiPd (the crystal structure of alloys becomes B19 also). As seen from Fig. 5 the calculated X-ray photoelectron spectra for ternary alloys are in reasonable agreement with experiment [10]. It is evident that the changes of the valence band due to Hf and Zr are less prominent.

The other electron characteristic, which can be calculated using ES of the binary and ternary alloys, is the electron energy-loss spectrum (EELS). This spectroscopic technique is precise and its result can be a good test for ES calculations. The intensity of a "white line" (a sharp maximum of an absorption coefficient in TM) reflects the change in the

filling up of the d-states, i.e. it decreases with increasing atomic number. As seen from the Fig. 6 the intensity of EELS for Fe, Co and Ni decreases in 3d-TiMe series in good agreement with the experimental result for pure metal but Ti band varies insignificantly. Our calculations predict the only slight change in the Ni, Ti L profile upon B2 $\rightarrow$ B19$'$ transformation as in the experiment [11]. These EELS changes can be apparently explained by insignificant change of ES during MT in TiNi. We also check will the chemical composition influence on the Ni spectrum. Our result reveals that the filling of the Ni states changes also insignificantly with alloying by Pd, Cu, Zr, Hf up to 25%. Unfortunately the supercell approach used often in the calculations has the lack because it ignores the effect of disordering. We investigate this effect for binary TM alloys also. The ES of the disordered alloys is less discussed in literature due to the difficulties of the band structure calculations for imperfect crystal. We found that the DOS change is similar in two series of TiMe alloys. As seen from Fig. 1 the width of DOS of the disordered alloys is approximately equal to that in the ordered state. The results are quite interesting because DOS of TiPd looks similar to that in the ordered state unlike other TiMe alloys. The valley in the middle region of DOS exists for TiPd only. The LDOS of Ti shifts upwards relative to that of Fe to fill up the energy gap and a peak appears at E_F in TiFe. As follows from obtained results the ordered state in considered TiMe alloys is highly stable. Our results indicate that possibility of disordering in TiPd exists and in this respect it is necessary to take into account in the microscopic description of the phase transformation. It has been reported that some intermetallic alloys could undergo a crystalline-amorphous transformation upon irradiation only. It is possible to compare the present result for TiFe with that from [12]. In our calculation the first peak is more expressed in contrary to old result. Moreover the Fermi level falls exactly in the peak that appears in the place of the dip for the ordered alloy but it was in the shoulder in previous calculation [12]. The reason of the discrepancy may be connected with non self-consistent approach used in [12]. We also check that our results for non-magnetic and magnetic disordered NiMn are in satisfactory agreement with results from [13]. DOS for disordered B2-NiMn looks quite different from that for TiMe alloys [14]. It is known that the ordered state of TiFe or TiNi is highly stable contrary to NiMn (the NiMn cubic phase exists with the long-range order parameter $\sim$0.6–0.8). Using the average T-matrix method we studied a few composition of pseudobinary NiMn(Ti) alloys in [14]. It was shown that the changes in electronic states are qualitatively due to Ti, irrespective of the partial replacement of Mn or Ni. The same trend is obtained for considered above ternary TiNi-based alloys using the supercell approach in the framework of the FLAPW method. Because the effect of disordering is not essential in Ti-based alloys the supercell approach leads to reasonable result for ternary alloys.

Recently the correlation between electronic structures of

binary TiMe alloys and the MT temperature was stressed in [15]. The authors have suggested the formula for estimation of MT temperature using the overlapping occupancies, shape factors of d–d and p–d partial DOS's as well as the lattice parameter. It should be noted that the overlapping occupancies are very critical in the respect to atomic radii used in LMTO approach. Besides our results show that the electronic structure changes insignificantly with addition of Zr and Hf whereas the MT temperature increases essentially in comparison with binary TiNi alloy (from 40 up to 180°C). One can see also that the increase of the MT temperature in the considered ternary alloys correlates well with increase of their unit cell volume. We think that the solution of this problem is more complicated than that suggested in [15] and the following study is desirable. As was shown in our paper [14], the change of the MT temperature with deviation from stoichiometry composition (with magnetic and non-magnetic impurities) is strongly affected by the competition of the following factors: the impurity scattering and the imperfect nesting. In the case of magnetic alloys the destruction of the magnetic order at the presence of the impurity it is necessary to take also into account.

In conclusion, we performed a comparative study for binary and ternary Ti-based transition metal alloys using the full-potential LAPW method. For the first time the influence of disorder was studied for two series transition metal alloys. The obtained electron characteristics are in good agreement with the experiment.

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