

Creep of the Ti_3AlC_2 MAX-phase ceramics

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The process of plastic deformation of multicomponent ceramics based on the MAX phase at room temperature and at higher (1000°C) temperature has been studied by dilatometry and microindentation. Based on the experimentally obtained dependence of the strain rate of the material on the magnitude of the applied load, conclusions were made about the mechanisms controlling the plastic deformation process in the samples under study.

Keywords: crystal creep, MAX phases.

Методами дилатометрії і мікроіндентування досліджено процес пластичної деформації полікомпонентної кераміки на основі МАХ-фази при кімнатній і більш високій (1000°C) температурі. На основі отриманої в експерименті залежності швидкості деформації матеріалу від величини прикладеної навантаження зроблено висновки про механізми, які контролюють процес пластичної деформації у досліджених зразках.

Повзучість (високотемпературна пластична деформація – "сгреп" кераміки МАХ-фази Ti_3AlC_2 . *Ю.І.Бойко, В.В.Богданов, Є.С.Геворкян, Р.В.Вовк, В.Ф.Коршак, В.А.Колесніченко.*

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1. Introduction

In modern materials science, special attention is paid to obtaining and using for many technical purposes of ceramic materials based on the so-called MAX phases. These materials belong to the class of ternary refractory compounds with varying stoichiometry and are described by the general chemical formula $M_{n+1}AX_n$, where M is the 3d transition metal, A is the p-element, X is carbon (C) or nitrogen (N).

Intensive research and practical use of such ternary compounds began in the early 2000s and are relevant to the present [1–4]. It was found that the MAX phases are characterized by a layered hexagonal crystal structure in which carbide or nitride blocks of close-packed octahedra $[M_{n+1}X]$ are separated by thin layers of atoms of the element A. Due to this specific structure, these materials have properties that combine both the properties of metals and the properties

of ceramics. In particular, materials based on MAX phases are characterized by unique mechanical properties: on the one hand, they have a high plasticity, like metals, on the other hand, they are characterized by high resistance to fracture (increased crack resistance), which is typical for multicomponent ceramics. The rather high plasticity of MAX phases at room temperature makes them easy to machine, which makes it possible to manufacture from these materials various products of complex geometric shape, used, in particular, in medicine (bone endoprostheses, implants, etc.).

An important aspect in the study of the properties of MAX phases is the study of the plastic deformation of this material as a result of the prolonged action of an external load at room and higher temperatures (the study of the creep process).

The study of the matter transport mechanisms during plastic deformation of materials with complex chemical and phase composition, as well as characterized by the presence of various types and sizes of structural elements, is one of the most actual problems of modern materials science.

This paper presents the results of a study of the process of plastic deformation of ceramics based on concrete MAX phase at ambient and higher temperatures under conditions of variation in the exposure time and the magnitude of the external load acting on the sample. The choice of such a research object is associated with its use as the basic material for the production of bone implants and endoprostheses in medicine.

The obtained experimental data on the rate of plastic deformation under the action of varying external load used to determine the mechanisms that control the matter transport in the material at various temperatures.

2. The possible mechanisms of plastic deformation of polycomponent materials

Polycomponent ceramic materials, as a rule, are characterized by the presence of crystalline elements (grains) from the material of the main phase in the form of solid precipitates. These precipitates can be realized either in the form of grains of a very small size of $\approx 1-10^2$ nm (nano-structured materials), or in the form of isomeric or shapeless solid inclusions with a size of $\approx 1-10$ μ m. In addition, at the initial stage of

the compacting process of ceramics (sintering), the boundaries of an extraneous phase often form in the form of liquid interlayers, which later turn into amorphous (non-crystalline) layers between the grains. Finally, such materials are characterized by the presence of voids in the form of pores or microcracks.

Depending on the chemical composition, structural state, as well as on the parameters of the deformation mode (temperature, magnitude of the applied load, loading method, etc.), multicomponent ceramic materials are characterized by the wide range of mechanical properties. For example, they may have such a unique property as "superplasticity", i.e. the ability to deform like rubber or liquid and, on the contrary, they can be characterized by increased strength (significant crack resistance), that is, the ability to resist plastic deformation up to destruction.

At high temperatures (much higher than room temperature) the diffusion of atoms is the limiting mechanism determining the matter transport in crystalline materials. However, due to the presence of precipitates (inclusions) of various phases, as well as due to the participation of grain boundaries, amorphous layers, etc. in the mass transfer process, the kinetic regularity that characterize the plasticity of the material can be very different.

