

Basic Properties of Fuel Determining its Behavior under Irradiation

I.I. Konovalov

Russia, Moscow 123060, Bochvar Institute (VNIINM), post box 369

The theoretical model describing a swelling of nuclear fuel at low irradiation temperatures is considered. The critical physical parameters of substances determining behavior of point defects, gas fission atoms, dislocation density, nucleation and growth of gas-contained pores are determined. The correlation between meanings of critical parameters and physical properties of substance is offered. The accounts of swelling of various dense fuels with reference to work in conditions of research reactors are given.

Introduction

The increase of volume of nuclear fuel under irradiation is caused by two basic processes - formation of two fission fragments with total volume more, than initial uranium atom, so-called "solid swelling", and formation of gas-vacancy porosity. Last process can proceed on two mechanisms: gas-driven and bias-driven.

The gas-driven mechanism assumes presence in fuel equilibrium bubbles and is supervised by absorption rate of fission gas atoms, basically Xe. The bias-driven swelling is supervised by absorption rate of vacancies by pores. As against the gas-driven mechanism the bias-driven mechanism results in the unlimited expansion of pore and can result in a catastrophic swelling.

For the theoretical description of a fuel swelling at low temperatures the DART-code [1] based on the gas-driven mechanism was offered.

During the further joint theoretical work of the Russian and American scientists the probability of some processes controlled by a superfluous flow of vacancies in a matrix, and opportunity of development of the undesirable phenomenon - vacancy swelling was found out. Some aspects of this problem are discussed in [2-4].

This paper is attempt to define under what irradiation temperature one may expect that or other mechanism of a swelling and to connect it with fundamental properties of fuel.

Density of gas-contained pores

Nucleation rate of bubbles on reaction $Xe + Xe + \text{vacancy}$ we shall define by expression

$$K_{nXe} = \alpha_{Xe} D_{Xe} C_v \frac{C_{Xe}^2}{2} \quad (1)$$

where: α_{Xe} is the coefficient taking into account radius r of interaction (merge) of two Xe atoms at the presence of vacancy, $r = 4\pi r / \Omega$ (Ω is the atomic volume), D_{Xe} is the diffusion coefficient of Xe, C_v is the vacancy concentration in a matrix, C_{Xe} is the Xe concentration in a matrix.

Rate of absorption of Xe atoms by already existing bubbles we shall define by expression

$$K_{aXe} = 4\pi R_p N_p D_{Xe} C_{Xe} \quad (2)$$

where: R_p and N_p are the bubble radius and its concentration accordingly.

Let's estimate the termination of nucleation process, when the probability of formation of a new bubble is significant less, than probability of Xe absorption by already existing bubbles. This condition we shall write down as $K_{aXe}/K_{nXe} = \eta$, where $\eta \gg 1$, or

$$\frac{K_{aXe}}{K_{nXe}} = \frac{4\pi R_p N_p}{\alpha_{Xe} C_v C_{Xe}} = \frac{\eta}{2} \quad (3)$$

At termination of bubble nucleation the Xe absorption rate by already existing bubbles prevails, and the expression for quasi-stationary Xe concentration has a view

$$C_{Xe} = \frac{K_{Xe}}{4\pi R_p N_p D_{Xe}} \quad (4)$$

where K_{Xe} is the generation rate of fission Xe atoms in relative shares.

For moderate irradiation temperatures, because of a practical immovability of vacancies and mobile interstitions, the equilibrium concentration of vacancies is determined by recombination, that is

$$C_v = \sqrt{\frac{K}{D_v \alpha_r}} \quad (5)$$

where: K is the generation rate of vacancies in relative shares, α_r is the recombination coefficient similar to α_{Xe} , D_v is the diffusion coefficient of vacancies.

The solving of (3) - (5) gives expression

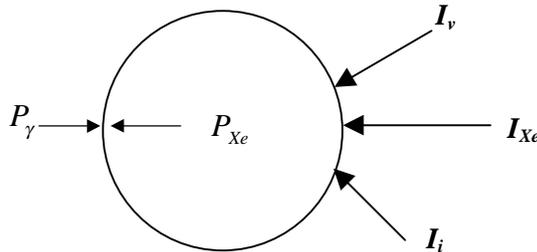
$$N_p = \left(\frac{\eta}{2}\right)^{1/2} \frac{1}{4\pi R_p} \left(\frac{\alpha_{Xe} K_{Xe}}{D_{Xe}}\right)^{1/2} \left(\frac{K}{D_v \alpha_r}\right)^{1/4} \quad (6)$$

The generation rate of vacancies and gas atoms are interconnected meanings and are function of fission rate: for uranium $K=10^{-18}G$ and $K_{Xe}=5.2 \cdot 10^{-24}G$, where G has dimension $\text{cm}^{-3}\text{s}^{-1}$.

