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THERMOMOLECULAR ENERGETICS: FUEL AND STRUCTURAL SAVING, ENVIROMENTAL SAFETY

Анотація – створено нове робоче тіло (репульсивний клатрат) і запропоновано науково-технологічний напрям у технічній термодинаміці під назвою «ТермоМолекулярна Енергетика», що вирішує завдання економії палива, конструкційних матеріалів, а також екологічної безпеки.

Аннотация – создано новое рабочее тело (репульсивный клатрат) и предложено научно-технологическое направление в технической термодинамике под названием «ТермоМолекулярная Энергетика», которое решает задачи экономии топлива, конструкционных материалов, а также экологической безопасности.

Abstract – a new working medium (repulsive clathrates) was made and a scientific and technological direction in technical thermodynamics called «Thermo-Molecular Energetics» was suggested, which solves the problems of saving fuel, structural materials and environmentally safety.

INTRODUCTION

A modern power system based on the conventional working medium “gas-steam” has reached its limits in term of technical and economical performance. The further growth of the energy power is related to increase of heat engines sizes with no significant improvement in their thermal efficiency.

In contrast to conventional working medium (gas or steam) for the first time in the world, professor Eroshenko from KPI suggested to use an interface area of the Lyophobic Heterogeneous Systems (LHS) or Repulsive Clathrates (RC) in thermo-mechanical systems to accumulate, dissipate and convert the mechanical and thermal energies. A new trend in industrial power engineering has been called Thermo-Molecular Energetics (TME).

THE PHYSICAL AND THERMODYNAMIC ESSENCE OF A NEW WORKINH MEDIUM

An extremely advanced interface area Ω (m³) of the surface contact between “nonwetting liquid” and “nanoporous solid matrix (pore diameter is 5–300 Å)” can be used as a new heterogeneous working medium for accumulation, dissipation and conversion of the mechanical and thermal energies [1–3]. The considered heterogeneous system (LHS) consists of two components: the liquid and the discrete nanoporous solid particles (matrix) that are non-wetted by this liquid (a liquid-solid contact angle $\theta \gg 90^\circ$).

By virtue of a phobic system, the liquid cannot fill the opened pores space of the matrix spontaneously. For forced intrusion of the liquid into the matrix pore space, the external pressure have to reach the threshold limit value, which is given by the Laplace capillary pressure P_L (here and further for simplicity, we will use an absolute value of $\cos\theta$), Pa

$$P_L = P_{\text{int}} = \frac{2\sigma \cos\theta_A}{r} \quad (1)$$

where σ is the surface tension of liquid at the border with gas (vacuum) in N/m; θ_A is a advancing

contact angle and r is the pore radius in m.

Volume of pore space of the matrix V_{inv} (m^3) actually determines the degree of compression dV of the considered HLS. Under thermodynamic consideration, the elastic deformation of the actual liquid and matrix was neglected resulting in:

$$dV \approx V_{inv} = \phi V_m = -kr d\Omega \quad (2)$$

where ϕ is a matrix porosity in m^3/m^3 ; k is a shape factor of the pores and the capillaries ($0.33 < k < 0.50$); $d\Omega$ is a variation of the area of surface contact between the liquid and solid phases during forced intrusion and spontaneous extrusion of the liquid clusters from the pores space in m^2 ;

The minus sign in equation (2) means, that during the system compression ($dV < 0$), forced advancement of the interface area of surface contact between the liquid and solid phases occur ($d\Omega > 0$) (i.e., an energy accumulated by the system through the formation of the interface area Ω). During the system expansion ($dV > 0$) (after the removal of external load), the spontaneous escape of the liquid clusters from the nanoporous particles with the reduction of the interface area ($d\Omega < 0$) occurs and simultaneously, release of previously accumulated energy and performance of useful work takes place [1–15].

The system expansion can be reversible ($P_{int} = P_{ext}$) or irreversible ($P_{int} \neq P_{ext}$). In the last case, the liquid phase will be expelled at a extrusion pressure P_{ext} , given by the following equation [4]

$$P_{ext} = \frac{2\sigma \cos \theta_R}{r} \quad (3)$$

where θ_R is a receding contact angle.

As a porous matrix, one can use silica gels, aluminum silicates, porous glasses and many others mediums of the extremely advanced specific surfaces (from 100 to 1000 m^2/g of the medium).

The possibility of ultrafine dispersion of the liquid (up to its molecular size) by means of these matrices explain the behavior under consideration repulsive clathrates. It is determined by their surface properties and phenomena and to a lesser extent depends on the bulk properties of the component of the system: the liquid and the solid phases.

