The change of electron energy loss spectra in NiTi$_2$ alloys

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Abstract. The electron energy loss spectra (EELS) and *d*-electron occupancy of Ti and Ni in NiTi$_2$ alloy has been studied in terms of white-line intensity. It is found that the change of *d*-electron occupancy of Ni is very small. However, *d*-electron occupancy of Ti changes considerable large in the alloy. The change of *d*-electron occupancy is discussed in terms of charge transfer and local charge neutrality (LCN) approximation.

Introduction

The Ti-Ni alloys possess lots of interesting mechanical and chemical properties, such as shape memory [1-4], hydrogen storage [5-7], and large negative energies of alloy-formation [8]. These properties have the origin in the electronic structure in essence. Therefore the study of the electronic structures of Ti-Ni alloys is important. However, up to till now the change of *d*-electron occupancy of Ti or Ni in Ti-Ni alloys is not clear. Saturation magnetic moments experiments showed that the mean moment fall rapidly with increasing concentration of Ti in Ni rich alloys [9], X-ray emission experiments showed that the degree of occupation of Ni 3*d* band in these materials increases gradually in order of Ni, Ni$_3$Ti and TiNi alloys [10], self-consistent-field (SCF)-*X*α calculation showed that in Ni$_3$Ti alloy charge transfer from Ti to Ni, and X-ray photoelectron spectra (XPS) [11] electron energy loss spectroscopy (EELS) and showed the transfer of Ni *d*-electrons is probably small. These discussions are mainly concerned on NiTi and Ni$_3$Ti alloys, the NiTi$_2$ alloy catches little attention in the literatures.

EELS is a powerful tool to probe the electronic structure in solids. Comparing to X-ray absorption spectroscopy (XAS), which probes the unoccupied electronic structure also, EELS has better spatial resolution [12] making it possible to study the electronic structure of materials down to sub-nanometer level like precipitates, grain boundaries and other lattice defects. The most distinctive features observed in the EELS of transition metals are the peaks known as "white-line" [13] due to the excitations of 2*p* core electrons in an atom to unoccupied *d* or *s*-final states according to the dipole selection rule. The probability of transition to *s*-final states is much smaller than that to *d*-states, so *d*-band is mainly taken into account. A number of studies have related the change of "white-line" intensity to the change of the occupation of *d*-band in terms of either the ratio of L$_3$/L$_2$ white-line intensity or the total white-line intensity. It was found that an almost linear relationship exits between the normalized total white-line intensity and the occupancy of the *d* band for 3*d* and 4*d* metals [14]. A number of EELS experiments had been carried out to measure the change of *d*-electron occupancy in alloys using this method.

In this paper we focused on the change of *d*-electron occupancy in NiTi$_2$ alloy. The EELS of NiTi$_2$ alloy was acquired and the *d*-electron occupancy of Ti and Ni is calculated in terms of white-line intensity. The concept of charge transfer and LCN approximation is discussed with the results.

Experimental methods

Disk-shaped samples of NiTi$_2$ alloys were thinned down to electron transparency by twin jet electropolishing followed by ion milling to remove the possible thin oxide layer on the surface. The EELS experiments were performed on a field emission gun transmission electron microscope (JEOL

2010F) equipped with a GIF 678 system at 200 kV. After examining the oxygen edge, Ti and Ni EELS of $NiTi_2$ was acquired in similar thickness areas. The microscope was operated in diffraction mode with the camera length of 80 mm and a spectrometer collection aperture of 3 mm. The energy resolution is typically 1.4 eV estimated from the width of half maximum of the zero-loss peak. The detector dark current and gain variation were corrected. The pre-edge backgrounds of all spectra were subtracted by fitting with the power-law function and then deconvoluted by the Fourier-ratio method. Before comparison the threshold position of experimental spectra were aligned together.

Results and discussion

EELS of Ti and Ni in alloys are shown in Fig.1. The L_2 and L_3 edges can be seen easily. The EELS of pure Ti and pure Ni [15] was put together for comparison. It can be seen that the shape of Ti EELS is very similar in $NiTi_2$ and pure Ti, but the white line intensity changes very noticeable. The white line intensity of EELS in $NiTi_2$ is much larger than that in pure Ti, implying that its unoccupied states are larger and d-electron occupancy decreases dramatically. The shape of Ni EELS in $NiTi_2$ and pure Ni is very similar also, and L_2 and L_3 edges shift to higher energy loss in $NiTi_2$.