The expression (6) becomes simpler at the assumption, that $\alpha_{Xe} \approx \alpha_r = \alpha$ and $R_p \approx r = \frac{\alpha \Omega}{4\pi}$, where $\alpha \approx 5.10^{16} \text{ cm}^{-2}$, $\Omega = 2.1 \cdot 10^{-23} \text{ cm}^3$. The meaning of η let's accept equal to 10.

Growth rate of gas-contained pore

The processes varying a volume of gas-contained pore at neglect of thermal vacancy evaporation is submitted on scheme.



The processes resulting in volume change of gas-contained pore

Index I designates the flows of defects of atomic level: vacancies, interstitions and fission gas atoms. Also in figure the "static forces" working on bubble are specified: surface energy P_γ and internal pressure of gas fission products P_{Xe} .

The increase of volume of gas-contained pore can be controlled by two mechanisms: by arrival of superfluous vacancies or arrival of fission gas atoms.

In case of the gas-driven mechanism, within the capillary model, the increase of bubble volume is connected with absorption of Xe atoms and "instant" transition in a new equilibrium state, determined by equality of P_γ and P_{Xe}

$$P_\gamma = \frac{2\gamma}{R_p} \quad (7)$$

$$P_{Xe} = \frac{n_{Xe}kT}{4\pi R_p^3/3 - b_{Xe}n_{Xe}} \quad (8)$$

where: γ is the surface energy, n_{Xe} is the number of Xe atoms in bubble, b_{Xe} is the Van-der-Vaals constant (for Xe $8.5 \cdot 10^{-23} \text{ cm}^3$).

The "instant" transition in a new equilibrium condition is caused by the fact that bubble under superfluous pressure begins "to draw" vacancies and "to push away" interstitions.

With increase of bubble radius the "constraining force" determined by a surface tension decreases, and the coming Xe atom occupies greater volume.

With accuracy of 10 % at equality (7) and (8) the following expression for volume occupied by one Xe atom in bubble is valid

$$V_{Xe} = b_{Xe} + 0.172 \sqrt{n_{Xe}^{3/2} kT / \gamma} \quad (9)$$

At the assumption that all Xe atoms are in bubbles (fairly for deep burnup), and their total output is $0.25B$, where B is the burnup expressed in number of splitted uranium atoms, we receive final expression for the gas-driven swelling S_g

$$S_g = 0.25B \left[b_{Xe} + 0.172 \left(\frac{0.25B}{N_p} \right)^{1/2} \left(\frac{kT}{\gamma} \right)^{3/2} \right] \quad (10)$$

Expression (10) for ideal gas at neglecting of b_{Xe} is transformed to the so-called kinetic law of "3/2" [5,6].

The swelling on the bias-driven mechanism is caused by an excess flow of vacancies due to absorption preference of interstitions by dislocations. The swelling rate in this case is determined by a difference between I_v and I_i .

Using some simplifications for moderate irradiation temperatures we receive the rate of bias-driven swelling

$$\mathcal{S}_v = \sqrt{\frac{KD_v}{\alpha_r} \cdot \frac{4\pi R_p N_p \rho_d (Z_i - Z_v)}{4\pi R_p N_p + \rho_d}} \quad (11)$$

where: ρ_d is the density of mobile dislocations, Z_i and Z_v are the efficiencies of interstition and vacancy absorption by dislocations.

At the assumption that dominant sinks are pores we simplify expression (11) and vacancy swelling determine as

$$S_v = \sqrt{\frac{KD_v}{\alpha_r}} \cdot \rho_d (Z_i - Z_v) \tau \quad (12)$$

where τ is the irradiation time.

Stationary density of mobile dislocations according to analytical accounts carried out by author on “loop-plane” model in dimension of cm^{-2} can be expressed

$$\rho_d = 10^{12} K^{1/6} \frac{D_v^{1/6}}{D_i^{1/3}} \quad (13)$$

where D_i - is the diffusion coefficient of interstitions.

