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Effect of additives on titanium-hydrogen interaction under ball milling of Ti powder probed by hard x-ray emission spectroscopy

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Titanium is well known as a light-weight hydrogen storage material that is applied as a component of hydrogen storage composites together with Mg and other metals. Amorphous boron, boron nitride, and graphite were used as additives to improve Ti-H₂ reactivity during ball-milling due to its anti-sticking and matrix-forming properties. The chemical state and local electronic structure of Ti atoms were studied by hard x-ray emission spectroscopy (XES). We have measured fluorescent Ti $K\beta_5$ ($4p \rightarrow 1s$ transition) x-ray emission spectra, which are very sensitive to the local surroundings of exciting atoms, and found additional features coinciding in energy with spectra of reference samples TiB₂, TiN, and TiC. Based on these measurements, it is concluded that atoms of additives form chemical bonding with Ti due to the occupation of interstitials in the host Ti-lattice. © 2011 American Institute of Physics. [doi:10.1063/1.3662200]

I. INTRODUCTION

The development of a metal-hydride technology requires a detailed study of hydrogen interaction with metals and alloys. Titanium is widely used as an ingredient of hydrogen storage materials. Titanium hydride TiH₂ has been an attractive material for the purpose of hydrogen storage.¹ For a successful application, fast and low-temperature preparation of metal-hydrides should be realized. TiH₂ can be prepared during reactive milling of Ti in a H₂ atmosphere, which is a highly effective technique to synthesize nanocrystalline Ti-hydride powder.^{2,3} Graphite addition considerably accelerates and increases hydrogen uptake.^{4,5} However, this additive can suppress Ti-H₂ interaction by blocking the Ti surface with carbon or TiC layers.⁵ Other additives (B, BN, V₂O₅ etc.) are also used to promote the mechanochemical synthesis of metal hydrides.^{6,7} The aim of this work is to study the local bonding structure of Ti atoms of Ti/C, Ti/B, Ti/BN, and TiH₂/BN nanocomposites and estimate the formation of Ti-C, Ti-B, and Ti-N bonds in these materials.

II. EXPERIMENTAL

Titanium powder (~250 μm sized spherical particles) with a purity of 99.5%, highly oriented pyrolytic graphite with a purity of 99%, boron with a purity of 99%, and hexagonal BN with a purity of 99% were used as starting materials. The graphite boron or boron nitride was added to Ti with an amount of 16.6 wt. %. Hydriding experiments were carried out in a flow mechanochemical reactor with an average energy intensity of 1.0 W/g in a 50–60 vol. % H₂/He gas mixture. The gas composition

was monitored by a gas-chromatograph combined on-line with the milling device.

The local bonding structure of Ti atoms in Ti/C, Ti/B, and Ti/BN nanocomposites was studied by means of hard x-ray emission spectroscopy.

X-ray emission Ti $K\beta_5$ ($4p \rightarrow 1s$ transition) spectra are obtained with the help of a Johann-type spectrometer FRS-KD-2⁸ with a curved ($R = 1.3$ m) quartz (1011) monochromator providing an energy resolution of 0.25 eV. The spectra were recorded using a linear position-sensitive detector similar to “Chevron”⁹ dividing the charges arising on the cathode. Spectra are excited with the help of a sealed Pd x-ray tube operated at $V = 25$ kV and $I = 40$ –50 mA. Polycrystalline samples (pressed pellets) are attached to the spectrometer sample holder using conductive adhesive tape. The signal/noise ratio was 20/1. Calibration of the experimental spectra was carried out using Ti $K\beta_5$ spectrum of pure titanium, the energy of which ($E = 4962.3$ eV) is taken from Bearden Tables.¹⁰ Before and after each measurement, a spectrum of pure titanium was recorded. All spectra were normalized after background subtraction. All measurements were performed at room temperature.

