

# MATERIALS – ADDITIVE OF KNOWLEGE PROPERTIES AND TECHNOLOGIES

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**Abstract:** Two tasks are enumerated: a task of hardening spheres with a radius of 50 nm and a task of crystallization - the underlying kinetic equation of formation of new phases. These tasks are rational bridges for multi-scale approach.

There is an opportunity to create additive production with traditional machines and technologies in the field of anti-pressure casting

**Keywords:** ADDITIVE MANUFACTURING GAS COUNTER-PRESSURE, „CORRELATION VOLUME“, 3D PRINTING

## 1. Introduction

Definition of the thermodynamics: Thermodynamics (from Greece) [1] is called the general science of energy dealing with the relationship between heat and mechanical energy and heat transformations at work and vice versa. The purpose of the article in [1] is to show the application of the two general principles (1) the Joule’s Law on Heat and Work Equivalence, and (2) the Carnot principle that the efficiency of a reversible engine depends only on the temperatures between which it does work;

The main content of thermodynamics - this is a description of the conversion of heat into work and, conversely, the conversion of mechanical work into heat [2]; Thermodynamics: the science that deals with heat and work, and those properties of matter that refer to heat and work [3]. Thermodynamics is a branch of physics that deals with heat and temperature and their relationship to energy, work, radiation, and the properties of the bodies of matter [5]. The main meaning in all definitions is preserved, which is an example of accurate knowledge.

The classical thermodynamics presented in the essay of Table 1:

**Table 1: Thermodynamics [1, 2, 4].**

1. LIQUIDUS IS HOMOGENEOUS OR HETEROGENEOUS OPEN THERMODYNAMICS SYSTEM; 2. PARAMETERS: VOLUME V PRESSURE PARAMETERS p TEMPERATURE T AND AGREGATE STATE; 3. FOR A SUBSTANCE VARIABLES V, p AND T ARE NOT INDEPENDENT BUT ARE CONNECTED IN THE STATE EQYATION  $f(p, V, T) = 0$  AND THE SOLUTION FOR EACH VARIABLE IS A FUNCTION OF THE OTHERS TWO; 4. EXTENSIVE QUANTITIES ARE: VOLUME (v), MASS (m), ENERGY (U), ENTALPY (H), ENTROPY (s), BECAUSE THEY ARE PROPORTIONAL TO THE QUANTITY OF MATTER. INTENSIVE QUANTITIES ARE: DENSITY ( $\rho = m/V$ ) AND TEMPERATURE T, WHICH DO NOT SATISFIES WITH THE CONDITION OF EXTENSIVE; 5. ANALYSIS APPROACH: THE HETEROGENEOUS SYSTEM IS DISTRIBUTED AT THE END OR EXRTEME NUMBER OF HOMOGENEOUS VOLUMES (PARTS). 6. THE STATE OF THERMODYNAMICS EQUILIBRIUM OF A SYSTEM IS SIMULTANEOUSLY THE THREE THERMAL, MECHANICAL AND CHEMICAL EQUILIBRIUM. THE DYNAMICALLY-THERMODYNAMIC STATE IS A COMBINATION OF DYNAMIC STATES THROUGH WHICH THE SYSTEM REPIDLY MIGRATES AS A RESULT OF MOLECULAR MOVEMENT; 7. THE SYSTEM HAS A STEADY EQUILIBRIUM WITH A MINIMUM OF FREE ENERGY; 8. THE CONVERSION OF THE SYSTEM STATUS IS EXCHANGED UNDER AN INCORRECT RANGE OF INTERMEDIATE CONDITION. THEREVERSIBLE TRANSFORMATION IS WHEN THE ARRAY OF INTERMEDIATE STATES ARE INFINITELY CLOSE TO THE EQUILIBRIUM; 9. INTERNAL ENERGY (U) IS THE SUM OF: THE TOTAL KINETIK ENERGY  $\Sigma E_{Cinetic}$  OF THE MOVMENT OF MOLECULES AND THE FULL POTENTIAL ENERGY  $\Sigma E_{Potential}$  OF ELECTROMAGNETIC INTERACTION KEEPS THE ELECTRONS IN THE ATOMS AND CONNECTS THE ATOMS IN MOLECULES AND CRYSTALS  $U = \Sigma E_{Cinetic} + \Sigma E_{Potential}$ ;