As a liquid, one can use water and water solution, salts, melts, low-temperature alloys and eutectics and other simple liquids.

The initial requirement to the pointed heterogeneous systems is its pronounced lyophobicity: $90^\circ \ll \theta \leq 180^\circ$. If a system is lyophilic (liquid spontaneously wets the matrix), the matrix can be made non-wettable, for example, using chemical modification of its surface [5].

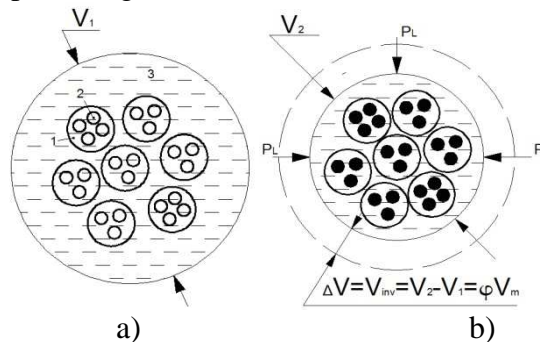


Fig. 1. a) Graphical interpretation of the RC: a) schematic presentation of the RC before the intrusion (1 – particle; 2 – pore; 3 – liquid); b) the state of the RC after the intrusion;

Fig. 1a presents a model of the lyophobic granular system with chaotic distribution of the matrix particles in the liquid. The matrix particles have nanopores, which are cavities between nanoglobules that form the carcass of these particles.

For simple liquids the relation between surface tension σ and temperature T is written down in

Wander-Waals form

$$\sigma \approx \sigma_0 (1 - T/T_{cr}) \quad (4)$$

where T_{cr} is a critical temperature ($\sigma=0$) in K; $d\sigma/dT = -\sigma_0/T_{cr}$ is a temperature coefficient of surface tension of the liquid in N/m·K.

As opposed to conventional working medias (with the state equation $PV=nRT$), the properties of the repulsive clathrates is given by two independent equations where T and Ω are independent parameters:

$$dP = -\frac{2 \cos \theta}{r} \frac{d\sigma}{dT} dT \quad (5)$$

$$dV = -kr d\Omega \quad (6)$$

Evidently, for the first time in the engineering thermodynamics, equations (5) and (6) allowed successfully break up the relationship between parameters P and V , which has opened opportunity of making more perfect energy device and reach the optimal working regime.

Fig. 2a presents the PV isotherm for the repulsive clathrates in terms of the uniporous matrix (e.g. zeolite with $r=CONS$). Apparently during 0-1 phase, the pressure increases do not cause a considerable compression of the quasi-condensed heterogeneous systems volume. During 1-2 phase (after the rich Laplace capillary pressure (1)), the intrusion of the liquid in the pore space of the matrix occurs and the system volume in the amount of porous volume V_{inv} considerably decreases: the interface area Ω reaches its maximum at the end of the compression process (see point 2 on the Fig. 2a and equation (2)).

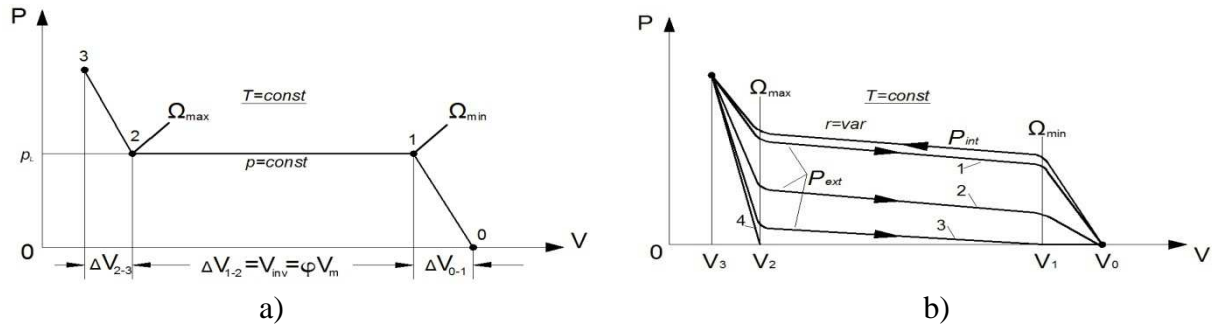


Fig 2. a) Example of the isothermal system compression: 0-1phase is the quasi-elastic deformation of the liquid and the matrix particles; 1-2 phase is advancement of the interface area between the liquid and solid phases; 2-3 phase is the RC compression with liquid-filled nanopores; b) Cycle of the isothermal compressive and expansion of the RC in terms of the heteroporous matrix.

