

Features of phase formation at the interfaces of structural elements in multi-component ceramics based on Ti–Al–C

Yu.I.Boyko, V.V.Bogdanov, R.V.Vovk, V.F.Korshak

V.Karazin Kharkiv National University, 4 Svobody Sq.,
61022 Kharkiv, Ukraine

Received June 10, 2019

The paper analyzes the features of the MAX phases formation in the Ti–Al–C system; in particular, the possibility of thin layers of the amorphous phase (Ti–Al) forming on the surface of the TiC grains is discussed. Such layers cause increased crack resistance of ceramic materials based on MAX phases such as Ti_2AlC , Ti_3AlC_2 , $TiAlC_2$, which are therefore durable and suitable for use as the basis for the manufacture of implants in medicine and biology.

Keywords: multi-component ceramics, MAX-phases, liquid-phase sintering, crack resistance.

Проаналізовані особливості процесу формування МАХ-фаз в системі Ti–Al–C, в частности, обговорюється можливість утворення на поверхні зерен TiC тонких шарів аморфної фази (Ti–Al), обумовлюючих підвищену тріщиностійкість керамічних матеріалів на основі таких МАХ-фаз, як Ti_2AlC , Ti_3AlC_2 , $TiAlC_2$, являючихся в силу цього зносостійкими і придатними для використання в якості основи для виготовлення ендопротезів і імплантів в медицині та біології.

Особливості фазоутворення на межах розділу структурних елементів у полікомпонентній кераміці на основі Ti–Al–C. Ю.І.Бойко, В.В.Богданов, Р.В.Вовк, В.Ф.Коршак.

Проаналізовано особливості процесу формування МАХ-фаз в системі Ti–Al–C, зокрема, обговорюється можливість утворення на поверхні зерен TiC тонких шарів аморфної фази (Ti–Al), які обумовлюють підвищену тріщиностійкість керамічних матеріалів на основі таких МАХ-фаз, як Ti_2AlC , Ti_3AlC_2 , $TiAlC_2$, які є через це зносостійкими і придатними для використання як основи для виготовлення ендопротезів і імплантів в медицині та біології.

1. Introduction

Currently, many researchers are focused on the synthesis and study of the properties of layered polycomponent compounds, i.e., ceramic materials characterized by the presence of structural elements (grains, refractory inclusions, etc.) separated by layers of different phases. The functional properties of these materials substantially depend on their phase composition [1]. A typical example of such compounds of great practical interest are materials based on the so-called MAX phases [2, 3].

MAX phases are the ternary layered compounds of various stoichiometric composition, described by the general chemical formula: $M_{n+1}AX_n$ ($n = 1, 2, 3...$), where M — 3d transition metal (Ti, Zr etc.), A — p-element (for example, Al, Si, Ge and etc.), X — carbon or nitrogen (C, N). These compounds have unique mechanical, thermal and electrical properties, combining the properties of both metals and ceramic materials. They are thermo- and crack-resistant, have high thermal and electrical conductivities, have a lower modulus of elasticity, and are also

very resistant to corrosion in various chemically aggressive environments.

Among the many MAX phases, the most famous and widely used in practice as their typical representative are the phases based on titanium, aluminum and carbon: Ti_2AlC , Ti_3AlC_2 , $TiAlC_2$. In this article, using the example of this compound, the features of the phase formation process are discussed, which ultimately determine the unique physical properties of this material, in particular, its increased crack resistance. This property determines the possibility of using this material in practice in medicine and biology for the manufacture of deterioration-resistant implants. In this regard, the study of the phase formation process and, accordingly, of the properties of ceramic material based on this compound is a very urgent task of modern materials science.

Synthesis of ceramics based on MAX phases, as a rule, is carried out by the traditional method of high-temperature isostatic pressing of a mixture of powders with the certain ratio of components. In addition to this method, the sintering method has also been used recently by passing pulses of high-ampere electric current through a powder billet (the electroconsolidation method) [4].

An important feature of the MAX phases formation process by these methods is that it occurs in stages. In the first stage, when the temperature ~ 1350 – 1500°C reaches, titanium interacts with carbon and aluminum, forming the refractory phase in the form of crystal grains of titanium carbide TiC and thin layers of the liquid phase $Ti-Al$, surrounding specified grains. With further cooling of the material crystallization (or solidification) of the melt occurs at the grain boundaries of TiC , accompanied by the formation of various crystalline (or amorphous) phases differing in stoichiometric composition. In this case, the phase formation process under these conditions is very complicated from the point of view of classical thermodynamics. This is due to the fact that as the thickness of the liquid layer decreases in the process of solidification, upon reaching of the nanometer size range (~ 10 – 100 nm) there are significant changes in the energy and boundary conditions that determine the process of phase formation. Firstly, in the ultra-thin layers, the surface and volume energies of the layer are comparable values, which causes a change in the thermodynamic equilibrium conditions of the phase formation process [5]. Secondly,

the phases formation in this case occurs on the surface of the grain, the lattice parameter of which is significantly different from the lattice parameters of the forming phases. The requirement of lattice parameters matching at the interface causes the appearance of a density gradient of the forming phase material, which is also accompanied by a change in the free energy value of the system and, accordingly, of the thermodynamic equilibrium conditions [6].

