Effect of alternative treatments methods on the electronic structure of ZrO_2-TiO_2

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Idea

Use of the XPS method to study the feature of the electronic structure ZrO_2-TiO_2-based composites before and after mechanochemical and ultrasonic treatment.

Method

X-ray spectrometer:"JEOL" JSPM-4610. Work pressure no less then 10^{-7} Pa.
X-ray source Mg K_α 1253.6 eV. Energy resolution 0.1 eV.

Results

To evaluate the distribution of components in the surface layer of the composites, a quantitative analysis was performed using the integral intensities of the XPS spectra - O1s, Ti $2p_{3/2}$ and Zr $3p_{3/2}$ taking into account the effective scattering cross sections (Table 1). Since the mechanical treatment showed a greater amount of oxygen on the surface, and considering the fact that there is a significant covalent chemical bonding component in these oxygen oxides, it can be assumed that there is an increase in the corrosion resistance of the composite.

Table 1. Chemical composition of the surface according to XPS (at.%).

Element / Sample	O, %	Ti,%	Zr,%	Ti/Zr
Initial sample	62.00	21.57	16.43	1.31
After machining treatment	65.83	18.43	15.74	1.17
After ultrasonic treatment	63.58	19.17	17.25	1.11

The dependence of the chemical shift on particle size has been studied [1]. A logarithmic dependence of the chemical shift value of the X-ray photoelectron line of metal ΔE_b(eV) on the particle area was established, where S_{part} - is the particle area on the surface, and S_0 - is the area of particles that do not experience the size energy shift.

$$\Delta E_b = ln(\frac{S_0}{S_{part}})$$

Using this formula for the peaks of titanium and zirconium, the ratio between the areas of the particles relative to the original sample was determined (Table 2).

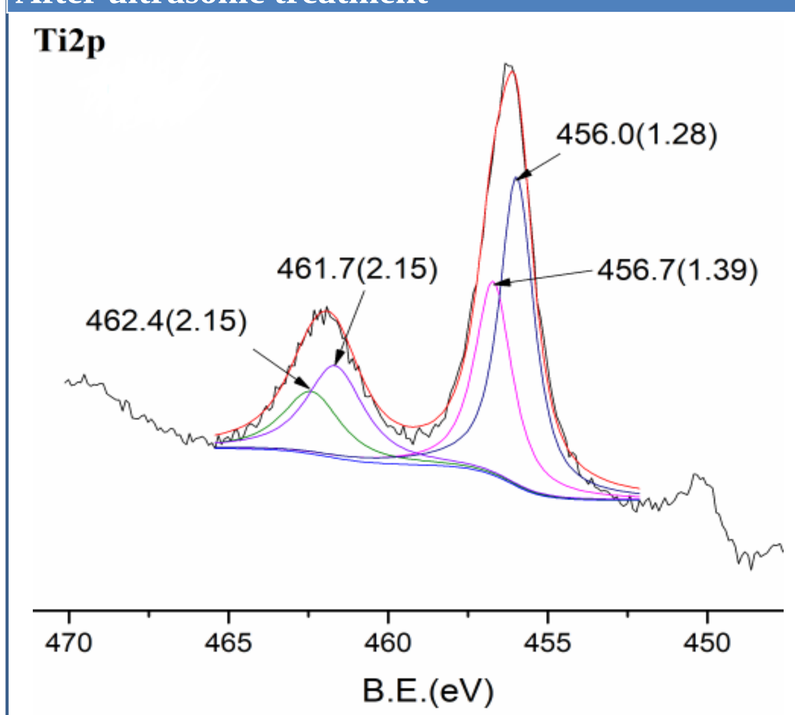
Table 2. Ratio of particle areas relative to the original sample.

	Ti $2p_{3/2}$, (eV)	Zr $3p_{3/2}$, (eV)	ΔE(Ti), (eV)	ΔE(Zr) , (eV)	S_0/S_p (Ti 2p)	S_0/S_p (Zr 3p)
Initial sample	456.21	333.09	-	-	-	-
After machining treatment	458.07	331.87	1.86	1.22	6.42	3.39
After ultrasonic treatment	456.72	331.67	0.51	1.42	1.67	4.14

