High-temperature physical properties of the electrodes based on MAX-phase Ti-Al-C produced by SHS-extrusion method

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Abstract. Physical properties of the Ti-Al-C compact rods with the content of the MAX phase have been studied. The rods were produced by energy-efficient SHS-extrusion method. It has been found that the oxidation mechanism is similar to nickel heat-resistant alloys, herewith the oxidation rate does not exceed 1 g/m²·h at 900 °C. The dependences of the corrosion resistance on stoichiometric parameters of green mixtures are reported. The electrical resistivity of the rods does not exceed 5-6 μΩm·cm at room temperature with a slight increase in value to 18 μΩhm·cm at 900 °C. These results can be useful for the potential applications of the rod as the high-temperature electrodes.

1. Introduction

Materials based on the MAX phase are thermodynamically stable layered ternary systems of the M₆₋₃AXn (n= 1…3) phases with hexagonal close packing. Here M is a transition metal, A is an element of group “A” of the periodic table, X is carbon or nitrogen [1]. Among the variety of this class, ternary carbides such as Ti-Al-C, Ti-Si-C combine mechanical and physical properties most successfully. It can be said that such compounds are metals and ceramics at the same time [2]. MAX phase has high electrical and thermal conductivity, high elastic modulus, good machinability, on the one hand, and oxidation resistance, low density and thermal stability on the other one [3]. There are several methods to produce dense MAX-phase containing material, such as hot isostatic pressing (HIP), spark plasma sintering (SPS) or pulse discharge sintering [4-6]. Self-propagating high-temperature synthesis (SHS) is another highly effective method, which contributes the energy-efficient way to produce ready-to-use items in a fast mode [7,8]. SHS-extrusion technique allows to combine a combustion process with the high-temperature plastic deformation and gets long thin rods. As a result, dense compacts with different shapes and high purity of compounds can be obtained [9,10]. Ti-Al-C-based phases are one of the most appropriate candidates for this method, because of the high exothermic reaction between Ti and C during the SHS [11,12]. Long rods were produced by SHS-extrusion method previously. Sheng et.al. [13,14] fabricated a Ni-Al-Ti-C based composite rods by SHS. However, their effective length does not exceed 15 mm. In the case of aluminum electrolysis application, a desirable content of the MAX-phase in the rod is estimated at 80-90% wt. The MAX phases are very good conductors of electricity, therefore it is expected that they will not react with the cryolite–alumina melt. That is why so important to investigate the temperature dependences of the electrical resistance of such materials as well as the high-temperature oxidation behavior of the extruded items. [15].
In the current work, the rods of 10 mm in diameter and more than 100 mm in length were prepared from the Ti$_2$AlC or Ti$_3$AlC$_2$ main phases with the 96-98 % density of the compact. For the investigations, a choice of such materials was motivated by their relatively high heat resistance, chemical inertness to the cryolite–alumina melt and low electrical resistivity, thus giving hope for the application of these compounds as the aluminum electrolysis electrodes. For these rods, the dynamics of high-temperature oxidation, the dependences of electrical resistivity on temperature up to 900 °C as well as the evolution of microstructure with heating were studied.

2. Experimental procedures
Commercially available powders were used for the green mixtures preparation, shown on Table 1. Initial pellets were prepared with the special stoichiometric ratios to ensure the fullest formation of MAX-phase (Ti$_2$AlC and Ti$_3$AlC$_2$). Before the cold pressing, the raw powders were initially dried for 24 hours, than the pellets were dried again within 4 hours before the combustion processes.

Table 1. Initial powders parameters

| Powder | Type  | Purity, % wt. | Dimensions |
|--------|-------|---------------|------------|
| Ti (titanium) | PTM   | 99,1          | 45         |
| C (carbon)   | PM-15T | 99,1          | 1          |
| Al (aluminium) | ASD-4 | 99,5          | 5          |

The stoichiometric ratios of the green mixtures were selected to ensure variability of aluminum content in the melt during the combustion. Some reports state that the exceeding of aluminum during the synthesis can improve MAX-phase content in the final product [16]. Table 2 shows the molar and mass ratios of green mixtures that were investigated in this paper.