Figure 1 shows results of fluorescence measurements of Ti $K\beta_{1,3}\beta_5$ XES of Ti metal. As can be seen, Ti $K\beta_5$ XES ($4p \rightarrow 1s$ transition) is almost 30 times weaker than Ti $K\beta_{1,3}$ XES ($3p \rightarrow 1s$ transition). For subtraction of Ti $K\beta_5$ XES the high-energy part of Ti $K\beta_{1,3}$ XES is approximated by the model function:

$$y = y_0 + A_1 \cdot e^{-(x-x_0)/t_1} + A_2 \cdot e^{-(x-x_0)/t_2} + A_3 \cdot e^{-(x-x_0)/t_3}$$

where y is the relative intensity, and x the energy. All other parameters were calculated by least-square method. The calculated part of Ti $K\beta_{1,3}$ XES is shown by solid line and the

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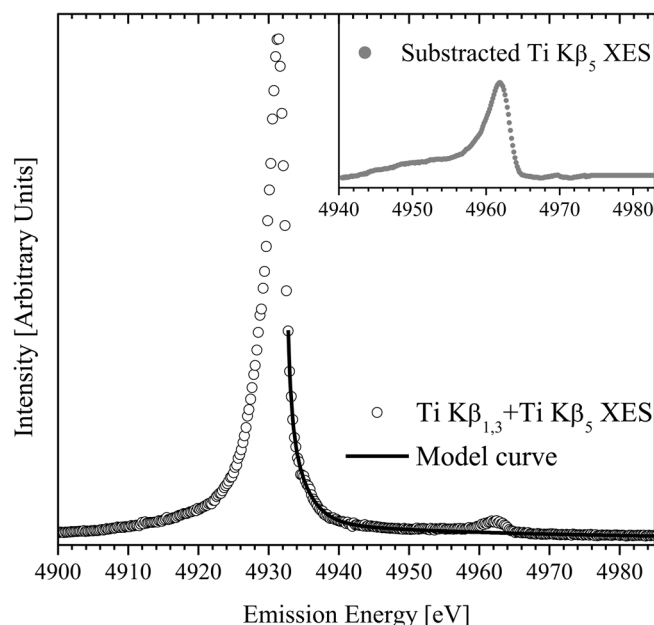


FIG. 1. Subtraction of Ti $K\beta_5$ XES from Ti $K\beta_{1,3}$ -line with help of model curve.

result of subtraction of Ti $K\beta_5$ XES of Ti metal is given in the inset.

III. RESULTS AND DISCUSSION

The results of measurements of Ti $K\beta_5$ XES of Ti hydrides TiH_x ($x = 1.15$ – 2.0) are presented in Fig. 2. As can be seen, Ti $K\beta_5$ XES of hydrides is split into two subbands A and B. The $I(B)/I(A)$ intensity ratio is increased with H-content, which indicates that the B-band reflects Ti $4p$ -H $1s$ bonding. On the other hand, the A-subband is close in energy to Ti-metal (see Fig. 3) and therefore is formed by Ti $4p$ -Ti $3d$ interactions in Ti hydrides. We need to point out that Ti $L_{2,3}$ XES ($3d4s \rightarrow 2p$ transition) of TiH_2 ¹¹ also shows an addi-

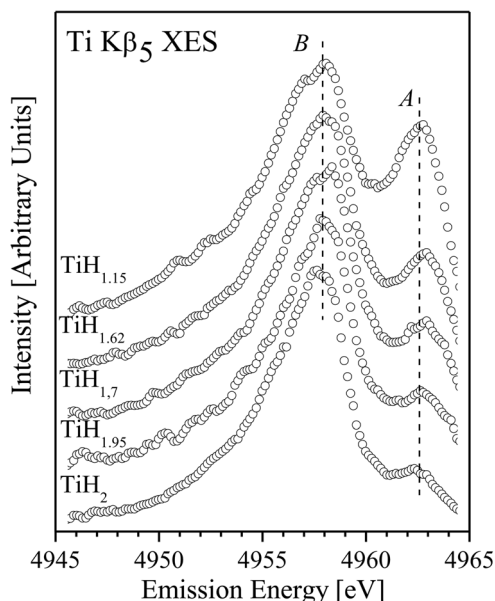


FIG. 2. Ti $K\beta_5$ XES of TiH_x ($x = 1.15, 1.62, 1.70, 1.95, 2.0$).