10. LAWS OF THERMODYNAMICS: ZERO LAW: IF THRMODYNAMICS SYSTEM A IS IN THERMODYNAMIC EQUILIBRIUM WITH SYSTEM B AND IN TURN SYSTEM B IS IN THERMODYNAMIC EQUILIBRIUM WITH SYSTEM C, THEN A AND C ARE ALSO IN THERMODYNAMIC EQUILIBRIUM. PHYSICAL PRINCIPLE EXPRESSING THE TRANSITIVITY OF THERMODYNAMIC EQUILIBRIUM AND DEFINING TEMPERATURE; FIRST LAW: THE CHANGE IN THE INTERNAL EMERGY U OF A THERMODYNAMIC SYSTEM IN AN RABITRARY THYERMODYNAMIC PROCESS WITH INITIAL AND FINAL STATE IS EQUAL TO THE QUANTITY OF HEAT Q INPUT OR OUTPUT FROM THE SYSTEM AND THE OPERATION W PERFORMED ON THE SYSTEM  $\Delta U = Q + W$  OR  $\Delta Q = dU + PdV$ ; CHANGE BETWEEN TWO EQUILIBRIUM STATEES: CLOSED SYSTEM  $\Delta E = \Delta E_{C(macro)} + \Delta E_{P(macro)} + \Delta U$ ; AND OPEN SYSTEM  $\Delta E =$

$\Delta E_{C(macro)} + \Delta E_{P(macro)} + \Delta U + m(u)_{inlet} - m(u)_{outlet}$ , WHERE MASS  $m(u)_{OUTLE(INLET)}$  ARE MASS FLOW ENTERING AND LIVING THE SYSTEM; 10.1 THERMODYNAMIC FUNCTIONS: *EMTALPY*  $H = U + pV$ ; *ENTROPY* (S)  $=$

$$S(A) = \int_0^A dQ/T$$

*dQ/T* OR 10.2 THE SECOND LAW: IT IS NOT A POTENTIAL PROCESS IN WHICH THE ONLY ULTIMATE RESULT IS TO SWICH TO THE HEAT OF A HEAT REMOVED FROM A SOURCE THAT ALWAYS HAS A SINGLE TEMPERATURE (KELVIN POSTULATE); IT IS NOT AN INHERENT PROCESS IN WHICH THE ONLY ULTIMATE RESULT IS A HEAT TRANSFER FROM A BODY HAVING A GIVEN TEMPERATURE TO A BODY WITH A HIGHER TEMPERATURE (CLAUSIUS POSTULATE) IF THE HEAT REMAINS FROM THE BODY A AND ANAOTHER B, THIS IS NOT A POSSIBLE PROCESS TO WHICH THE ONLY END RESULT IS TO BE TRANSFERRED TO THE HEAT FROM B TO A (OTHER CLAUSIUS POSTULATE); SECOND LAW: THE ENTROPY OF A CLOSED SYSTEM THAT IS NOT IN EQUILIBRIUM INCREASES WITH TIME REACHING ITS MAXIMUM VALUE WHEN EQUILIBRIUM  $\Delta Q \leq TS$ ; 10.3 THERMODYNAMIC POTENTIALS OF THE SYSTEM: INTERNAL EMERGY  $dU = Tds - PdV$ , IN VARRIABLES S, P, V, T; POTENTIAL ENTROPY  $H = U + PV$  OR  $dH = d(U + PV) = dU + PdV + VdP = Tds + VdP$  IN VARIABLES S, P, V, T; HELMHOLTZ’S FREE ENERGY  $F = U - TS$  ( $dF = -SdT - PdV$ ) IN VARIABLES T AND V; POTENTIAL OF GIBBS  $G = U + PV - TS \equiv H - TS$  IN VARIABLES T AND P; OFEN G IS CALLED FREE ENTALPY; THE RANOME CHOICE OF THE INITIAL STATE O INTRODUCES INTO THE ENTROPY S AN UNDETERMINED ADDITIVE CONSTANT. 10.4 THE THIRD LAW OF THERMODYNAMICS OR THEOREM OF NERNST: THE ENTROPY OF ANY SYSTEM AT ABSOLUTE ZERO CAN ALWAYS BE ASSUMED TO BE ZERO. 11. ASSESSMENT OF THERMODYNAMICS: FROM ALL POSSIBLE STATE, WHICH OF THEM IS EQUILIBRIUM. MAKE THE RELATIONSHIP BETWEEN I-st LOW AND II-nd THE THERMODYNAMICS LAW OF THE TIPE  $dU + PdV = \Delta Q \leq Tds$  AT  $dp = dT = 0 \Rightarrow dG \leq 0$ . i.e.  $G \rightarrow \min$ . ANALOGGUE WHEN SET V AND T,  $dV = dT = 0 \Rightarrow dF = dU - Tds - SdT \leq -PdV - SdT$  and from  $dV = dT = 0 \Rightarrow F \rightarrow \min$ . IN FUTURE AMENDMENS WITH FAST FREQUENCY CONFLICTS FREEFIELD PHRASES  $dF = dU - Tds - SdT = -PdV - SdT$  AND GIBBS POTENTIAL  $dU = PdV = \Delta Q = Tds$  WE HAVE AN EQUALITY WE HAVE EQUALITY MARK. HERE ARE FOLLOWING RELATIONS: AT  $F \rightarrow \min$   $(\partial F/\partial V)_{T,N_k} = -P$   $(\partial F/\partial T)_{V,N_k} = -S$ ; AT  $G \rightarrow \min$   $(\partial G/\partial p)_{T,N_k} = V$   $(\partial G/\partial T)_{p,N_k} = -S$ .