Basic properties of fuel determining its swelling

The leading mechanism, gas or vacancy, depends on a parity of the swelling rates determined by (10) and (12).

Let's allocate temperature-dependent parameters of substance and its physical properties influencing the swelling.

With the account of (6) and (10) expression for the gas-driven swelling is

$$S_g = Const_1 \left[Const_2 + \left(\frac{D_{Xe}}{K} \right)^{1/4} D_v^{1/8} \left(\frac{kT}{\gamma} \right)^{3/2} B^{1/2} \right] B \quad (14)$$

With the account of (12) and (13) bias-driven swelling we determine

$$S_v = Const_3 \frac{D_v^{2/3}}{(KD_i)^{1/3}} (Z_i - Z_v) B \quad (15)$$

For a gas-driven swelling (14) critical parameter is the surface energy (tension) γ and D_{Xe} .

In a case of bias-driven swelling (15) critical parameters are $(Z_i - Z_v)$ and D_v , to a lesser importance is D_i .

For the normal diffusion mechanism the expressions for the appropriate coefficients look like in cm^2/s

$$\begin{aligned} D_{Xe} &= C_v 0.01 \exp(-E_{mXe}/kT) + D^R \\ D_v &= 0.01 \exp(-E_{mv}/kT) + D^R \\ D_i &= 0.01 \exp(-E_{mi}/kT) + D^R \end{aligned} \quad (16)$$

where: E_{mXe} , E_{mv} , E_{mi} are the activation energies of Xe, vacancy and interstition diffusion accordingly, k is the Boltzman's constant, T – is the irradiation temperature, D^R is the irradiation component of diffusion; C_v is defined by (5).

Proceeding from theoretical considerations of Konobeevsky [7] about atom mixing in quasi-liquid area caused by braking fission fragment, and numerical accounts which have been carried out by the author [8], irradiation component of diffusion D^R can be expressed (cm^2/s)

$$D^R = A \frac{G}{(T_m - T)^4} \quad (17)$$

where: G is the fission rate in cm^3 per second, T_m is the melting temperature, A is the constant dependent from thermo-physic properties of a substance, and having the order of meaning $n \times 10^{-18}$. For uranium and its alloys $A \sim 4 \cdot 10^{-18}$.

Within the capillary model surface energy we shall define from parity $E_{fv} = \gamma S_a$, where S_a is the free surface formed at removal of one atom from a crystal lattice

$$\gamma = \frac{E_{fv}}{4\pi \left(\frac{4\Omega}{3\pi} \right)^{2/3}} \quad (18)$$

where E_{fv} is the formation energy of vacancy.

As a first approximation the energetic parameters of substance can be received by empirical dependencies establishing correlation between activation energy of self-diffusion and melting temperature $E_{sd} = AkT_m$, where A is the constant. For 90 % of all metals having dense-packed lattices the calculated meanings of energy are in an interval of data at $A = 17.3$ (analysis is made on the data given in [9]).

Let's determine energetic parameters as follows:

$$\begin{aligned} E_{sd} &= 17.3kT_m, \text{ eV} \\ E_{mv} &= 0.45E_{sd} \quad E_{fv} = 0.55E_{sd} \\ \gamma &= 1.9 \cdot 10^{14} E_{fv}, \text{ eV/cm}^2 \end{aligned} \quad (19)$$

Migration energy of interstition on the basis of results received on processes of loops nucleation in Al, Au, Fe, Mo and V [10,11] is possible to accept

$$E_{mi} = 0.15E_{mv} \quad (20)$$

The author's analysis of data on volume thermal Xe diffusion [12-15] shows affinity of meanings of E_{mXe} and E_{mv} .

Thus the energetic parameters of substance at a first approximation can be received from one fundamental property of a material - melting temperature.

Some uncertainty is caused by a choice of preference meaning Z_i-Z_v .

Meaning of $Z_i-Z_v \sim 0.1$ is predicted by the simplified analytical decision for continuous matter [16-18].

These meanings contradict the basic data file on vacancy swelling of reactor materials. For explanation of data the meaning of Z_i-Z_v should lay in limits from 0.005 up to 0.05.