The general equation describing the deformation rate of the crystalline material of a polycomponent composition and characterized by a complex structural state has the form:

$$d\varepsilon/dt = A\sigma^n(1/d)^m \exp(-Q/kT). \quad (1)$$

Here A is a numerical coefficient, σ is the effective stress, d is the characteristic size of the main structural element (grain), Q is the activation energy of the process that controls creep, k is the Boltzmann constant, n , m — exponents, the values of which depend on the specific mechanism of deformation, changing in the interval $\approx 1-10$ and $0-3$, respectively. If, for example, diffusion of atoms is the controlling mechanism of matter transport, the value of the index $m = 2$ for lattice diffusion (in the volume of the crystal grain) (Nabarro-Herring mechanism) and $m = 3$ (Koble mechanism) in the case when the process controls by the diffusion of atoms along the grain boundaries. In both of these mechanisms, the index $n = 1$. Accordingly, for these cases, equation (1) takes the form:

Table. Mechanisms of matter transport in the process of plastic deformation of materials characterized by different structural state, phase and composite state. n — stress exponent value σ , m — exponent grain size values d , D_v — diffusion coefficient in the volume of grain, D_b — diffusion coefficient in the boundaries between grains, GR — reaction of various point defects in the grain boundaries

The mechanism of matter transport	n	m	Controlling process
Diffusion Creep (Nabarro-Herring) [5, 6]	1	2	D_v
Grain boundary creep (Coble) [7]	1	3	D_b
Dislocation Creep (Ashby) [8]	3–8	0	D_v
Dislocation creep (Ashby-Ferral) [9]	2	1	D_b
Grain boundary sliding [10]	2	3	D_b
Grain boundary sliding [10]	2	2	D_v
Inclusions dissolution [11]	1	3	D_b
Inclusions dissolution [12]	3	1	GR
Viscous grain boundary "flow" (presence of amorphous phase) [13, 14]	1.5	1.7	GR
Viscous grain boundary "flow" (presence of liquid phase) [15]	2	1.2	GR

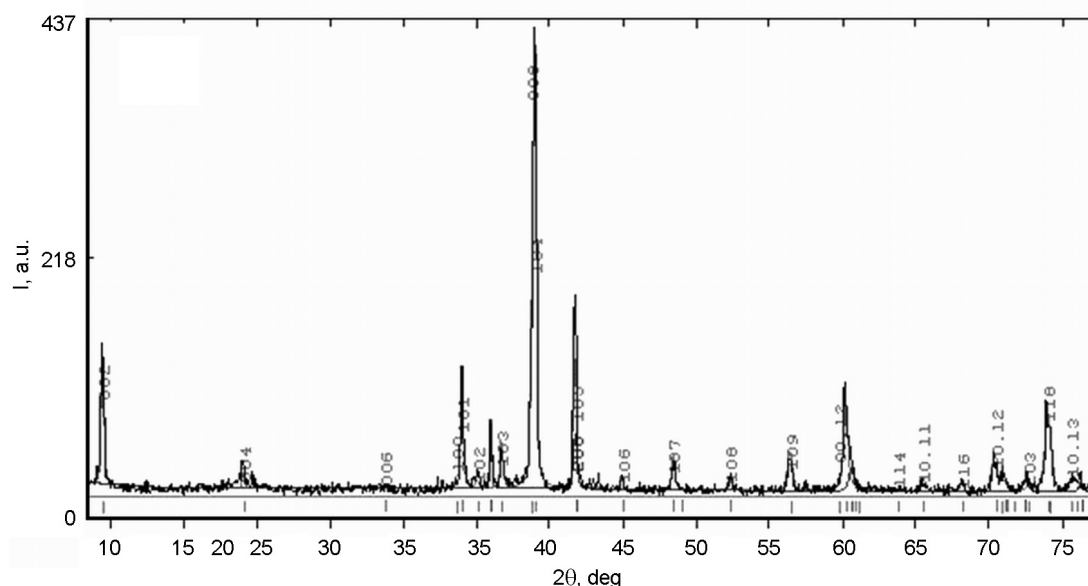


Fig. 1. Diffractogram of a ceramic sample based on the MAX phase, indicating the presence of two phases in it: Ti_3AlC_2 and TiC .

$$d\varepsilon/dt = D_{eff}\Omega\sigma(kTd^2), \quad (2)$$

where Ω is the atomic volume, D_{eff} — effective diffusion coefficient, defined as follows:

$$D_{eff} = B_1D_v + B_2\delta D_b/d. \quad (3)$$

Here D_v and D_b are the diffusion coefficients in the grain volume and in the grain boundary, δ is the width of the boundary between grains, B_1 and B_2 are numerical factors.