THE CHEMICAL COMPOSITION DETERMINES THE AMOUNT OF  $N_k$  OF EACH COMPONENTS k IN EACH PHASE  $\phi$  I.E.  $K\phi$  ARE QUANTITIES WHERE K – THE NUMBER OF COMPONENTS AND  $\phi$  – THE NUMBER OF PHASES. THE MAGNITUDE  $N_{k\phi}$  DENOTES THE CHEMICAL COMPOSITION WHICH FOR EACH PHASES. THE MAGNITUDE  $N_{k\phi}$  IS UNICUELY

CHARACTERIZED BY  $K - 1$  PARTS:  $x_{k\phi} = N_{k\phi} / \sum_{i=1}^K N_{i\phi}$ , BUT ALSO THE TOTAL QUANTITY OF SUBSTANCE AS THE AMOUNT OF SUBSTANCE

$\forall$  PHASE  $\phi$  IS EQUAL TO  $\sum_{i=1}^K N_{i\phi}$ . EXTENSIVE  $\Psi$  FOR HETEROGENEOUS MIXTURE IS OBTAINED BY SUMMING (ADDITIVE RULE)  $\Psi = \Sigma \Psi_i$ ; THE RELATION  $\Psi(\alpha N_1, \alpha N_2, \dots, \alpha N_k) = \alpha \Psi(N_1, N_2, \dots, N_k)$  IS TRUE; MATHEMATICAL REPRESENTATION OF THE EXTENSIVE DIMENSIONS ARE HOMOGENEOUS FUNCTIONS OF THE 1-ST DEGREE AND IS TRUE EULER’S THEOREM  $\Psi = \Sigma (\partial \Psi / \partial N_i) N_i$ , WHILE FOR ANY FUNCTIONS  $\Xi$  IT IS ONLY THE CORRESPONDING DIFFERENTIAL RATIO TRUE  $d\Xi = \Sigma (\partial \Xi / \partial N_i) dN_i$ .

The basic processes of material science, casting and heating flow in open thermodynamic systems [2, 3, 4, 5 ana 6]. The two processes are irreversible phase transitions of the first and second order. The classical thermodynamics Table 1, [2, 3 and 4] is used to describe the casting process that is basically considered. Mathematics is presented alongside the laws of thermodynamics, showing in depth the historical development. We also use the synergistic approach [18, 19, 20, 21 and 22]. The overall dynamic state of the system in the synergistic approach [18, 19, 20, 21 and

