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Elastic properties of ceramics based on Ti_3AlC_2 MAX phase

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The unique mechanical properties of ceramics based on MAX phases (high hardness, thermal and crack resistance combined with the possibility of plastic deformation) make it a widely used multifunctional material. Therefore, the study of its elastic properties, i.e., obtaining information about the value of elastic constants: Young's modulus and Poisson's ratio, is very actual. The values of these constants in a ceramic material substantially depend on the stoichiometry and chemical composition of its phases, as well as on the structure of the material. In particular, in the process of its synthesis by isostatic pressing, crystalline grains of the main phase are formed, inclusions of the initial or secondary phases appear, and a certain number of different voids are formed: isolated pores, their clusters (capillaries), microcracks, etc. These structural elements cause a significant heterogeneity of ceramics, which leads to a change in many physical properties of this material, including elasticity. As a result, the numerical values of the elastic constants of the ceramic material differ distinctly from the values of similar constants characterizing the initial components from which the MAX phase is formed.

The paper presents the results of the effective elastic constants characterizing ceramics based on the Ti_3AlC_2 MAX phase study. It is shown that the elastic modulus of the ceramic material is characterized by the value exceeding ≈2,5 times the elastic modulus value of the studied phase material itself and reaches the value of ≈ 320 GPa. The observed change in the elastic modulus is due to the heterogeneity of the ceramic material structure and is caused by the presence of hard TiC phase inclusions in it. This conclusion is confirmed by varying the content of TiC phase inclusions in the composition of the MAX phase Ti_3AlC_2.

Keywords: ceramics, MAX phases, mechanical properties, elastic modulus.

Пружні властивості кераміки на основі MAX-фази Ti_3AlC_2

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Унікальні механічні властивості кераміки на основі MAX-фаз (висока твердість, термо- і тріщиностійкість в поєднанні з можливістю пластичної деформації) роблять її широко використовуваним багатофункціональним матеріалом. Тому дослідження її пружних властивостей, тобто отримання інформації про величину пружних констант: модуля Юнга і коефіцієнта Пуассона, є дуже актуальним. Значення цих констант в керамічному матеріалі істотно залежать від стехіометрії та хімічного складу фаз, що утворюються, а також від структури матеріалу. Зокрема, в процесі його синтезу методом ізостатичного пресування під тиском формуються кристалічні зерна основної фази, виникають включення вихідних або другорядних фаз, а також утворюється певна кількість різних порожнеч: ізольованих пор, їх скупчень (капілярів), мікротріщин та ін. Ці структурні елементи обумовлюють істотну неоднорідність кераміки, що призводить до зміни багатьох фізичних властивостей цього матеріалу, в тому числі пружності. Як наслідок, числові значення пружних констант керамічного матеріалу помітно відрізняються від значень аналогічних констант, що характеризують вихідні компоненти, з яких формується MAX-фаза.

В роботі представлені результати дослідження ефективних пружних констант, що характеризують кераміку на основі MAX-фази Ti_3AlC_2. Показано, що пружний модуль керамічного матеріалу характеризується значенням, що перевищує у ≈2,5 рази значення модуля пружності власне речовини досліджуваної фази і досягає величини ≈ 320 GPa. Виявлену зміну модуля пружності пов'язано з неоднорідністю структури керамічного матеріалу і обумовлено наявністю в ньому жорстких включень фази TiC. Цей висновок підтверджується при варіюванні вмісту включень фази TiC в складі MAX-фази Ti_3AlC_2.

Ключові слова: кераміка, MAX-фази, механічні властивості, пружний модуль.

Упругие свойства керамики на основе MAX-фазы Ti_3AlC_2

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Уникальные механические свойства керамики на основе MAX-фаз (высокая твердость, термо- и трещиностойкость в сочетании с возможностью пластической деформации) делают ее широко используемым многофункциональным материалом. Поэтому исследование ее упругих свойств, т. е. получение информации о величине упругих констант: модуле

Юнга и коэффициенте Пуассона, является весьма актуальным. Значения этих констант в керамическом материале существенно зависят от стехиометрии и химического состава образующихся его фаз, а также от структуры материала. В частности, в процессе его синтеза методом изостатического прессования под давлением формируются кристаллические зерна основной фазы, возникают включения исходных или второстепенных фаз, а также образуется определенное количество различных пустот: изолированных пор, их скоплений (капилляров), микротрещин и др. Эти структурные элементы обусловливают существенную неоднородность керамики, что приводит к изменению многих физических свойств этого материала, в том числе и упругости. Как следствие, численные значения упругих констант керамического материала заметно отличаются от значений аналогичных констант, характеризующих исходные компоненты, из которых формируется MAX-фаза.