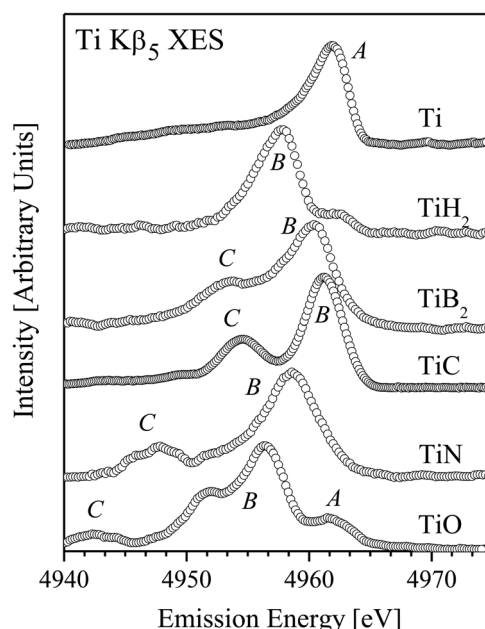


FIG. 3. Ti $K\beta_5$ XES of reference samples (Ti, TiH_2 , TiB_2 , TiC, TiN, TiO).

tional low-energy subband (compared to that of Ti-metal) which has the same origin and is due to Ti $3d$ -H $1s$ hybridization. However, the relative intensity of this subband is much lower than observed in Ti $K\beta_5$ XES: The intensity ratio ($I(B)/I(A)$) is 4.93 and 0.54 for Ti $K\beta_5$ and Ti $L_{2,3}$ XES, respectively. Such high relative intensity of the B-subband in Ti $K\beta_5$ XES is due the fact that $4p$ -states are absent in free Ti atoms and are populated only under the formation of a solid. In accordance with the concept developed in Refs. 12 and 13, the intensity distribution of the $K\beta_5$ -spectra is determined by interaction between the $4p$ states of the exciting atom with the valence states of the neighboring atoms. Therefore, Ti $K\beta_5$ XES reflects more electronic states of neighbor atoms surrounding the exciting Ti-atom that are easily hybridized with Ti $4p$ -states due to the diffuse character of Ti $4p$ -wave functions. This conclusion is confirmed by the results of band structure calculation of Ti and TiH_2 (Fig. 4), which is made in the same manner as in Ref. 5. According to this calculation, Ti $4p$ -states form a two-subband (A and B) structure in the valence band of TiH_2 where the shape and energy position of the A-band is close to Ti $3d$ -band and the B-band reproduces that of hydrogen $1s$ -band. The energy difference of calculated A and B bands as well as their ratio are very close to those of experimental Ti $K\beta_5$ XES of TiH_2 (Fig. 2). In the case of Ti-metal, only atoms of the same sort are located in the first coordination sphere of Ti-exciting atom, and as result the Ti $K\beta_5$ XES has one band structure that is determined by Ti $4p$ -Ti $3d$ hybridization.