22]. is the extended form of I. Prigogine's second law of thermodynamics [18] in the view:

$$\left[ \frac{\text{Entropy of OTS}}{\text{Time}} \right] = \left[ \left( \frac{\text{Internally entropy production of irreversible processes (crystallization) in OTS}}{\text{Time}} \right) + \left( \frac{\text{Externally entropy flow by interaction OTS with environment}}{\text{Time}} \right) \right]$$

$$\frac{dS}{dt} = \frac{dS_i}{dt} + \frac{dS_{EX}}{dt} \quad (1)$$

The thermodynamic driving force  $\Delta\mu > 0$  of the phase transition of first order and at crystallization of melts [15, 16, and 17]

$$\Delta\mu = \Delta S_m(T_m - T), \quad (2)$$

Where  $T_m$  - the temperature of phase transition. Temperature of undercooling is defined from Stefan's problem. The work  $W_n$  for the formation of n-atoms complex in the system  $\Delta V$  under the influence of the case eq. (2) we have

$$W_n(\Delta\mu) = -n\Delta\mu + F_n(\Delta) \quad (3)$$

For description the nucleation and growth we use fundamental kinetic equation phase transition of Kashchiev [30]. It expresses a balance between the distribution function  $Z_n(t)$  of new phase complex of n-atoms and its total change  $dZ_n(t)/dt$

$$\frac{dZ_n(t)}{dt} = \sum_{m=1}^n [f_{nm}(t)Z_m(t) - f_{nm}(t)Z_n(t)] + K_n(t) - L_n(t) \quad \text{at } t \in [0, t_f] \quad (4)$$

With a suitable definition of the transition frequencies  $f_{nm}(t)$  the equation (4) is valid not only for the initial stage of nucleation, but also for coagulation from unified point of view. The general number  $N(T)$  of the over-nuclei complex in the subsystem  $\Delta V$  is obtained. So as the rate of nucleation  $J(t)$

$$N(t) = f|Z_n| \cdot J(t) = \frac{dN(t)}{dt} \quad t \in [0, t_f] \quad (5)$$

The equations (2-5) introduce the phase transition of first order of the three levels [31]. The local function

$$\sigma_S = F[N(t), J(t)] \quad \text{at } t \in [0, t_f] \quad (6)$$

We separate the volume of the open thermodynamic system in macroscopic cells  $\Delta V_i, i=1, \dots, N$  and the phase transition of first order is

$$\sigma_S = \sum_i \sigma_S^i \quad \text{for time:} \quad t = \sum_i t_f^i \quad (7)$$

Thus with eq.(7) a generalized model of phase transition of first order in the complex casting process is present.

In order to have a technology we can reproduced in every local volume  $\Delta V_i$  degradation of energy and condition.

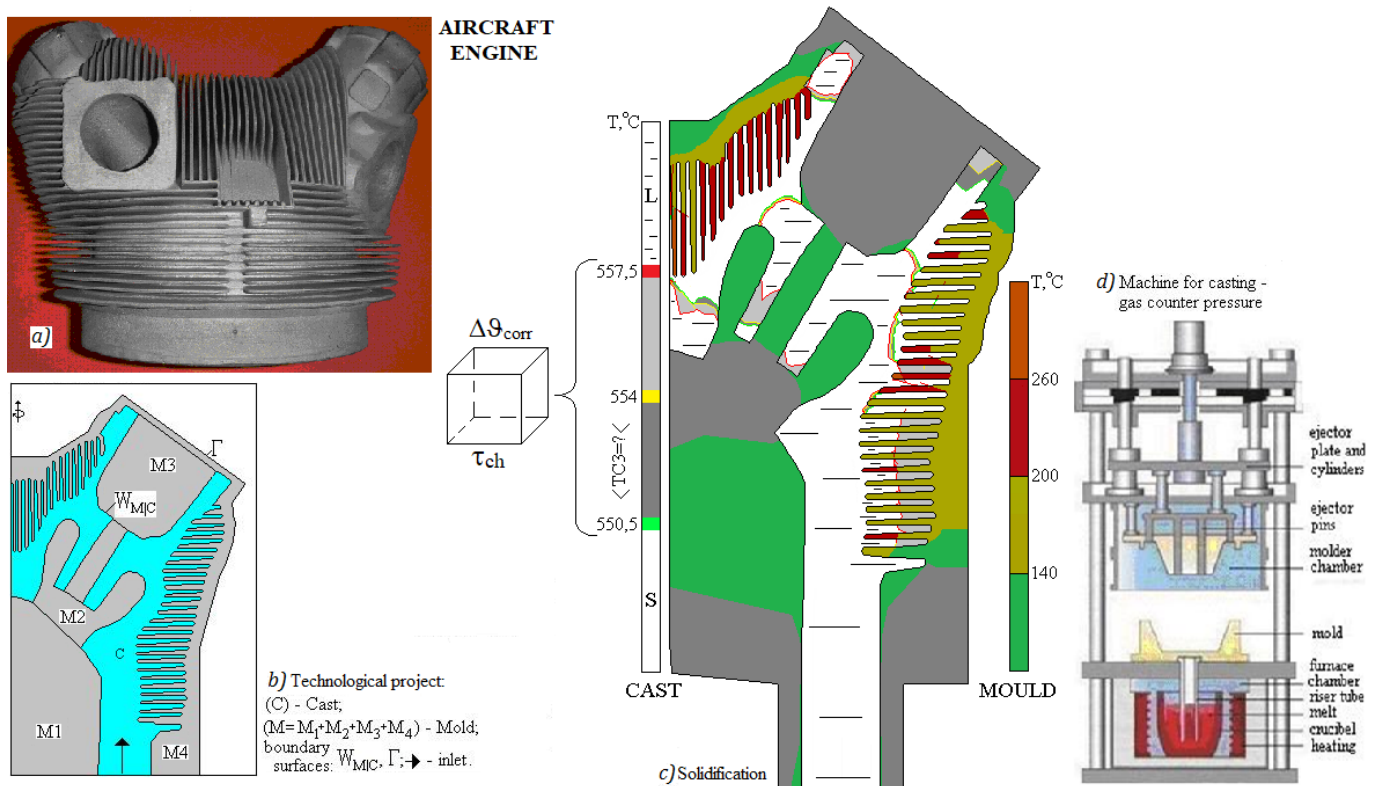
$$\sigma_S^i \leq J_i(t) \quad \text{at } t \in [0, t_f^i]$$