In addition to the above mechanisms of plastic deformation, there are also many other mechanisms that control the matter transport, affecting the magnitude of the

strain rate, and, accordingly, change character of the dependence $d\varepsilon/dt = f(\sigma, d, D_v, D_b)$. In particular, the mechanism of diffusion-dislocation slipping of grains is possible, the mechanism of the "viscous flow" of material with the participation of intergranular or interfacial liquid or amorphous interlayers (boundaries), etc. Table shows the theoretical values of the indices n and m , and also indicates the specific controlling mechanism of matter transport for various cases.

3. Experimental

Samples for the study were obtained by the method of hot isostatic pressing under pressure ≈ 30 MPa at the temperature $1350^\circ C$

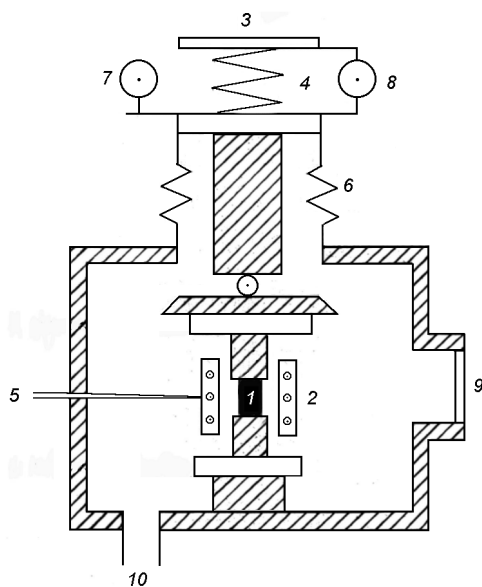


Fig. 2. Installation scheme for studying creep of ceramics based on MAX phase Ti_3AlC_2 : 1 — test sample; 2 — heater matrix; 3 — press up to 10 kN; 4 — calibrated spring; 5 — thermocouple; 6 — bellows; 7 — device that controls the change in sample size in the creep process; 8 — spring compression device; 9 — observation window; 10 — output to the pump.

of the mixture of powders (2–10 μm) of titanium carbide (TiC) and of aluminum (Al) with the required molar ratio of the components. The exposure time under pressure at the specified temperature during the preparation of the samples was ≈ 30 min.

As a result of the synthesis, ceramic samples were obtained based on the MAX phase of the following composition: 89 wt.% Ti_3AlC_2 + 11 wt.% TiC. The phase composition of the samples was controlled by X-ray diffraction (Fig. 1). The obtained samples had the shape of parallelepipeds of size $6 \times 4 \times 4$ mm³.

The high-temperature plastic deformation of the samples was studied by placing the sample in a special chamber (see Fig. 2), in which the sample is heated to a temperature $\leq 1000^\circ C$ under the action of a uniaxial load with its variation from zero to ≈ 10 kN, which corresponds to the stresses in the sample up to 500 MPa. As a parameter characterizing the plastic deformation of the sample, dimensionless dilatation $\epsilon = (h_0 - h)/h_0$ was taken, where h_0 and h are the initial and current sample heights. Measurements of the sample shrinkage ϵ were carried out depending on the exposure time under conditions of varying external load

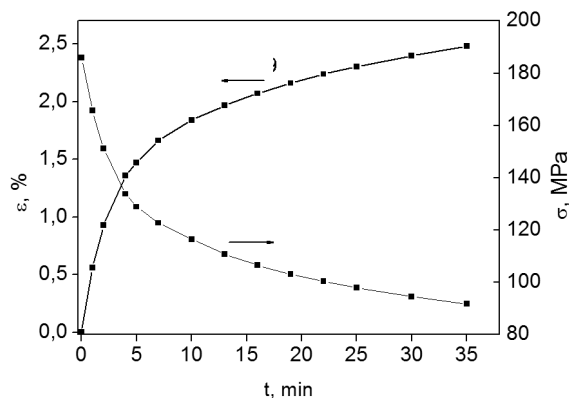


Fig. 3. Graphs of time dependence of relative deformation (ϵ) of sample of multicomponent ceramics based on Ti_3AlC_2 and of values of uniaxial compressive stresses acting in the sample at a temperature $1000^\circ C$.