Disagreement of theoretical and experimental meanings can be connected with impurity atmospheres, which essentially deform elastic stress fields, and dislocation pinning. These reasoning prove to be true because the close to theoretical preference meaning is received only for high-purity metals [19].

According to the analysis made by the author for explanation of vacancy swelling of uranium the most probable meanings should be in limits from 0.004 up to 0.01.

For computation the meaning of parameter Z_i-Z_v is accepted to be 0.01.

Swelling computation

For swelling computation the following T_m (K) were used: $U_6Me \sim 1070$, $U_3Si \sim 1270$, $U+10wt.\%Mo - 1520$, $U_3Si_2 - 1930$, $UC - 2660$, UN и $UO_2 \sim 3070$.

For definition of fundamental energetic parameters of substance their correlation with melting temperature described above were used.

The gas swelling was calculated by (10) and vacancy - by (11).

The rate of the solid swelling was accepted to be 6.4 % on burnup of 10^{21} cm^{-3} .

The computed results are submitted on Fig.1 - 3.

From Fig.2 follows that there is some critical temperature at which the change of the gas-driven on bias-driven mechanism occurs.

The rate of gas swelling is less, than solid swelling due to accumulation of fission fragments. It means that the rate of distance increase between bubbles at expansion of a matrix surpasses rate of bubble growth. Thus, originally arisen bubbles under condition of their immobility never will merge. It is visible from computed pore morphology of U-10wt.%Mo at 100 and 200°C in Fig.3.

As the rate of vacancy swelling surpasses solid swelling, it is necessary to expect merging of pores and catastrophic swelling. The beginning of this process is shown in Fig.3 on model structure of the alloy at $B=2 \cdot 10^{21} \text{ cm}^{-3}$ и $T=300^\circ\text{C}$.

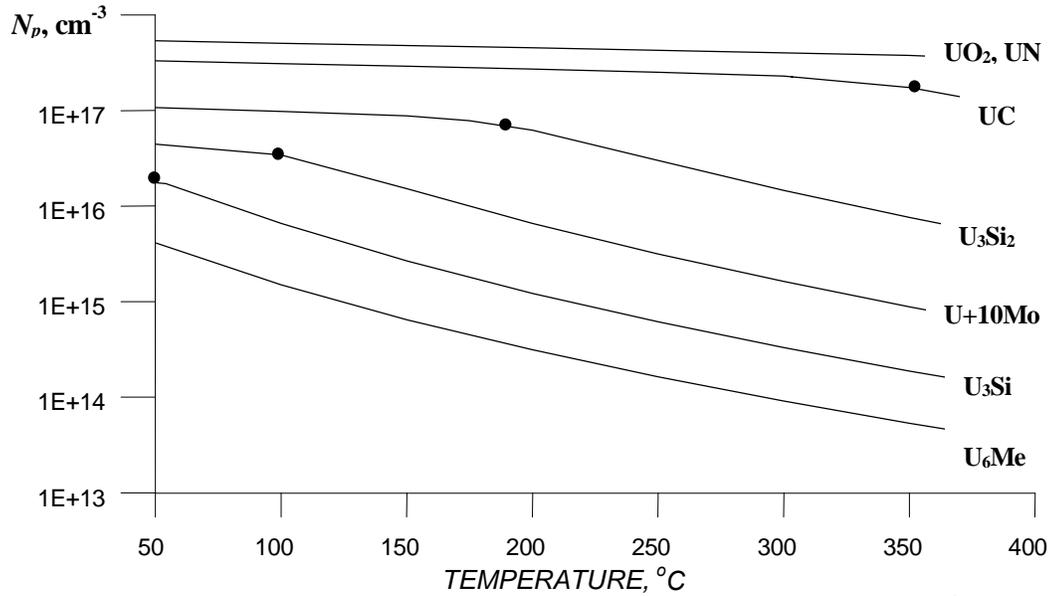


Fig.1. Computed temperature dependence of steady-state bubble density at $K=10^{-4}$ dpa/s ($G=10^{14}$ $\text{cm}^{-3}\text{s}^{-1}$). The points designate temperature when $D_v^{\text{Th}}=D_v^{\text{R}}$.