В работе представлены результаты исследования эффективных упругих констант, характеризующих керамику на основе MAX-фазы Ti_3AlC_2. Показано, что упругий модуль керамического материала характеризуется значением, превышающим в ≈2,5 раза значение модуля упругости собственно вещества изучаемой фазы и достигает величины ≈ 320 GPa. Обнаруженное изменение модуля упругости связано с неоднородностью структуры керамического материала и обусловлено наличием в нем жестких включений фазы TiC. Этот вывод подтверждается при варьировании содержания включений фазы TiC в составе MAX-фазы Ti_3AlC_2.

Ключевые слова: керамика, MAX-фазы, механические свойства, упругий модуль.

1. Introduction

MAX-based ceramics is a widely used multifunctional material [1] – [4]. This material belongs to the class of ternary refractory compounds with variable stoichiometry, which are described by the general chemical formula: $M_{n+1}AX_n$. Here M is the 3d transition metal (for example, Ti, Zr, etc.), A is the p-element of the 3A or 4A subgroup of the periodic system (for example, Al, Si, etc.), X is carbon (C) or nitrogen (N). Intensive studies of properties, as well as study of practical use possibility of ceramic materials based on these phases, began in the early 2000s and are very relevant to the present (see [5] – [7], etc.). Interest in these materials, in particular, in the Ti_2AlC_3 compound, is due to the specific physical properties of this class of matter: on the one hand, they are characterized by high hardness, by increased thermal and crack resistance, and on the other hand, under certain conditions, they are easily amenable to plastic deformation. The latter fact greatly simplifies the process of machining this material in the making of products of complex geometric shape. In addition, these materials have significant thermal and electrical conductivity, which is not characteristic of traditional ceramic materials [8].

An important aspect of these materials properties studying is the study of their elastic properties, that is, information obtaining about the magnitude of elastic constants: Young's modulus and Poisson's ratio. The values of these constants in the considered compounds substantially depend on the stoichiometry and chemical composition of the resulting phases, as well as on the structure of the material. In particular, in the process of ceramic materials synthesis, crystalline grains of the main phase are formed, in certain conditions there are inclusions of initial or secondary phases, and some voids are formed (isolated pores, their aggregations (capillaries), microcracks, etc.). These structural elements cause a significant heterogeneity of ceramics, which leads to a change in many physical properties of this material, including its elasticity. As a result, the values of the elastic constants of the ceramic material are distinctly different from the values of the analogous constants characterizing the initial components of which the MAX phase is formed. The elastic properties of ceramics are described by the effective values of the corresponding constants. [9] – [11].

This paper presents the results of the effective elastic constants study characterizing ceramics based on the Ti_3AlC_2 MAX phase. In recent years, this material, as an alternative to metals (Ti), (Ni) and their alloys, has been used for medical and biological purposes for the various types of endoprostheses and bone implants production. In this regard, the study of the elastic properties of this material is an actual problem not only from a scientific, but also from a practical point of view.

2. Experiment and Results

Investigated Ti_3AlC_2 MAX phase samples were obtained by isostatic pressing under 30 MPa at the temperature of 1350ºC of titanium carbide (TiC) and aluminum (Al) powders mixture with the corresponding molar ratio of the components. The size of the powders in the initial state was characterized by a range of values ≈ 2 ÷ 10 mkm. The exposure time under pressure in the process of the samples pressing was 30 minutes. The samples prepared for the study had the shape of parallelepipeds with the sizes of 6×4×4 mm. The phase composition of the samples was controlled using x-ray analysis, and their structural state was studied by optical and electron microscopy (see Fig. 1 and Fig. 2). To measure the values characterizing the elastic properties of the studied material, we used the method of measuring the longitudinal and transverse elastic (reversible) deformation of the sample (ε) under conditions of uniaxial compressive stress (σ). The load was controlled using a pre-calibrated dial gauge, and the deformation was measured using a special electronic device that allows you to record the change in the relative sample size with an accuracy of $\approx 5 \cdot 10^{-6}$ [12].