The high sensitivity of Ti and V $K\beta_5$ XES to the local surroundings of exciting metal atoms was used to study oxygen vacancies in non-stoichiometric oxides TiO_x and VO_x ^{14,15} and can also be applied to study the role of additives C, B, BN under ball milling of Ti-powder in hydrogen flow. Our previous studies of this problem based on Ti $L_{2,3}$ XES measurements have shown^{5,11,16,17} that the atoms of additives can enter the host lattice of Ti-metal occupying

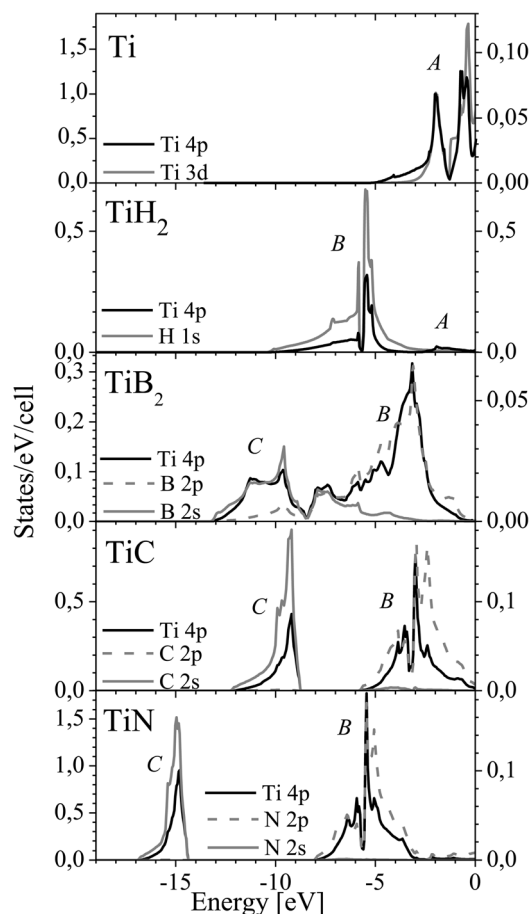


FIG. 4. Calculated partial DOSes of Ti, TiH₂, TiB₂, TiC, and TiN. Right axis for Ti 4*p* states, left axis for all others.

octahedral interstitials and form chemical bonds with Ti-atoms.

Figure 3 shows Ti $K\beta_5$ XES spectra of reference samples: Ti, TiH₂, TiB₂, TiC, TiN, and TiO. As can be seen, in the case of TiH₂, only one additional low-energy subband *B* is observed, whereas in spectra of TiB₂, TiC, and TiN, two low-energy subbands *B* and *C* are present. This is due to the fact that hydrogen has only 1*s* valence state but B, C, and N have 2*p* and 2*s* valence states. According to our previous studies^{11,18} the *B* and *C* subbands are connected with 2*p* and 2*s* states of light elements (B, C, N) and are observed in Ti $K\beta_5$ XES due to their hybridization with Ti 4*p*-states. This is confirmed by band structure calculations (Fig. 4). The energy position of *B* and *C* subbands is different in different compounds (following the energy 2*s*-2*p* difference in B, C, and N atoms) enabling use of them to reveal additional chemical bonds of Ti atom with light elements in the products of chemical reactions occurring under ball milling. As can be seen, the low-energy subband at $E \cong 4943$ eV connected with O 2*s*-states is absent in reference spectra of Ti, TiB₂, TiC, and TiN, allowing to conclude that these reference spectra were not oxidized.

Figure 5 illustrates how we can identify the formation of an additional energy subband in Ti $K\beta_5$ XES spectra in the product of 1 h ball milling of Ti with graphite additive in H₂/He flow. The experimental Ti $K\beta_5$ XES is presented in the