Table 2. Stoichiometric and mass ratios of green mixtures

| Molar ratio, %, Ti- Al - C | 3 : 1 : 2 | 2 : 1,5 : 1 | 3 : 2,3 : 2 |
|---------------------------|-----------|-------------|-------------|
| Mass ratio, %             | 74 : 14 : 12 | 65 : 27 : 8 | 63 : 27 : 10 |

Heat resistance tests of electrodes were carried out in special ceramic crucibles, which passed an oxidation atmosphere through and ensured the preservation of crumbling scale. The crucible with the samples was placed in an oven on ceramic supports. Before testing, the crucibles were calcined to constant weight. The quantitative characteristics of the heat resistance of the samples were determined by the weighing method based on analytical balance controlling the increasing sample’s weight. Samples were weighed with an accuracy of 10$^{-6}$ g after 2, 4, 9 and 16 hours of annealing at 900 °C. The true rate of weight increase of the samples ($V_q$) was calculated as the first time derivative of the specific mass loss of the oxidized sample. Let’s use the equation (1) for calculating the true rate of the samples:

$$V_q = \frac{dq}{dt} = \frac{1}{S} \frac{dm}{dt},$$

where $dt$ is the oxidation time of the samples, $dm$ is the mass change of the samples over the considering time, $S$ is the surface area of the entire sample.

The electrical resistivity of the samples was measured by the four-point method, the scheme of such measurements is shown in Figure 1. The contacts were fixed in four places to the sample. An electric current I14 was excited through two contacts (1, 4), and the potential difference U23 was measured at the other two (2,3) contacts. From the measured values of the potential difference between points 2 and 3 and the current flowing through the points 1 and 4 the resistance was determined. The electrical resistivity was recalculated by equation (2):
Ω = R * S/l, \hspace{1cm} (2)

where $R$ is the measured resistance, $S$ is the cross-sectional area of the sample, $l$ is the distance between points 2 and 3.

Figure 1. The scheme of the electrical resistivity measurement of the extruded long rods.

The microstructure of the obtained items was studied by scanning electron microscopy (SEM) on a Zeiss Ultra Plus field emission scanning electron microscope equipped with an INCA 350 Oxford Instruments X-ray microanalysis attachment, which makes it possible to study the shape and size of the particles with a resolution of up to 2 nm.

3. Results and discussion

Figure 2 shows the dependences of the specific mass increase on the annealing time for the tested samples. This method also was used to determine the weight gain for a nickel heat-resistant EP741-NP alloy.

Figure 2. Dependences of specific weight gain on annealing time.

It was revealed that all the studied samples of stoichiometric ratios are possessing the characteristic oxidation curve dependences typical for the heat-resistant alloys. In the first stage of oxidation, the largest mass gain is caused due to the formation of oxide films on the surface, which is subsequently impede the penetration of oxygen into the samples. This oxidation stage is occurring during the first two hours. In order to evaluate the corrosion resistance of the samples, the specific rates of their oxidation
were calculated as the specific values of the mass gain given by the exposure time. Figure 3 shows the curves of growth rates (Vq) on the exposure time for each oxidized sample.

![Figure 3](image)

**Figure 3.** Oxidation rate of the extruded rods during 16 hours of annealing

As may see in Figure 3, after 4 hours of annealing, the oxidation rate of the samples after 4 hours of oxidation reaches a plateau, due to the oxide film formation at the samples surface. The obtained values of the oxidation rates for the studied samples were found to be close to that one for the EP741-NP alloy. Moreover, for 3Ti:2,3Al:2C and 3Ti:1Al:2C compositions, the oxidation rate was found to correspond to 0.65 g/m² • h, which is by a factor of 1.5 less in comparison with that one for the EP741-NP alloy. The observed oxidation rate values mean that the nature of the oxidation process for all the samples in study is similar to that of corrosion resistant alloys. The rason of the samples mass gain by the oxidation process relates to the surface oxide film formation, which slows down the penetration of oxygen into the samples. The previously described oxidation rates (20 h of oxidation) for the SHS electrodes were found 0.84 g/m² h and 1.09 g/m² h for the 3Ti:1Al:2C and 3Ti:2,3Al:2C compositions, respectively. We assume that the following oxidation will not lead to a sharp increase of the sample’s weight. Moreover, after recalculating, taking into account the oxidation time, the estimated oxidation rate at 100 h should decrease and may reach 0.5 g/m²*h, which is on the level of the heat-resistant industrial alloys. For example, typical oxidation rate for the nickel-based alloys measured at 900 °C, 100 h duration of oxidation is in the range of 0.25-0.85 g/m²*h, depending on composition. It is also a known fact that the intense oxidation occurs at the sites of defects. Therefore, to reduce the oxidation rate, it is necessary to further reduce the surface imperfection by grinding and polishing the surfaces of oxidizable samples. As an example, Figures 4a and 4b show a sample of 2Ti:1,5Al:1C composition before and after the high-temperature annealing.

