



Paradox Kobasko as Green Avenue for Design Super Strong Materials

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Abstract: In the paper the three principles of transient nucleate boiling are used to explain why during quenching in cold fluid, performed under increasing pressure, very important for the practice paradox takes place. Its essence consists in simultaneously increase surface temperature and quick decrease core temperature of quenched steel part when heat transfer coefficient tends to infinity. The discovered paradox can be explored for designing super strong bainite via intense quenching combined with the low and high temperature thermomechanical treatment. The paradox is observed when quench tank is hermitized, the probe is immersed into quenchant and pressure is immediately increased. The two generalized fundamental equations related to transient nucleate boiling and convection create the basis for designing software that governs intensive quenching (IQ) process and bainitic transformations. The schematic installations for quenching samples in cold fluid under pressure is discussed in the paper. Example of calculation is provided. The article can be used by students, engineers, professors and just by good people who are interested in achievements of physics.

INTRODUCTION

When somebody says that during quenching in cold fluid surface temperature of steel probe increases while the core temperature decreases, it sounds as a nonsense. Such statement makes a smile on the faces of physicists and brings amusements to specialists involved in steel hardening. Therefore, the author of current article takes full responsibility for such unusual statement. Friends and colleagues jokingly referred to this statement as the Kobasko's paradox, so it appears in the title of this article as a gratitude. The previous two publications [1, 2] discussed in detail the three fundamental principles of transient nucleate boiling, which easily explain the existence of the paradox during quenching in cold vaporable cold fluids used as the quenchants in heat treating industry. For the first time, the paradox was discovered by accurate experiments when quenching steel probes in special chamber with cold fluid and increased versus time pressure [3]. Along with discovering the paradox, the so- called self - regulating thermal process was observed during hardening of steels [4, 5]. It means that surface temperature of probes during transient nucleate boiling maintains at the level of boiling point of fluid insignificantly differs from the average value of the fluid overheat. This fact opens green avenue for bainitic transformations since it creates possibility to delay martensitic transformations via increase boiling point of a boundary layer to martensite start temperature M_s and keep surface temperature of quenched steel parts at this level until core temperature quickly drops to the temperature of bainitic transformations. Also, high and low temperature thermomechanical treatments are possible to create high strengthened bainitic microstructures [6]. Theory and practice for obtaining super durable and ductile bainite is presented in scrupulous investigations of author [7, 8]. Current article serves as a green avenue for optimizing bainitic transformations in condition

when cooling process is extremely intensive. There are two types of bainitic microstructure distribution though section of quenched steel parts. The bainitic microstructure forms throughout all section of the steel part or surface optimal layer consists of super strengthened martensite while the core of steel part consists of the fine bainitic microstructure. The optimal hardenability steel and method for its composing are widely discussed in the books [9, 10]. Very useful information on cooling intensity of different quenchants and methods of their testing one can get from the Refs [11, 12 and 13]. More detail information on intense performance of bainitic transformations and mentioned above paradox are discussed below.

EXPERIMENTS SUPPORTING EXISTANCE OF PARADOX

The experimental system for investigating quenching process in cold fluids under pressure for the first time was discussed in the book [3]. The main details on apparatus and experimental data are presented below (see Fig. 1). The system consisted of an induction heating device (5), a tightly closed quenching chamber (2), a vacuum pump for evacuation and for creation of an under pressure in the chamber, a cylindrical pressure vessel (7) with the compressed air, and measuring devices (8-10) for monitoring temperature fields in test specimens and pressure in the chamber [3, 4]. Inside the chamber was an inductor (4), induction installation (5), coil pipe (1) for cooling (quenchant), electric heaters, and a test specimen (8) suspended on a mobile rod, which moves up and down by turning a solenoid (6) on or off. Observation windows on lateral walls permitted visual monitoring of the formation of vapor films throughout the process. Compressed air was introduced into the chamber from a tank (7), which was used for cooling specimens under pressure. A vacuum pump was connected here for the creation of under pressure above the bath and for vacuum cooling test specimens. The temperature of the quenchant was measured at different points in the tank by using chromyl-copper thermocouples delivered through the bottom of the chamber to potentiometer. The temperature of the specimen was determined by using thin thermocouples inserted into the chamber through the seal in the top cover. Temperature fields were recorded using two potentiometers and an oscillograph [3]. Tests were performed using a cylindrical specimen of 20-mm diameter made of AISI 304 steel. Stainless steel specimen material was used because when steel is austenitized, its thermal and physical properties differ very little from the thermal and physical properties of AISI 304 steel. Differential thermocouples were made of 0.2-mm-diameter wire