A further increases in pressure (after filling the pores and capillaries), during 2-3 phase, does not reduce the system volume significantly (it is again quasi-condensed).

Cycle of the isothermal compression and expansion of the repulsive clathrates in term of the hetero-porous matrix ($r = var$) is shown in Fig. 2b. As can be seen, after reaching Laplace capillary pressure, the process 1-2 of filling (at a pressure $P_{int} = var$ (1)) firstly large pores and capillaries, and then smaller ones occurs. During the process of spontaneous extrusion of the liquid clusters from the pores space (at a pressure $P_{ext} = var$ (3)) in reverse order, the liquid is forced out from the small pores first, and then from the larger ones.

The difference between the intrusion and extrusion pressures is a characteristic of a hysteresis phenomenon, which can be expressed as

$$H = \frac{P_{int} - P_{ext}}{P_{int}} \quad (7)$$

It is evident from the equation (7), that the systems can vary from reversibly transforming ($H=0$, see Fig. 2b, line 1) to completely irreversible ($H=1$, see Fig. 2b, line 4), when no

extrusion clusters of liquid from porous space occurs (black hole). Cycles of the repulsive clathrates with large hysteresis (Fig. 2b line 3) are applicable for effective energy dissipation (bumpers, damper and etc.) [6–8]. The repulsive clathrates with small hysteresis (Fig. 2b line 2) can be applied to accumulate (autonomous executive mechanism [9–11]) and convert energies (heat engine and refrigerator) [12–13].

Let us consider the equation of internal surface energy of heterogeneous lyophobic system U (neglecting of their bulk component and accordingly the internal energy of the bulk phase) [14–15]:

$$dU = dU_v + dU_\Omega \approx dU_\Omega = \delta W_\Omega + \delta Q_\Omega \quad (8)$$

The mechanical work (Gibbs work) δW_Ω exchanged during intrusion and extrusion can be written for a two- and three-dimensional process, respectively, as [15]

$$\delta W_{\Omega_{\text{int}}} = P_{\text{int}} dV = P_{\text{int}} \phi V_m = \sigma \cos \theta_A d\Omega \quad (9)$$

$$\delta W_{\Omega_{\text{ext}}} = P_{\text{ext}} dV = P_{\text{ext}} \phi V_m = \sigma \cos \theta_R d\Omega \quad (10)$$

During intrusion a certain amount of energy from work is stored in the system. The larger is pressure of intrusion or the porous volume, the larger is the stored energy. During expulsion, a certain amount of energy is released, which is always smaller than the amount of work previously done on the system ($90^\circ < \theta_R < \theta_A$).

In the case of reversible process, interfacial surface variation $d\Omega$ and work δW_Ω are defined as [15]

$$\delta W_\Omega = \delta W_{\Omega_{\text{int}}} = \delta W_{\Omega_{\text{ext}}} = P_L dV = \sigma \cos \theta d\Omega \quad (11)$$

where $\theta = \theta_A = \theta_R$ is a static contact angle.

The heat exchanged during reversible process can be expressed as

$$\delta Q_\Omega = T dS_\Omega = T \left| \frac{d\sigma}{dT} \right| \cos \theta d\Omega = T (kr)^{-1} \left| \frac{d\sigma}{dT} \right| \phi V_m \cos \theta \quad (12)$$

It is evidently from the equations (11)–(12) that there are two different heat effects during the intrusion and extrusion. There is an endothermic effect ($\delta Q_\Omega > 0$) during intrusion ($d\Omega > 0$) that becomes exothermic ($\delta Q_\Omega < 0$) during extrusion ($d\Omega < 0$). This effect is directly proportional to the area of the interface Ω [14–15].

THERMODYNAMIC CYCLE OF THE HEAT ENGINE BASED ON THE RC

The essence of the thermodynamic cycle of the heat engine with external heat supply based on the RC will be shown on the example of a single rigid pore and liquid cluster (Fig. 3a) [12–13].