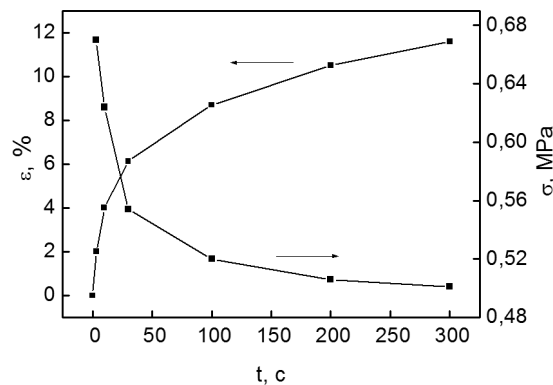


Fig. 4. Dependences on exposure time under load of the indenter of PMT-3 device of the relative deformation values (ϵ) of a ceramic material based on Ti_3AlC_2 and of the stresses (σ) acting in the sample under the indenter at room temperature. The load on the indenter ≈ 7 N.

on the sample. The temperature and the magnitude of the initial load were varied. All measurements were carried out in vacuum $\approx 10^{-2}$ mm Hg.

In the experiments at room temperature, the standard method of the microhardness value measuring was used, varying the exposure time at constant load on the Vickers indenter (PMT-3 microhardness tester). The change in the size of the forming footprint as a function of the exposure time at constant load was measured using an optical microscope. The value of the relative deformation of the material under the indenter was calculated by the formula $\epsilon = (d - d_0)/d_0$, where d is the current indenter footprint diagonal size, d_0 is the size of the footprint diagonal with minimum material load time (≈ 1 s). To calculate the magnitude of the

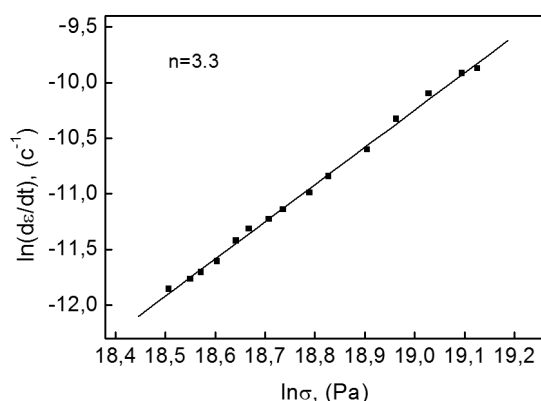


Fig. 5. Presented in Fig. 3 dependence of plastic strain rate $d\varepsilon/dt$ on the magnitude of the applied stresses σ in logarithmic coordinates. Index n in $d\varepsilon/dt \sim \sigma^n$ dependence is equal 3.3.

stresses acting on the material from the indenter, a formula to calculate the microhardness value was used: $\sigma \approx 0.189 P/d^2$, where P is the indenter load, d is the length of the diagonal of the residual indenter footprint.

4. Discussion

Figures 3 and 4 shows the data obtained in our experiments on the dependence of the relative deformation of samples ε on time with variations in the applied stresses and temperature. Figures 5 and 6 shows the results of the experimental results processing in double logarithmic coordinates of the plastic strain rate $d\varepsilon/dt$ vs. applied stresses σ . From the above data it follows that in our experiments, at different temperatures, in accordance with theory, regularity $d\varepsilon/dt \sim \sigma^n$ with different exponents: $n = 8$ (at room temperature) and $n \approx 3$ (at the temperature of 1000°C) is performed.

5. Conclusions

These results give reason to believe that the most likely mechanism for mass transport in the process of plastic deformation of the material at room temperature is dislocation creep (Ashby mechanism). At high temperatures ($\approx 1000^\circ\text{C}$) the creep process of the material under study is controlled by the mechanism of a viscous grain-boundary "flow" involving the dissolution of solid phase inclusions. Moreover, this process is limited by the reaction of point defects (va-

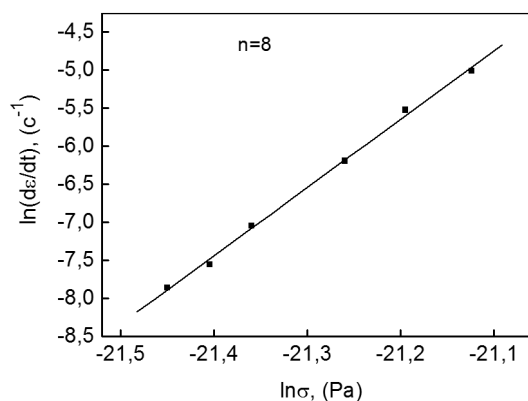


Fig. 6. Presented in Fig. 4 dependence of plastic strain rate $d\varepsilon/dt$ of the material under the indenter on the magnitude of the effective stresses σ in logarithmic coordinates. Index n in $d\varepsilon/dt \sim \sigma^n$ dependence is equal 8.

cancies) and linear defects (dislocations) directly at the boundaries of solid inclusions (see Table). The most likely solid "inclusions" of this type in the material under study are particles of refractory titanium carbide (TiC).

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