![Figure 4](image)

**Figure 4.** Extruded rod before (4a) and after (4b) annealing for 16 h.
The microstructure of the cross-section of the 2Ti:1.5Al:1C extruded electrode is presented in Figure 5. This sample is interesting to consider because of the lowest oxidation resistance among the entire series, so it was curious whether some morphological change occurs or not. The cross-section was taken from the central part of the rod. It can be noticed that the oxidation curve of this sample has almost full matching with that one for the heat-resistant EP741-NP alloy, which was shown in Figure 2. As may see in Figure 5a, the microstructure of the non-annealed electrode depicts a typical dendritic MAX phase grains reaching up to 10 μm in length and no more than 1 μm in width. The predominant phase corresponds to Ti$_2$AlC with Ti$_3$AlC$_2$ inclusion, by prior results. The orientation of dendrites is mainly elongate toward the direction of the heat sink, but it depends on the particular side of the rod. After the annealing at 900 °C, 16 hours, no severe morphological changes revealed, including a grain growth or mutual phase’s diffusion. In this particular case, the presence of intermetallic compounds such as Ti$_x$Al$_y$ (5-8% wt.) promotes increased mobility of the titanium carbide grains (10-15% wt.) during the heating, Figure 5b. We are considering that this occurs because of the diffusion mobility of the TiC grains at the temperatures above 882 °C. As a result, multiple micro-defects appear along grain boundaries, which leads to intensifying oxygen penetration into the sample. Based on the experimental high-temperature testing and subsequent calculation results, the following practical advice can be drawn; the decreasing of TiC grains in the SHS-extruded Ti-Al-C rods leads to enhancing of the high-temperature corrosion resistance.

The electrical resistivity of the samples with nominal compositions 3Ti:1Al:2C, 2Ti:1.5Al:1C and 3Ti:2.3Al:2C was measured in the temperature range of 25 – 900 °C. The samples were placed in a furnace, which was heated up to 900 °C with increments of 15 deg/min.

**Figure 5.** Backscattered electron images of cross-sections of the 2Ti-1.5Al-1C extruded rods before (a) and after (b) annealing at 900 °C after 16 hours.

**Figure 6.** The temperature dependences of electrical resistivity of the samples.
The measurement results are presented in Figure 6. As can be seen from the experimental graphs, for the 3Ti:2,3Al:1C sample, the electrical resistivity value is 5-6 μOhm*cm at room temperature. Whereas in the case of other systems, the value does not exceed 40 μOhm *cm. As the temperature increases to 900 °C, the electrical resistance increases to 18–20 μOhm*cm and 130-155 μOhm * cm for the 3Ti:2,3Al:2C and 2Ti:1,5Al:1C, 3Ti:2Al:1C samples, respectively. An order of magnitude difference between these values can be caused by the low content of TiC grains in the last two samples.

4. Conclusion
This work dedicated to high-temperature physical properties of the dense compact rods prepared by self-propagating high-temperature synthesis with subsequent extrusion from Ti, Al and C initial powders. The series of the ready-to-use samples with 3Ti:2Al:1C, 2Ti:1,5Al:1C and 3Ti:2,3Al:2C stoichiometric ratios were examined at 900 °C. It has been revealed that the visual dendritic structure of TiAlC MAX-phase do not undergo severe morphological changes under 900 °C of annealing, whereas its physical properties are changing slightly. The high-temperature oxidation mechanism for the studied SHS rods has been found to be similar to the nickel-based heat-resistant alloys, exhibiting the oxidation rate in the range of 0.65-1.05 g/m²* h at 900 °C, depending on the carbides and intermetallic contents. For the samples in study, a monotonous increase of the electrical resistivity with temperature was observed. The reported results can be useful for the potential high-temperature application of such rods, especially as the electrodes for aluminum electrowinning process.

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