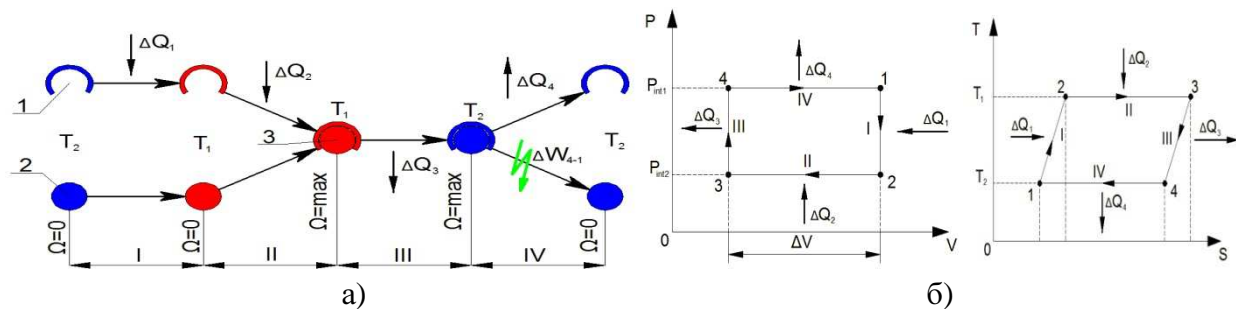


Fig. 3 a) Thermodynamic cycle on the example of a single rigid pore 1 and liquid cluster 2, forming a repulsive clathrate 3; b) PV and TS – diagram of the cycle

Stroke I. At the initial stroke, the pore 1 and the liquid cluster 2 have temperature of T_2 (cold source). The external pressure P applied to the system is less than the capillary pressure P_L (1). Moving the system (pore and cluster) into the region of high temperature T_1 and neglecting the change in heat capacity of the pore 1 c_1 and the liquid cluster 2 c_2 , it can be assumed that at the end of the first stroke the pore and the liquid cluster have temperature of the heat source T_1 . During

the first stroke, the cluster does not change their volume (the liquid is almost incompressible) and their heating due to heat of the hot source ΔQ_1 (the heat supplied from outside) can be described as the isochoric ($V = \text{const}$) and the isosurface ($\Omega = \text{const}$). The heat ΔQ_1 can be expressed as

$$\Delta Q_1 = T_a \Delta S_{1-2} = (c_1 \rho_1 V_1 + c_2 \rho_2 V_2) \cdot (T_1 - T_2) \quad (13)$$

where $T_a = (T_1 - T_2) / \ln(T_1 \cdot T_2^{-1})$ is a mean-temperature of the system during first stroke; $\Delta S_{1-2} = C_\Sigma \ln(T_1 \cdot T_2^{-1})$ is a variation of the entropy during first stroke; $C_\Sigma = c_1 \rho_1 V_1 + c_2 \rho_2 V_2$ is a total heat capacity of the system (c_1 and c_2 are specific heat capacity of the liquid and the pore material in J/kg·K; ρ_1 and ρ_2 are density of the liquid and the pores material in kg/m³; V_1 and V_2 are volume of the pore material and the liquid in m³)

Stroke II. At higher temperature T_1 , the capillary pressure P_L decreased by an amount of dP (5) through the reduction of the surface tension with increasing temperature (4). In this case, the liquid cluster 2 can be easily embedded into pore 1 at a low pressure P_{L_2} ($P_{L_2} = P_L - dP$) and the system external pressure $P = P_{L_2}$ performs the work of interface formation from 0 to Ω_{max} , according to equation (11). As already was mentioned above, the formation of the interface area is endothermic ($\Delta Q > 0$), therefore one should lead to the system heat ΔQ_2 to be equal to the heat of interface area formation in the isobaric-isothermal conditions (12).

Stroke III. During third stroke, which occurs at a constant system volume and interface area, the working medium is cooling down to T_2 due to the removal of heat ΔQ_3 from the system by the cold source. At the end of stroke III, the system pressure (the pressure in pore) increases to the Laplace pressure P_L due to decreasing temperature and increasing surface tension (see Eqs. 4 and 1). The heat ΔQ_3 by analogy with Eq. (14) can be expressed as

$$\Delta Q_3 = -T_a \Delta S_{3-4} = C_\Sigma \cdot (T_1 - T_2) \quad (14)$$

Stroke IV. By virtue of the increased capillary pressure, the liquid cluster 2 is pushed out of pore space. The isobaric-isothermal reversible reduction of interface area contact between the liquid and the solid phase takes place ($\Delta \Omega < 0$). During this process, the heat of the reduction area ΔQ_4 is released into the environment to ensure isothermality of the process. Extruded at a pressure P_L , the liquid cluster performs mechanical work of the isobaric-isothermal expansion of the working medium (the reduction of the surface (11)). Stroke IV ends with the return of pore 1 and cluster 2 in the initial states (start of Stroke I in Fig. 4a)