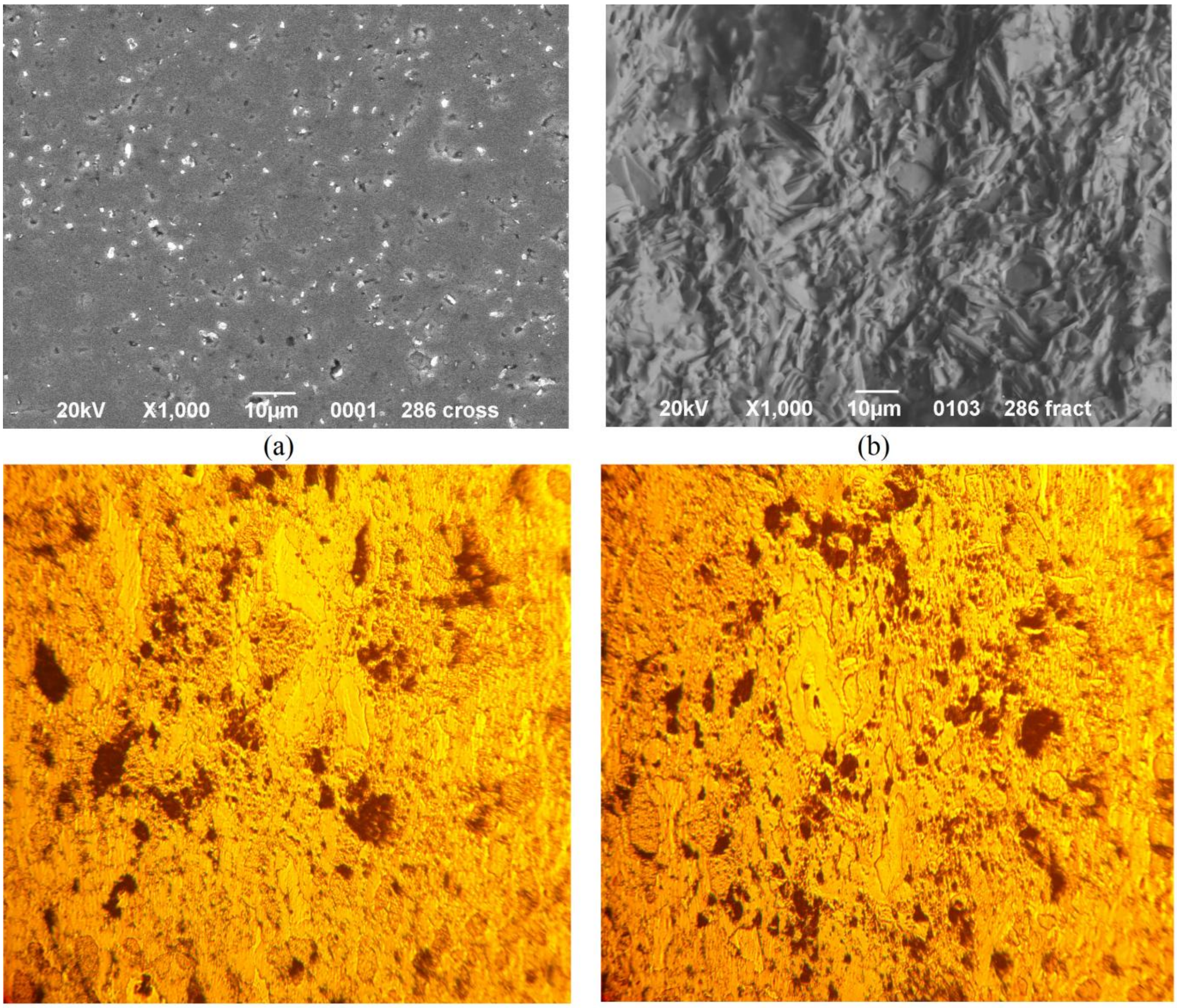
The quantitative values of the effective elastic constants of the material under study, measured at room temperature, were as follows: the elastic modulus $E \approx 200$ GPa (with uniaxial load of 250 mN), and the Poisson's ratio $\upsilon \approx 0{,}2$. The X-ray analysis of studied samples chemical composition showed that they consist of the following phases (weight %): $89Ti_3AlC_2 + 11TiC$. The density of the ceramic material under study (ρ), measured by weighing the sample and then normalizing its mass to a unit volume, turned out to be $\approx 3{,}98$ g/cm^3.

Note that according to the literature data, the x-ray density (density of the substance itself) of the MAX phase (Ti_3AlC_2) and titanium carbide (TiC) are characterized respectively by the values: $\approx 4{,}2$ g/cm^3, $\approx 4{,}92$ g/cm^3, and the elastic constants of the same substances are characterized by the following values: MAX-phase: $E_0 \approx 140$ GPa , $\upsilon \approx 0{,}2$; titanium carbide: $E_0 \approx 450$ GPa, $\upsilon \approx 0{,}18$ [13].

Let us discuss the results obtained and try to find out the reasons for the effective values of the elastic constants of the material under study observed in the experiment.