Accounting for both of these factors leads to the fact that in the specific conditions it is possible formation of phases that don't exist in massive samples of identical chemical composition at the same temperature. It is very important that in the case under discussion, when phases are forming it becomes possible to form not only different crystalline phases, but also an amorphous phase, that is, a phase characterized by a disordered arrangement of atoms [6].

This paper is devoted to the analysis of the features of the MAX phases formation in the system $Ti-Al-C$, in particular, the possibility of an $(Ti-Al)$ amorphous phase forming on the surface of TiC crystal grains is discussed. In our opinion, the presence of such a phase causes an increased crack resistance of the material under study.

2. Features of the phase formation process on the surface of TiC refractory crystal grains in the $Ti-Al-C$ system

In the case of MAX phases formation of the $Ti-Al-C$ system, on the surface of the crystalline grains of the refractory TiC compound, immersed in the $(Ti-Al)$ melt layer at the initial stage, depending on the temperature and concentration of the components, various crystalline phases can form during crystallization: $TiAlC_2$, Ti_2AlC , Ti_3AlC , Ti_3AlC_2 [7]. In the investigated samples obtained by hot isostatic pressing of powders, as evidenced by X-ray analysis, the main phases are TiC and Ti_3AlC_2 . Wherein the Ti_3AlC_2 phase has a layered structure, in which the carbide Ti_3C_2 layers interconnected by very thin (≈ 10 nm) layers of aluminum ($Ti-Al$ connection). The presence of such a layered structural state in samples of this compound is confirmed by electron microscopic studies [8].

The presence of ultra-thin layers during the phases formation at the interfaces of structural elements, as already mentioned, from the thermodynamics point of view

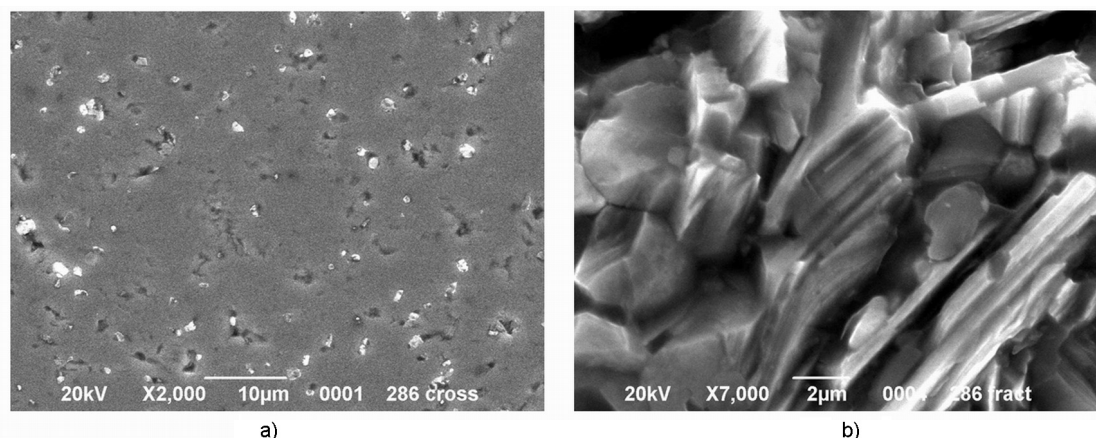


Fig. 1. The structure of ceramics based on MAX-phase (Ti-Al-C) system: a — SEM microsection picture, b — SEM sample break picture.

leads to realization of possibility of an amorphous phase formation of [6]. Specifically in this case, such an amorphous phase can be a phase based on (Ti-Al) [9].

This fact can cause responsible for the high fracture toughness of the ceramic material [10, 11]. Indeed, according to the theoretical calculations described in the paper [6], taking into account the previously mentioned specific conditions of the phase formation process, critical layer thickness, upon reaching which it is possible to form not crystalline, but amorphous phase, can be estimated using the following relation:

$$d^* \approx 2 \frac{a_{cr}^6}{|a_0^6 - a_{cr}^6|} \sqrt{3 \frac{\alpha_{cr}}{f_{cr}} \left[\left(\frac{a_0}{a_{cr}} \right)^3 - 1 \right]}. \quad (1)$$

Here a_0 — parameter of crystal lattice of the grain, on the surface of which the phase formation process takes place, (in our case it is a structural element in the form of a refractory crystalline phase TiC), a_{cr} — the lattice parameter of one of the possible crystalline phases forming in the layer surrounding the grain (TiAl, TiAl₂, TiAl₃ or Ti₃Al, see Fig. 1), α_{cr} — coefficient taking into account the dependence of free energy of the system on the density gradient at the "grain-forming phase" interface, f_{cr} — free energy density of the forming phase.