The functional relation between kinetic motion and velocity of crystallization  $v_{crys}$  is driving force of crystallization  $\Delta T_k$  at three growth mechanisms: 1. 2D nucleus formation  $V_{crys} \sim \Delta T_k$ ; 2. through screw dislocation  $V_{crys} \sim \Delta T_k^2$ ; 3. Continuous growth  $V_{crys} \sim \Delta T_k$ . Character macro- and micro-scales on the base of [11] in [8 and 9] is obtained:  $\Delta v_{corr} = t_{corr}^d \tau_{ch}^{-1} = D \Delta v^{-2/d} \quad d = 1, 2, 3 \quad (8)$

where  $\Delta v_{corr}, t_{corr}^d$  are correlations scales and local characteristics

volume and time  $\tau_{ch}$   $d$  is growth directions; and from [2] we accept  $\tau_{ch} = t_f \Leftrightarrow \Delta \theta^{2/d} / D = \Delta \mu / \Delta T_f V_f \quad (9)$

where  $D, \Delta T_f, V_f$  are coefficient of diffusion, locals temperature gradient and velocity of solidification. On Fig.1 present gas counter-pressure technology



**Fig.1 Integration** of casting technology to produce an article whose material has a particular structure and working properties for the longest possible life of the product. **Integration of Foundry Technologies** we consider as hybrid technology - a combination of foundry machines and 3D printers [25, 26, 27 and 28]. We wanted correlation volume eq. (8) and (9) with condition of solidification. The idea is produce cast with simple geometry and finish with 3D printer

## 2. Materials science in foundry – sciences and technologies

Bridge to unite science and technology in materials science is the basic process - the phase transition of the first order is the

fundamental task at foundry Stefan-Schwarz problem (St-Sch) Fig. 2 and 3 are shown the choice of  $\Delta\vartheta_{corr}$  and  $\tau_{ch}$  two bridge tasks: solidification of spheres with radius 50 nm and solution of eq.(4)