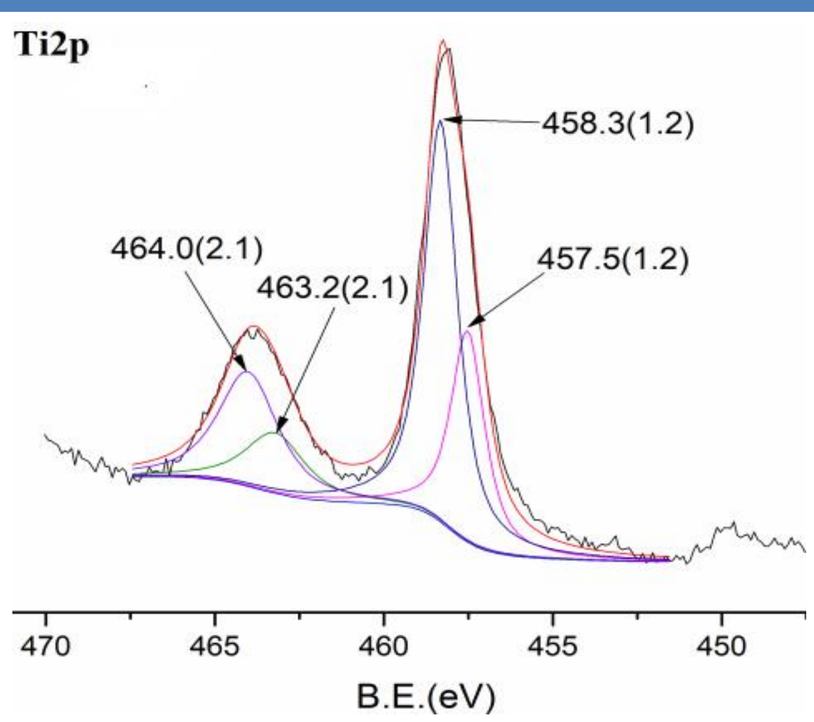
The change in the Ti $2p_{1/2}$ - Ti $2p_{3/2}$ splitting indicates a significant change in the first coordination sphere of the element. The 0.15 eV increase in Ti $2p_{1/2}$ - Ti $2p_{3/2}$ distance may indicate a possible phase transition (Table 3). Thus, it can be assumed that after the ultrasonic treatment, part of the sample experienced the anatase-rutile phase transition..

Table 3. Ti $2p_{1/2}$ - Ti $2p_{3/2}$ splitting

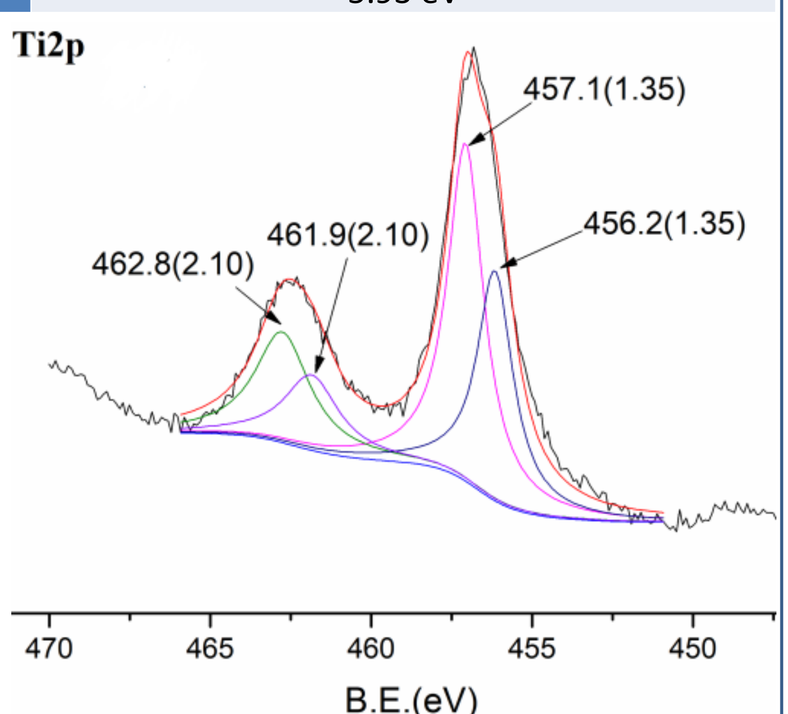
Initial sample	5.78 eV
After machining treatment	5.74 eV
After ultrasonic treatment	5.93 eV



XPS Ti 2p initial sample



XPS Ti 2p after machining treatment



XPS Ti 2p after ultrasonic treatment

Conclusions

The effect of different treatment methods, in particular, mechanochemical and ultrasonic treatment of ZrO_2-TiO_2 composites on the electronic structure was investigated. At mechanochemical treatment of samples, the increase in oxygen is 3.83 at. %, and at ultrasonic treatment - 1.58 at. %. Thus, the mechanical treatment of ZrO_2-TiO_2 composite leads to a significant increase in corrosion resistance compared to ultrasonic treatment.

In the process of ultrasonic treatment, there is an increase in the contribution of surface atoms of titanium and a decrease in the contribution of surface atoms of zirconium in the integral intensities of metal spectra. This effect can be attributed to the fact that during ultrasonic treatment in comparison with mechanochemical treatment there is an increase in the nanocrystalline X-ray amorphous phase of titanium oxide and a relative decrease in the X-ray amorphous phase of zirconium.

Both mechanochemical and ultrasonic processing of the ZrO_2-TiO_2 composite contribute to a more homogeneous composition of the composite compared to the original sample. During the processing of the composite, part of the titanium oxide may have experienced a phase transition from anatase to rutile.

[1] Surf. Interface Anal. – 2010. – **V. 42**, No. 6-7. - 850–854