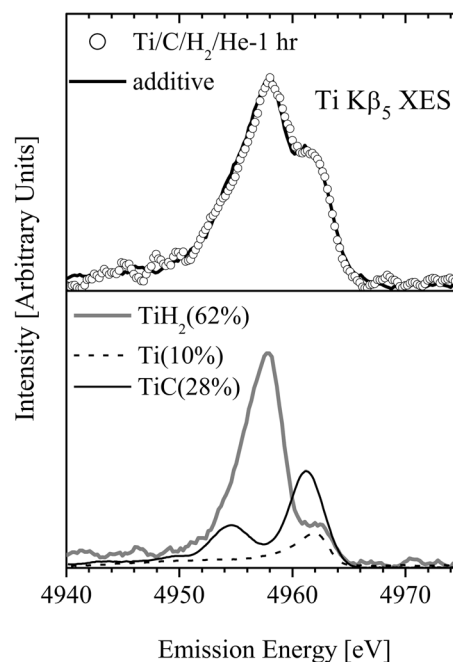


FIG. 5. Ti $K\beta_5$ XES of Ti/C/H₂/He (upper panel) and superposition of spectra of reference samples (lower panel).

upper panel. One can see that the fine structure of the spectrum resembles that of TiH₂ (see Fig. 2) except for a higher relative intensity of maximum of *A*-band. Spectra of reference samples given in lower panel demonstrate that it is due to the contribution of TiC (28%) and unreacted Ti (10%). The additive spectrum reproduces the experimental spectrum quite well (we estimate the accuracy of such superposition as 5%). Similar results are obtained in study of Ti $K\beta_5$ XES of Ti/B/H₂/He-1 hr (Fig. 6) and Ti/BN/H₂/He-3.5 hr (Fig. 7). One can see that in both cases, the double-peak structure of

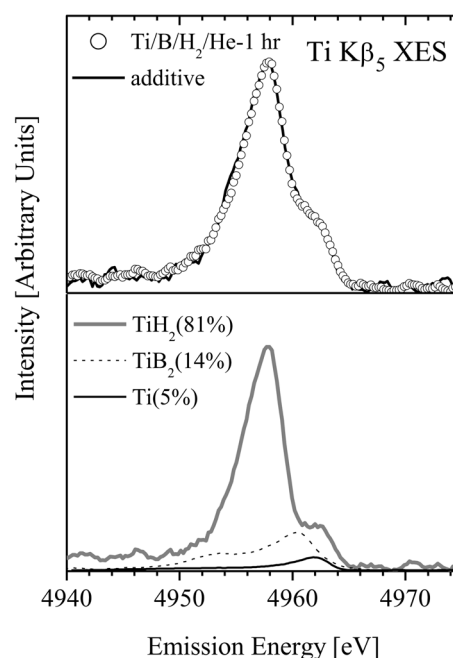


FIG. 6. Ti $K\beta_5$ XES of Ti/B/H₂/He (upper panel) and superposition of spectra of reference samples (lower panel).

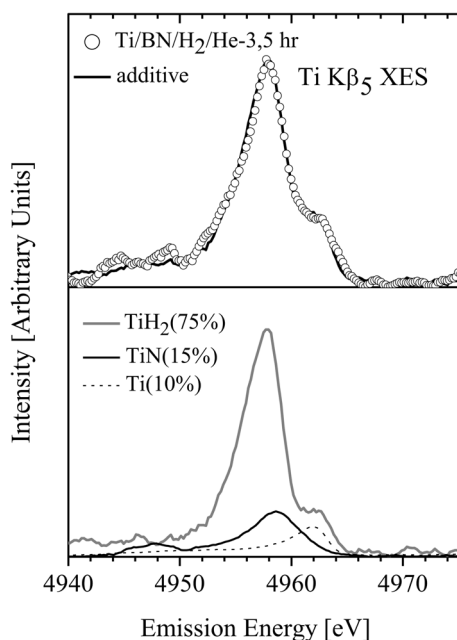


FIG. 7. Ti $K\beta_5$ XES of Ti/BN/H₂/He (upper panel) and superposition of spectra of reference samples (lower panel).