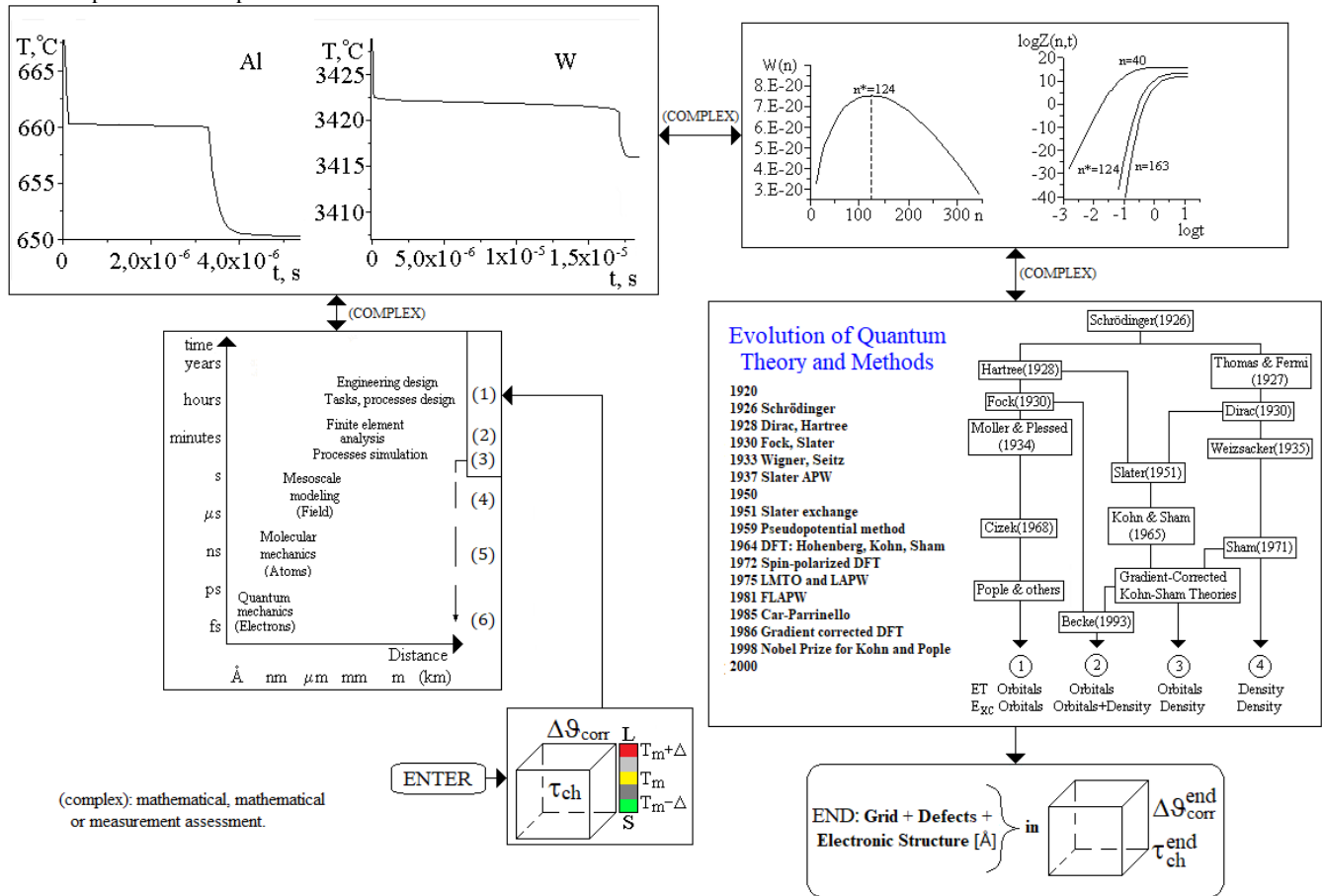


Fig.2. Determination of correlation volume  $\Delta\vartheta_{corr}$  and characteristic phase transition time  $\tau_{ch}$  of first order. We use a multi-scales approach.

