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Abstract

The electronic structure of the MAX-phase Ti_2AlC was investigated by soft x-ray emission spectroscopy. This nanolaminated carbide compound represents a class of layered materials with a combination of properties from both metals and ceramics. The bulk-sensitive soft x-ray emission technique is shown to be particularly useful for detecting detailed electronic structure information about internal monolayers and interfaces. The Ti-Al bonding is manifested by a pronounced peak in the Ti L-emission of Ti_2AlC, which is not present in the binary TiC system. The spectral shape of Al L-emission in the MAX-phase is strongly modified in comparison to metallic Al. By replacing the constituting elements, a change of the electron population can be achieved causing a change of covalent bonding between the laminated layers, which enables control of the macroscopic properties of the material.

Introduction

Recently, the interest in ternary carbides and nitrides, so-called $M_{n+1}AX_n$-phases has grown significantly both from a scientific and technological point of view [1]. Generally, there are three different kinds of crystal structures (stoichiometries) of these materials, classified as 211 (n=1), 312 (n=2) and 413 (n=3) phases. The letter M denotes an early transition metal, A is an element in the groups III-V and X is either carbon or nitrogen. The MAX-phases exhibit a unique combination of metallic and ceramic properties, including high strength and stiffness at high temperature, resistance to oxidation and thermal shock, and display high electrical and thermal conductivity [1]. The unique macroscopic properties of the MAX-phases are related to the internal nanolaminated crystal structure, as well as the electronic structure and the chemical bonding between the individual atomic layers. For the 211-crystal structure, there are about 50 different carbides, among which Ti_2AlC can be anticipated to be one of the most technically useful. Sintered bulk MAX-compounds are useful in many technological high-temperature applications such as heating elements in ovens and combustion engines. In other applications where tribological properties e.g., low-friction and wear resistance are useful, high-quality thin film coatings of MAX-phases can be utilized.

In this paper, soft x-ray emission (SXE) spectroscopy was applied to probe the internal electronic structures of Ti_2AlC and TiC. The photon-in-photon-out SXE spectroscopic technique is element selective and more bulk sensitive than electron-based techniques such as x-ray absorption and x-ray photoemission spectroscopy [2-4]. This makes it possible to obtain information about the buried internal monolayers and interfaces in the compounds. The internal electronic structure of each constituent atomic element in the MAX-phase compound can be probed separately and provide elemental as well as chemical information about the partial electronic structure of the occupied valence band projected by the dipole transition selection rules to the core level of each element.

Experiment

The SXE measurements were performed at the undulator beamline I511-3 at MAX II (MAX-lab National Laboratory, Lund University, Sweden), which includes a 49-pole undulator and a modified SX-700 plane grating monochromator [5]. The SXE spectra were recorded with a high-resolution Rowland-mount grazing-incidence grating spectrometer [6] with a two-dimensional detector. The Ti *L* and C *K* x-ray emission spectra were recorded using a spherical grating with 1200 lines/mm of 5 m radius in the first order of diffraction. The Al *L* spectra were recorded using a grating with 300 lines/mm, 3 m radius in the first order of diffraction. During the SXE measurements at the Ti *2p*, C *1s* and Al *2p* edges, the resolutions of the beamline monochromator were 1.6, 1.0 and 0.3 eV, respectively. The SXE spectra were recorded with spectrometer resolutions 0.7, 0.2 and 0.2 eV, respectively. The measurements were performed with a base pressure lower than 5 x 10^{-9} Torr. In order to minimize self-absorption effects [7], the angle of incidence was 20 degrees from the surface plane during the emission measurements. The x-ray photons were detected parallel to the polarization vector of the incoming beam in order to minimize elastic scattering. The deposition procedure of the epitaxially grown thin film coatings are described elsewhere [8].
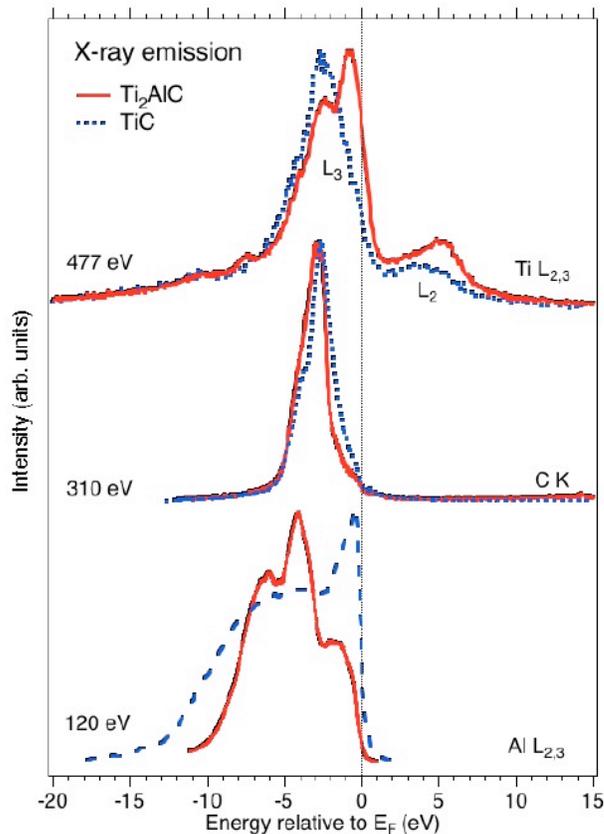
Figure 1: (Color) Ti *L*, C *K* and Al *L* x-ray emission spectra of the MAX phase Ti_2AlC compared to TiC. The excitations were made nonresonantly at 477 eV, 310 eV and 120 eV, respectively. The spectra were aligned on a common energy scale relative to the Fermi level (E_F) by using core-level XPS binding energies [8] (454.2 eV, 281.9 eV, 72.5 eV, respectively). The measured spectral profile of Al in Ti_2AlC is compared to a spectrum of pure Al from Ref. [9] (dashed line).