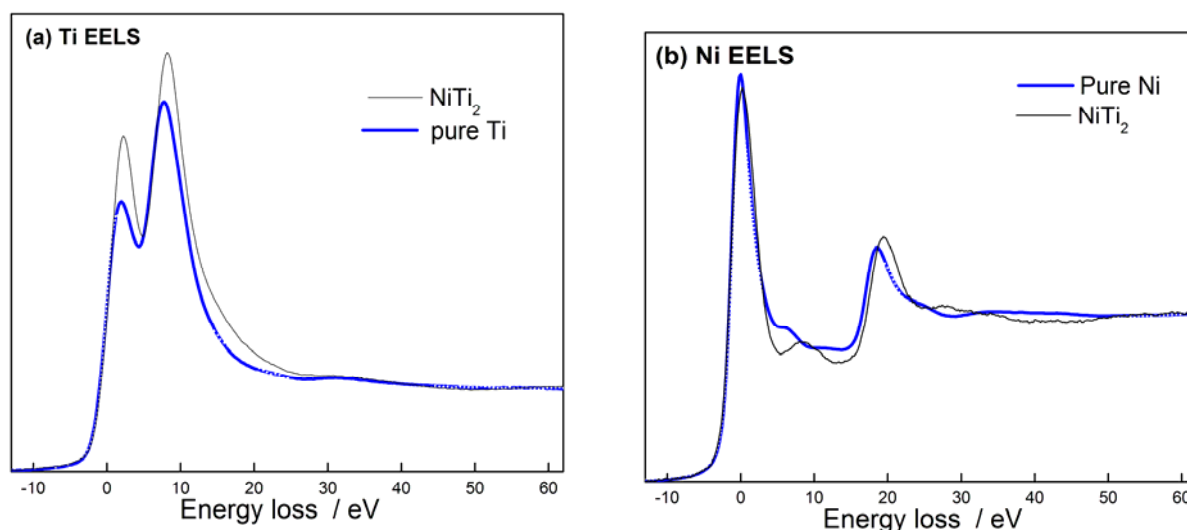Figure 1. (a) Ti EELS and (b) Ni EELS of some Ti_xNi_{100-x} alloys.

The change of d-electron occupancy of Ti and Ni in $NiTi_2$ are calculated from Pearson's method [15]. In this method, a step function is constructed as the continuum background of EELS so that the white line intensity is isolated. The normalized windows are set 50 eV after L_3 edges. The d-electron occupancy of pure Ti and pure Ni is 2.49 and 8.80 respectively. The results show that the change of d-electron occupancy of Ni in $NiTi_2$ relative to pure Ni is only -0.12. This is qualitatively in agreement with the results of Fuggle *et al.* [11] and Potapov *et al.* [16]. However, Ti d-electron occupancy in $NiTi_2$ decreases very noticeably relative to pure Ti, and the number is -1.35. It seems that charge transfer exits among atoms during formation of compounds. The results of Ti is accord with saturation magnetic moments [9], X ray emission experiments [10], and SCF-Xα calculation, because the results of all these experiments or calculation all concluded that d-electron occupancy of Ti decreases and d-electron occupancy of Ni increases in Ti-Ni alloys compared with that of the pure metal.

Charge transfer and the LCN approximation is frequently addressed by both experiments and calculations in the literatures. Recent results of XAS and EELS showed no significant change of d-electron occupancy in transition metal [16-20]. The change of d-electron occupancy of Ni, for example, is typically smaller than 0.2. It is appeared that the LCN approximation rather than the charge transfer plays a role upon the formation of the compound. In our EELS experiments, the change of d-electron occupancy of Ni is also smaller than 0.2, hence we also conclude that the LCN approximation plays an important role in Ti-Ni alloys if only the change of d-electron occupancy of Ni is taken into account. However, if the change of Ti d-electron occupancy is taken into account we

think that LCN approximation may be not adequate to explain the change of *d*-electron occupancy, because the change of Ti *d*-electron occupancy is accord with charge transfer mechanism. The charge transfer mechanism suggests that charge transfer between elements was governed by the difference in electronic chemical potential of pure metals [21,22]. The solve of the disagreement needs further studies.

Summary

We acquired the electron energy loss spectra (EELS) of Ti and Ni in $NiTi_2$ alloy and measured *d*-electron occupancy of Ti and Ni from white line intensity. The results show that the change of *d*-electron occupancy of Ni is very small, but *d*-electron occupancy of Ti decreases considerably.

Acknowledgment

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