Parameter $(\alpha_{cr}/f_{cr})^{1/2}$ has dimension of length and is the characteristic distance at which the elastic deformation in a crystalline material decays. In order of magnitude, this parameter in crystalline materials is characterized by the value $\approx 10^{-7}$ m [12]. Substituting this parameter value, as well as the value $(a_0 - a_{cr})/a_{cr} \approx 0,1$, charac-

terizing the described compound, in the formula (1), we have the estimate: $d^* \approx 10$ nm.

Thus, in the ultra-thin layer (Ti-Al) on the surface of the TiC grains during the formation of the MAX phases in the system Ti-Al-C the formation of layers of the amorphous phase separating the indicated structural elements is very likely. The conclusion is confirmed by the experimental results presented in Fig. 1. The structural state and phase composition of the samples were controlled by scanning electron microscopy (SEM) and X-ray diffraction.

From Fig. 1 it follows that the main structural elements of the studied material are grains surrounded by different phases. X-ray data [11] indicate the presence of the following crystalline phases: TiC, Ti₃AlC and Ti₃AlC₂. Other possible equilibrium crystalline phases, for example: TiAl₃, TiAl₂, Ti₃Al and TiAl, as indicated by X-ray diffraction [11] are absent. This result is in accordance with the above conclusion about the formation of the amorphous phase (Ti-Al) in a thin layer directly on the surface of the crystal grains of titanium carbide TiC.

The indicated structural state and specific phase composition of the studied Ti-Al-C ceramics cause its increased crack resistance. Indeed, high brittleness of materials (tendency to cracking under the influence of mechanical stress), including ceramics, due to their crystalline structure, i.e. to the presence of long range order in atomic arrangement [13]. Crack propagation occurs along the so-called "cleavage plane", formed by ordered atoms. Due to the presence of amorphous interlayers, the mechanical damage (cracks) is localized within individual grains in the ceramic material under investigation and, therefore, its structural and

phase condition is unfavorable for the development of macroscopic damage in general, i.e. this material is crack resistant. This fact is confirmed by the experimental data obtained by us on the value of the coefficient characterizing the crack resistance of the studied material: $K \approx 7,4 \text{ MPa}\cdot\text{m}^{1/2}$ [11].

3. Conclusion

The studied ceramic material based on the MAX-phase of the Ti–Al–C system is characterized by high crack resistance and, therefore, is durable and applicable as a basis for the production of implants in medicine and biology.

This unique property of the material studied is due to the peculiarities of the structural state and specific phase composition, characterized by the presence of ultrathin ($\approx 10 \text{ nm}$) amorphous (Ti–Al) layers on the surface of the crystalline grains of titanium carbide TiC. Amorphous layers localize microcracks within the grains and prevent their growth, i.e. transformation into macroscopic defects causing material destruction.

References

1. P.H.Shingy, B.Huang, S.R.Nishitani, S.Nasy, *Trans. Jap. Inst. Metals*, **29**, 3 (1988).
2. M.W.Barsoum, *Prog. Solid State Chem.*, **28**, 201 (2000).
3. M.W.Barsoum, M.C.Flemings, E.J.Kramer et al., in: *Encyclopedia of Materials Science and Technology*, Elsevier, Amsterdam (2006).
4. E.S.Gevorkyan, V.O.Chishkala, M.V.Kislitca, *Sb. Nauchnyh Trudov UkrDUZT*, **160**, 75 (2016).
5. V.M.Apalkov, Yu.I.Boyko, V.V.Slezov, *Z. Metallkunde*, **94**, 1162 (2003).
6. V.M.Apalkov, Yu.I.Boyko, V.V.Slyozov, *Vestnik KhNU, Ser. Fizika*, **476**, 59 (2000).
7. M.P.Slavinskij, *Fiziko-himicheskie Svoystva Elementov*, Nauch. Tehn. Izdatelstvo po Chernoj i Cvetnoj Metallurgiyi, Moscow (1952) [in Russian].
8. A.A.Smetkin, Yu.K.Majorova, *Vestnik PNIPU*, **17**, 120 (2015).
9. N.P.Lyakishev (red.), *Diagrammy Sostoyaniya Dvojnyh Metallicheskih System*, Mashinostroyeniye, v.1, 225 (1996) [in Russian].
10. Yu.I.Boyko, *Vestnik KhNU, Fizika*, **962**, 54 (2011).
11. Yu.I.Boyko, V.V.Bogdanov, R.V.Vovk et al., *Functional Materials*, **25**, 708 (2018).
12. S.P.Timoshenko, Dz.Gud'yer, *Teoriya Uprugosti*, Nauka, Moscow (1979) [in Russian].
13. V.M.Phinkel, *Fizika Razrusheniya, Metallurgiya*, Moscow (1970) [in Russian].