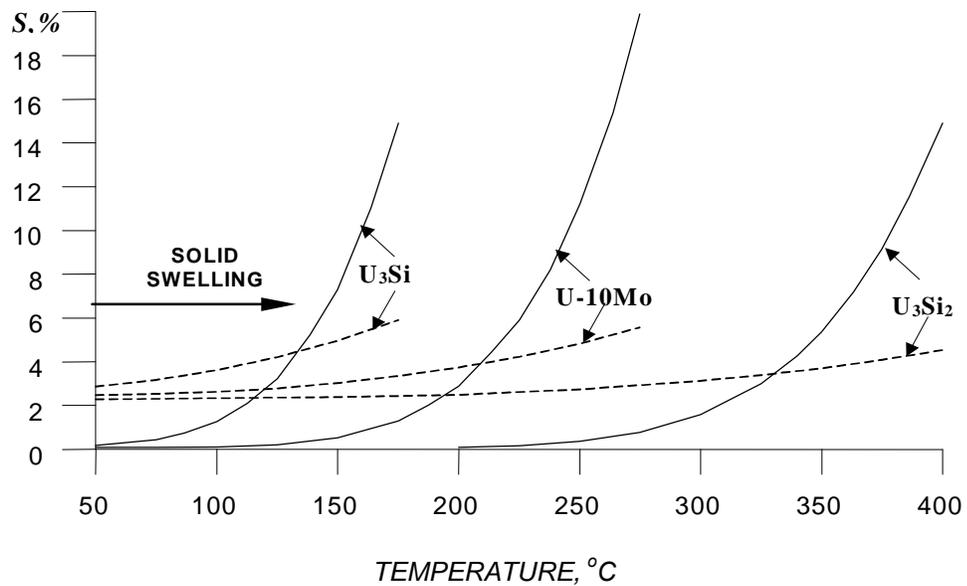


Fig.2. Computed swelling of various substances at $B=10^{21}$ cm^{-3} and $K=10^{-4}$ dpa/s ($G=10^{14}$ $\text{cm}^{-3}\text{s}^{-1}$): Dotted line - gas-driven model, continuous lines - bias-driven model.