3. The calculated values of the effective elastic constants of the material under study and their comparison with experimental data

In the general case, the real structure of polycomponent ceramics, including ceramics based on MAX phases, is characterized by the presence of microcrystals (grains) of the main phase, as well as by formation of a certain number of inclusions of accompanying (minor) phases. In addition, the presence of free volume in the form of individual pores or their aggregations (hollow channels), microcracks, etc. is characteristic of a ceramic material. The theoretical analysis and calculation of the effective elastic constants of the medium containing various kinds of



(a) (b)

(c) (d)

Fig. 1. The typical structures of the studied ceramic Ti_3AlC_2 MAX-phase material a) and б) – SEM snapshots, c) and d) – optical images.

inhomogeneities was carried out in the works [9] – [11]. So, for a porous medium in the case of a uniaxial load, according to the calculations made in [9], the value of the effective modulus of elasticity E is described by the following relation:

$$E = E_0\,(1 - \varphi). \qquad (1)$$

Here E_0 is the elastic modulus of matter without voids, φ is the porosity, i.e. a parameter characterizing the fraction of the volume of the medium occupied by voids:

$$\varphi = (V_к - V_м) / V_к. \qquad (2)$$

$V_к$ is the ceramics volume (medium containing voids), $V_м$ is the actual material volume without voids. Easy to make sure that $\varphi = (1 - \rho/\rho_0)$, were ρ and ρ_0 are respectively, the real and x-ray density of the substance of the ceramic material.

Thus, from (1) and (2) it follows that the effective modulus of elasticity of the medium containing voids should be described by the following relation: $E = E_0(\rho/\rho_0)$. At the same time, according to the calculations, the change in Poisson's ratio in the interval of $\upsilon_0 \approx (0{,}1 \div 0{,}3)$