Results and Discussion

Figure 1 shows a set of soft x-ray emission spectra excited nonresonantly above the Ti *L*, C *K* and Al *L*, edges for Ti_2AlC and TiC. The excitation energies were 477 eV, 310 eV and 120 eV, respectively. For comparison, the spectra are normalized to unity and plotted on a common photon energy scale relative to the Fermi level (E_F) using the core level XPS binding energies of Ti_2AlC [8]. For Ti $2p_{3/2}$, C *1s* and Al $2p_{3/2}$, 454.2 eV, 281.9 eV and 72.5 eV binding energies were used, respectively.

In the Ti $L_{2,3}$ spectra at the top of Fig. 1, the main L_3 and L_2 emission lines dominated by *3d* final states are observed at -2.5 eV and 3.7 eV and the intensity of the L_3 emission line is about 6 times higher than the L_2 intensity. The measured peak splitting due to the spin-orbit interaction is 6.2 eV. Considering the L_3 region, the most significant difference between the two systems is the pronounced double peak in the Ti_2AlC system. The peak splitting of the double peak is 1.5 eV.

In the C *K* spectra, the main peak is found at –2.6 eV and there are shoulders on both the low- and high-energy sides of the main peak at -4.2

eV and -2 eV. The high-energy shoulder is more pronounced in Ti_2AlC while the low-energy shoulder is more pronounced in TiC.

The Al $L_{2,3}$ spectrum of Ti_2AlC, has the main peak at -3.9 eV and is dominated by *3s* final states. Al *3p* states dominate close to E_F but are effectively dipole forbidden at the *2p* edges and only contribute indirectly to the Al *L* SXE spectrum. The spectral profile of Al in Ti_2AlC also differs substantially from the spectrum of pure Al metal, which has a sharp and dominating peak structure close to E_F [9]. A similar spectral profile as in Al of Ti_2AlC has been observed in the metal aluminides [10].

Considering the Ti $L_{2,3}$ spectrum of Ti_2AlC, the main peak at -1 eV mainly originates from Ti *3d* - Al *3p* hybridization, an interpretation that is also consistent with bandstructure calculations [11,12]. The -1 eV peak is absent in TiC which instead is dominated by a carbide-type of peak at -2.5 eV due to Ti *3d* - C *2p* hybridization. The broad peak structure observed approximately at -10 eV in both the Ti $L_{2,3}$ spectra of Ti_2AlC and TiC is not observed in Ti $L_{2,3}$ spectra of pure Ti [13]. The -10 eV structure can therefore be attributed to hybridization with carbon due to Ti *3d* - C *2s* hybridization. In the C *K* emission spectra, the main peaks and the shoulders correspond to the occupied C *2p* orbitals hybridized with the Ti *3d* states of the valence band. A comparison between the spectral profiles of measured MAX-phases and electronic structure calculations including core-to-valence dipole transition matrix elements is presented elsewhere [8] yielding a qualitative agreement in the interpretation between experiment and theory.

Conclusions

Soft x-ray emission spectra of the MAX-phase Ti_2AlC in comparison to TiC are presented. The largest difference between the two compounds is a double peak in the Ti $L_{2,3}$ emission of Ti_2AlC. This originates from the fact that the Ti-Al bond region at -1 eV is significantly closer to the Fermi level than the Ti-C bond regions at -2.5 eV and at -10 eV. The $L_{2,3}$ x-ray emission spectral profile of Al in Ti_2AlC is found to be very different in comparison to pure Al metal. This strongly modified spectral structure is due to significant hybridization with the surrounding Ti and C atoms. By replacing Al with other elements, the achieved change in the valence electron population and thus the modified chemical bonding scheme implies a change of the macroscopic material properties.

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