Fig. 3b shows the PV- and TS-diagrams of the working stroke. As a result of four-stroke cycle the system performs some effective work that can be calculated as

$$\Delta W = \Delta W_{2-3} + \Delta W_{4-1} = (P_{L_1} - P_{L_2}) \Delta V = \left| \frac{d\sigma}{dT} \right| \cdot \frac{2 \cos \theta}{r} \cdot V_{\text{inv}} \cdot (T_1 - T_2) \quad (15)$$

Work ΔW was done by the heat accumulated in the system during the cycle ΔQ

$$\Delta Q = \Delta Q_1 + \Delta Q_2 - \Delta Q_3 - \Delta Q_4 = \Delta Q_2 - \Delta Q_4 = \left| \frac{d\sigma}{dT} \right| \cdot \cos \theta \cdot \Omega_{\text{max}} \cdot (T_1 - T_2) \quad (16)$$

The thermal cycle efficiency is calculated by the formula

$$\eta = \frac{\Delta Q}{\Delta Q_1 + \Delta Q_2} = \eta_c \cdot \left(1 + \eta_c \cdot rk \sum c_i \rho_i V_i \cdot \left(V_{\text{inv}} \left| \frac{d\sigma}{dT} \right| \cos \theta \right)^{-1} \right)^{-1} \quad (17)$$

The inequality $rk \sum c_i \rho_i V_i \ll V_{\text{inv}} |d\sigma/dT| \cos \theta$ can be implemented by selecting the physical characteristics of the liquid and the matrix ($V_{\text{inv}}, d\sigma/dT, \theta, c_1, c_2, \rho_1, \rho_2$). As a matrix is

recommended to use particles with pores of molecular dimension (e.g., zeolite), as a result the thermal efficiency of the considering cycle may be close to the limit efficiency $\eta_c = 1 - T_2/T_1$ of Carnot cycle ($\eta \rightarrow 0.8 - 0.9$), but never reach it, because it requires to satisfy the condition: $r=0$. But it is physically impossible, since the liquid molecules have a finite size, so the minimum pore radius cannot be less than the radius of the liquid molecules.

Indirect implementation of the thermodynamic cycle allows generation of cold, which opens up opportunity for refrigerators without freon system.

OTHER ENGINEERING SOLUTIONS BASED ON THE RC

Self-contained actuator for space applications (Fig. 4) [11] is an example of a constructive combination of accumulator and actuator that can be used as a “device for deploying solar panels and the removal of optical instruments on satellites and spacecraft”.



Fig. 4. Photo of self-contained actuator for space applications.

The old design was based on the use of 13-15 “cleverly” connected Hooke springs (to make more flat characteristic “force displacement”). Project task: displacement is 100 mm, the force in the working cycle can reduce from 20 to 13 kN. A new working medium has provided the same displacement with a constant force of 80 kN with the octuple improvement in overall weight and dimension performance.

Shock absorber (Fig. 5) is based on the RC [7–8] and dissipates the design energy of the external mechanical perturbation using 15 cm³ of HLS (hydrophobized silica and water) while the traditional shock absorber is provided with a 1500 cm³ technical oils.

Specific power dissipation of energy with the new shock absorber (30 – 50W/cm³) is hundreds of times higher compared to traditional (oil) shock absorbers (0.10 – 0.15 W/cm³). The absorber uses clathrates with a large hysteresis in the parameter “pressure in the compression-decompression cycle” (in Fig. 2b, curve 3). Appropriate selection of porous matrices can optionally change the slope of the characteristics P_{int} and P_{ext} . Given the fact that the shock absorber on the repulsive clathrates does not require any oil to dissipate energy, it has no equal in the world on environmental requirements. Every year, about 100 million shock absorbers filled with oil are thrown to the landfills. A Sign of impending ecological disaster only through road transport.



Fig. 5. Photo of Shock absorber.

CONCLUSIONS

An application of a new heterogeneous working medium (repulsive clathrates RC, heterogeneous lyophobic system HLS) for accumulation, dissipation and conversation of mechanical and thermal energy in a new generation of thermo-mechanical energy devices was shown. Energy devices based on the RC have much better energy performance in comparison with the conventional devices, and these devices are environmentally safe.

Physical and thermo-dynamical nature of repulsive clathrates and the genesis of the thermal effects of compression and decompression of the bulk phase and forced advancement (reduction) of the interface area during intrusion and extrusion liquid clusters into pore space of the matrix were

shown.

Remark: The direction of Thermo-Molecular Energetics was given approval by the scientific community and successfully has been developing in many countries: Japan, France, Russia, USA, China, South Korea and others.

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