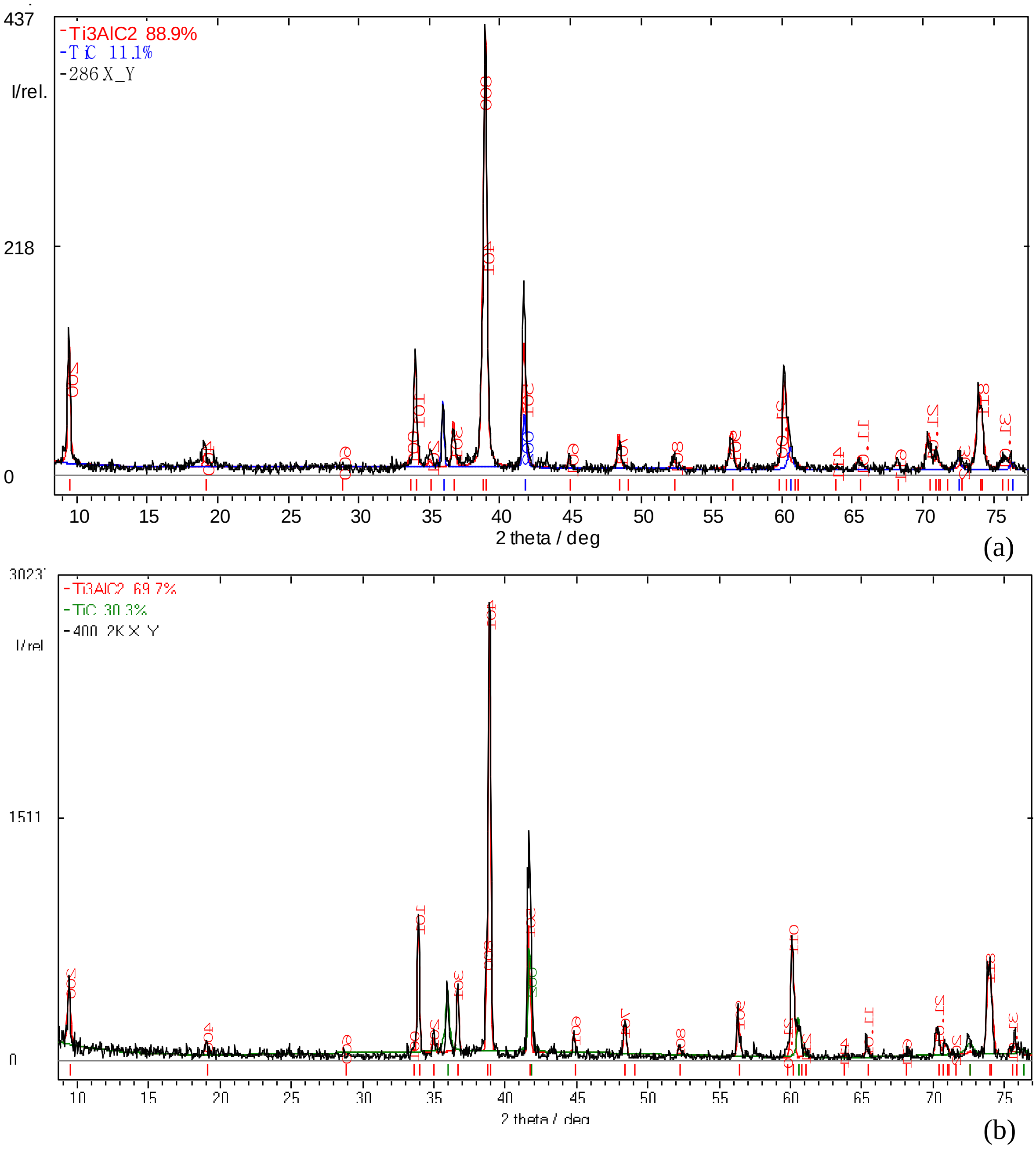


Fig. 2. X-ray diffractograms of the material under study: a) – Ti_3AlC_2 89 mass%, TiC 11 mass%; b) – Ti_3AlC_2 69 mass%, TiC 31 mass%.

practically does not affect the value of E [9]. In addition, the Poisson's ratio of the porous medium practically does not change with increasing porosity of the medium up to $\varphi \approx 0,5$.

In the case when the ceramic material is characterized by the presence of hard inclusions, i.e., inclusions that have a significantly larger elastic modulus compared to the main phase, the effective elastic modulus is described by the ratio:

$$E = E_0 \, exp\,(2,5\Omega). \quad (3)$$

Here $\Omega = (4\pi/3)\cdot N\cdot r^3$, were r is average radius of hard spherical inclusions, N is number of inclusions per unit volume of medium. The Ω parameter characterizes the fraction of the volume occupied by hard inclusions in an inhomogeneous medium. [11].

Thus, from the above relations (1) and (3), it follows that the elastic modulus of the medium containing voids and hard inclusions should decrease with increasing porosity and increase with increasing volume of hard inclusions. The presence of these structural elements (voids and hard inclusions), practically does not lead to a change in the Poisson's ratio [9] – [11].

In our studies, the experimentally measured quantity $\rho/\rho_0 \approx 0,94$ and, therefore, the calculated value of the effective elastic modulus E, taking into account the presence of voids in the material under study, in accordance with (1), should be characterized by ≈ 130 GPa. In reality, the experiment observed the value: E ≈ 200 GPa. This result indicates that in the material under study, the change in the value of E is primarily due to the presence of a certain number of hard inclusions. To confirm the correctness of the conclusion we made the following control experiment. By slightly changing the molar ratio of the initial components and the sintering regime, we prepared a ceramic sample based on the Ti_3AlC_2 MAX phase with the same porosity as the original samples ($\varphi \approx 0,16$), however, it contained a significantly larger amount of titanium carbide inclusions.: 69 mass % Ti_3AlC_2 + 31 mass % TiC (see. Fig. 2b). Measurements have shown that for this ceramic material the Poisson's ratio has not changed much ($\upsilon \approx 0,2$) , and the magnitude of the elastic modulus increased to E ≈ 320 GPa. If we now take into account the correction related to the effect of porosity on the elastic modulus of the sample under study (ratio 1), then the effective value of E should be characterized by the value ≈ 340 GPa , i.e. $E/E_0 \approx 2,4$. Accordingly, if only the presence of hard inclusions is taken into account, then from the relation (2) it follows that the parameter $(2\pi\,\Omega) \approx 1$, i.e. the fraction of the hard inclusions volume Ω in the sample under study is ≈0,15. The values obtained in our control experiment E/E_0 and Ω correspond to the values of these parameters, observed in special model experiments, in which the elastic properties of an inhomogeneous medium containing hard inclusions were studied [11]. Thus, the results of our control experiment indicate that in the material under study the change in the elastic modulus is mainly due to the presence of hard inclusions.

Conclusions

Our studies suggest that the elastic modulus of a ceramic material based on the Ti_3AlC_2 MAX phase characterized by a value exceeding in ≈2,5 times the value of the elastic modulus of the studied phase substance and reaches ≈ 320 GPa.

This change in the modulus of elasticity is due to the heterogeneity of the ceramic material structure, which is caused by the presence of hard inclusions of the TiC phase.

The presence of voids and hard inclusions has almost no effect on the value of the Poisson's ratio of the material under study. $\upsilon \approx 0,2$.

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