Ti $K\beta_5$ XES is found as in the case of Ti/C/H₂/He-1 hr (reminding of that of TiH₂); however, the relative intensity of A-band is lower for spectra of Ti/B/H₂/He-1 hr and Ti/BN/H₂/He-3.5 hr. The intensity of the A-band is lower for spectra of Ti/B/H₂/He-1 hr and Ti/BN/H₂/He-3.5 hr. The superposition of reference spectra shows that the best fitting with experimental spectra is found when the contribution of Ti-B (14%) and Ti-N (15%) bonds is less than the contribution of Ti-C (28%) bonds. However, the formation of a thick TiC layer can suppress Ti-H₂ interaction and therefore boron and BN additives seem to be more efficient than carbon additive to increase hydrogen uptake. Another important conclusion is that under ball milling of Ti with a BN additive, only nitrogen atoms have entered into the host Ti-lattice forming Ti-N bonds. This is in agreement with our previous study of soft x-ray spectra of Ti/BN/H₂/He⁶ and results of electronic structure calculations,^{6,7} according to which addition of carbon or nitrogen does indeed improve the bonding of hydrogen in Ti lattice. On the basis of these calculations, one can conclude that under ball milling the BN molecules are partially decomposed into nitrogen and boron atoms at the Ti surface, and consequently the nitrogen atoms enter the Ti lattice, occupying octahedral interstitial sites or perhaps vacancies in the Ti lattice.

We have also studied the local bonding structure of Ti-atoms of mechanically activated TiH₂/BN mixtures (Fig. 8). These data show that additional Ti-N and Ti-B bonds are formed due to an interaction of TiH₂ nanoparticles with the additives. Mixed configurations around Ti atoms with proportional contributions of local Ti-H, Ti-N, and Ti-B bonds reproduce the experimental Ti $K\beta_5$ spectrum quite well. Therefore one can conclude that the H₂ loss in the TiH₂ lattice is accompanied by incorporation of nitrogen and boron atoms into host material with formation of additional Ti-N and Ti-B bonds.

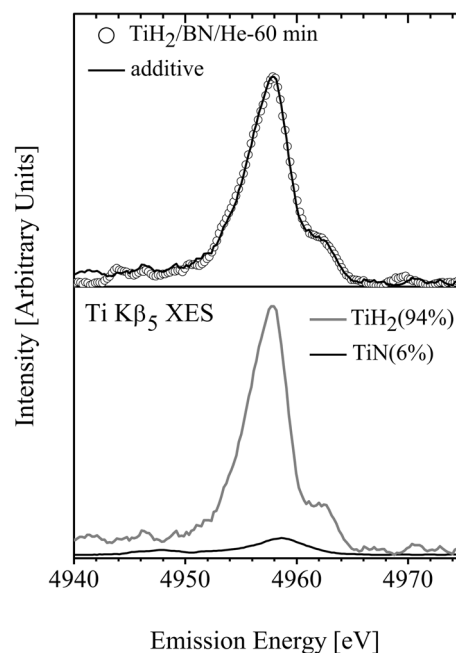


FIG. 8. Ti $K\beta_5$ XES of TiH₂/BN/H₂/He (upper panel) and superposition of spectra of reference samples (lower panel).

IV. CONCLUSIONS

In conclusion, we have studied Ti/C, Ti/B, Ti/BN, and TiH₂/BN mechanically activated nanocomposites with help of hard x-ray emission spectroscopy. The local bonding configuration of Ti-atoms was studied with help of Ti $K\beta_5$ x-ray emission spectra. The formation of additional Ti-C, Ti-B, and Ti-N bonds is found by detection of additional low-energy subbands, which are absent in spectra of the pure metal and are due to hybridization of Ti $4p$ -states with p - and s -states of ligand atoms. It is found that combinations of spectra of reference samples (Ti, TiH₂, TiB₂, TiC, and TiN) reproduce the experimental spectra quite well and can be used for an estimation of the ratio of Ti-H, Ti-C, Ti-B, and Ti-N bonds. Based on these measurements, one can conclude that under ball milling the additive atoms enter to the host lattice (Ti or TiH₂) and form chemical bonds with Ti atoms.

ACKNOWLEDGMENTS

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