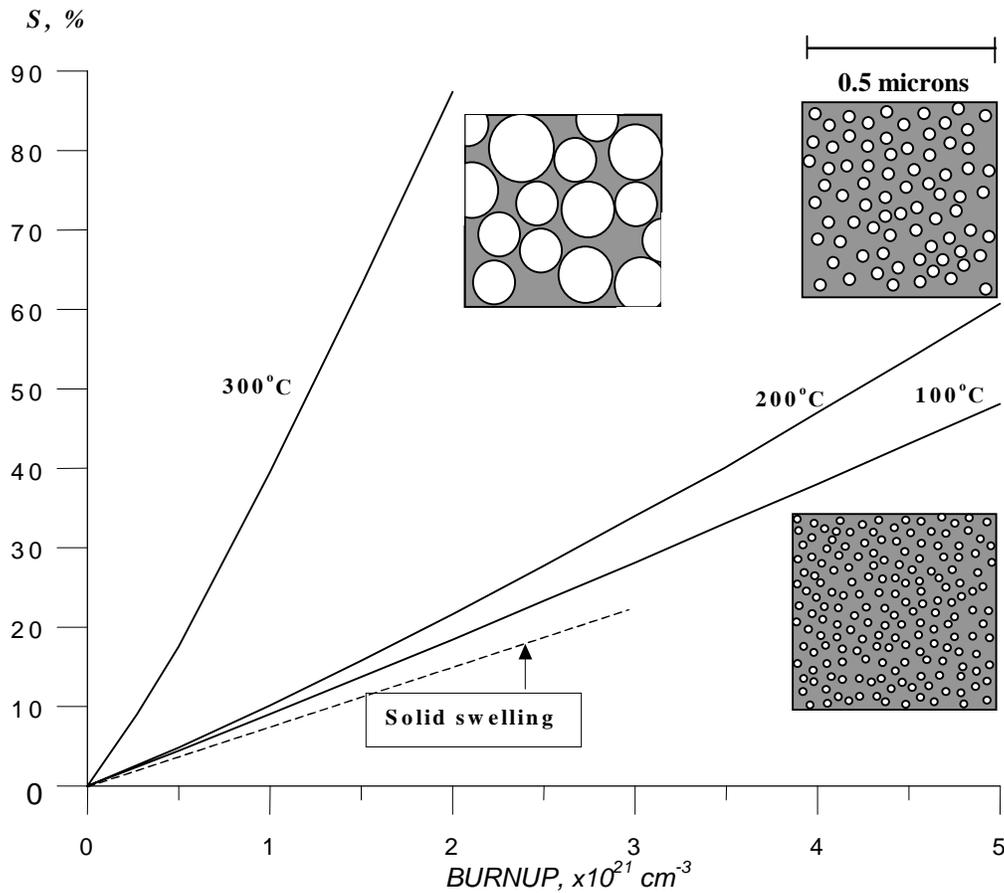


Fig.3. Computed total (solid + bubble) swelling of U-10wt%Mo at various temperatures and computed morphology of gas-contained pores, $K=10^{-4}$ dpa/s.

Conclusions

Use of the considered models and mathematical tools predicts change of stable gas swelling on catastrophic vacancy swelling at excess of some critical temperature.

The temperature of transition from gas to vacancy swelling is determined by energetic parameters of substance: activation energy of vacancy and fission gas diffusion, surface energy.

The energetic parameters of substance can be correlated with its fundamental characteristic - melting temperature.

According to carried out computation the fuel on a base of Uranium and its alloys with melting temperature higher than 1400 K keeps serviceability under temperature and burnup conditions of research reactors.

The calculated upper admissible temperature for U-10 wt.%Mo is about of 220°C.

References

1. Rest J. DART (Dispersion Analysis Research Tool), ANL-95/36 (USA), 1995.
2. Rest J., Hofman G.L., Coffey K.L., Konovalov I.I, Maslov A.A. – “Analysis of the Swelling Behavior of U-alloys”, 20th RERTR International Meeting, Jackson, Wyoming, USA, October 1997.
3. Rest J., Hofman G.L., Konovalov I.I, Maslov A.A. – “Experimental and Calculated Swelling Behavior of U-10 wt.% Mo Under Low Irradiation Temperatures”, 21st RERTR International Meeting, Sao Paulo, Brazil, October 1998.
4. Rest J., Hofman G.L., Konovalov I.I, Maslov A.A. – “Calculation of the Evolution of the Fuel Microstructure in U-Mo Alloys and Implications for Fuel Swelling” 22nd RERTR International Meeting, Budapest, Hungary, October 1999.
5. Greenwood G.W., Foreman A.J.E. and Rimmer D.E. – J. Nucl. Mat., 1959, 4, p.305.
6. Greenwood G.W. – UKAEA (Harwell) report, AERE-R3468, 1960.
7. Konobeevsky S.T. e.a. Atomic Energy, 1958. V.4. p.34. (*in Russian*)
8. Konovalov I.I. Questions of Nuclear Science and Engineering. Series: Applied Metallurgy and New Materials. 1998. 1(55). p.5. (*in Russian*)
9. Zelensky V.F. e.a.« Irradiation Defects and Swelling of Metals». Kiev, Naukova Dumka, 1988. (*in Russian*)
10. Kiritany M. - CONF-751006-P2: Fundam. Asp. of Radiat. Damage in Met., Proc. Int. Conf., Gatlinburg. Wash.(D.C.), 1976, v.2, p.695.
11. Eyre B.L., Loretto M.H. and Smallman R.E. - Vacancies'76. Proc. Conf. Point Def. Behav. and Diffus. Process, Bristol, 1976. London, 1977, p. 63.
12. Spedding R.H. e.a. - USAEC Report MUC-NS-3067, 1943, USA.
13. Ziemen K.E. and Schemiling P. – Zs. fur Electrochemie, 1954, 58, p.599.
14. Holden A.N. (1958) – Physical Metallurgy of Uranium, Addison-Wesley Pub. Co, Massachusetts, USA.
15. Rothman S.J., Hines J.J., Gray J. e.a. - J. Appl. Phys., 1962, 33.
16. Heald P.T. – Phil. Mag., 1975, 31/3, p.551
17. Speight M.V. – Phil. Mag., 1975, 32/6, p.1101
18. Miller K.M. – J. Nucl. Mat., 1079, 84(1/2), p.167
19. Demin N.A. e.a. – Questions of Nuclear Science and Engineering. Series: Physics of Radiation Damage and Metallurgy of Reactor Materials, 1982, 3(22), p.13 (*in Russian*)