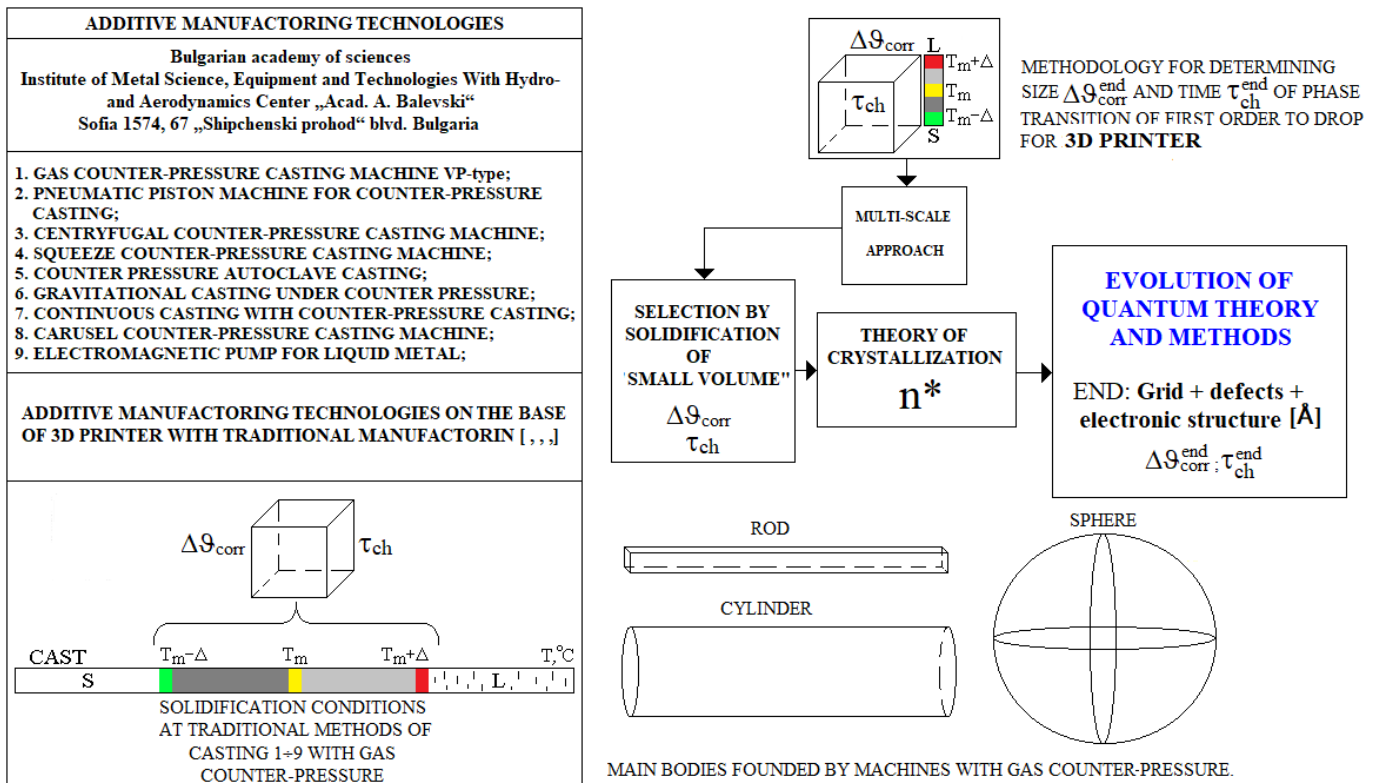


Fig. 3. Additive manufacturing gas counter-pressure casting machines: Castings with simple geometry and final operation with 3D printer.

From Fig. 1, 2 and 3, the correlated volume and the characteristic phase transition time  $\Delta\sigma_{corr}^{and}$  and  $\tau_{ch}^{and}$  we take for a drop size of a 3D printer. This way we can preserve the capabilities of the machines, technologies and materials of our institute. Tasks for solidification of spheres with a radius of 50 nm are key, and the solution of eq.(4) represents the number of nuclei-forming particles. This information is very close to the actual structure of the material. Using quantum mechanics allows you to get complete information about the real structure i.e. the properties of the material.

The multi-scales approach by the bridge tasks of solidification and crystallization are shown interacts with thermodynamics [1, 2, 3, 4, 5, 6]; material science [12, 13, 14]; synergy and methodology of science [18, 19, 20, 21, 22]; metal science [8, 9, 11]; metallography [23]; solid state physics and quantum physics [7, 10, 24, 29]. By choosing a correlation volume, phase transition conditions [25, 26, 27, and 28] allow to transfer through a 3D printer

### 3. Conclusions

Bridged tasks such as solidification a sphere with a radius of 50 nm and a crystallization task are selected.

Nano-scale and number of nuclei-forming particles are robust scientific and technological tools in multi-scale approach and additive production.

An additive manufacturing methodology is created by choosing a drop size for a 3D printer.

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