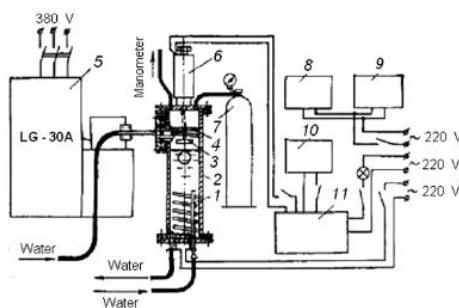


Fig. 1: Installation used for quenching steel specimens in liquid media under controlled pressure [3]: 1, coil pipe; 2, chamber; 3, test specimen; 4, inductor; 5, induction installation; 6, solenoid; 7, tank with compressed air; 8 and 9, potentiometers; 10, oscillograph; 11, rectifier.

Fig. 2 presents numerical FEM calculations concerning quenching cylindrical probe 20 mm diameter in water under variable pressure which was increasing linearly from 0.1 MPa to 2 MPa (see Fig. 2) on the bottom. Calculation shows that surface temperature of the probe at the beginning of cooling increases and then after 7 seconds decreases. The increase of surface temperature is possible if transient nucleate boiling takes place and heat flux density from inside of probe prevails the heat flux density that takes place at the beginning of convection, *i.e.* $q_{nb} > q_{conv}$.

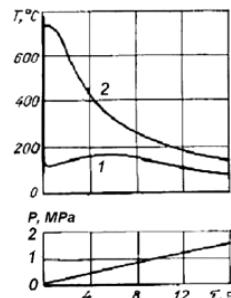


Fig. 2: Numerical calculations representing the effect of variable pressure during a change in temperature at the surface and core of a 20-mm-diameter cylindrical Kh18N9T (AISI 304) steel test specimen during cooling in water at 20°C [3]: a, numerical calculation; b, experimental data; 1, at the surface; 2, at a point a distance of 6.2 mm from the center.

Similar behavior of surface cooling curve was recorded by experiment. Experimental data presented in Fig. 3 show increase surface temperature versus time while core temperature rapidly decreases. The pressure in both cases was increased from 0.1 MPa to 2 MPa. Surface temperature after reaching maximum value at a time 6 seconds started to decrease (see Fig. 2 and Fig. 3).

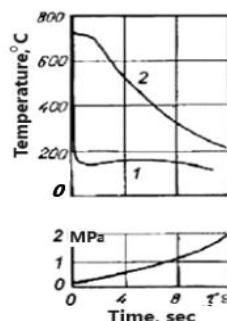


Fig. 3: Experimental data representing effect of variable pressure on surface and core temperatures during quenching in water of cylindrical probe 20-mm-diameter made of AISI 304) steel test specimen during cooling in water at 20°C [3]: a, numerical calculation; b, experimental data; 1, at the surface; 2, at a point a distance of 6.2 mm from the center

Obtained numerical calculations and experimental data were compared with experiments where quenching was performed at the elevated non variable pressure 0.1 MPa and 0.7 MPa (see Fig. 4). As seen from Fig. 4, according to the first principle of transient nucleate boiling, surface temperature of probe drops very rapidly from 800°C to boiling

points of fluids. Developed transient nucleate boiling starts at a time 1 second when pressure in chamber was 0.1 MPa and at 1.5 seconds when pressure was 0.7 MPa. After establishing transient nucleate boiling surface temperature decreases very slowly known as the first type boundary condition where analytical solution exists [16]. Exact solution of such task was obtained for non - linear third type of boundary condition by authors [16, 17].

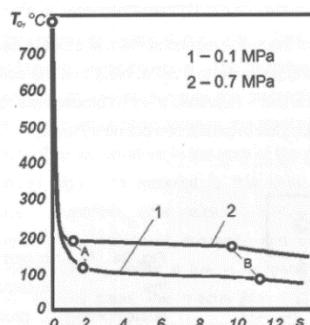


Fig. 4: Cooling surface curves when quenching cylindrical AISI 304 steel probe 20 mm diameter in water under pressure [3]: 1 - 0.1 MPa, 2 - 0.7 MPa.

Fig. 4 shows that surface temperature during quenching under pressure 0.1 MPa and 0.7 MPa drops almost instantly close to boiling point of water and then maintains at this level relatively a long time. When pressure in chamber is 0.1 MPa surface temperature maintains at the level of 100°C while at the elevated pressure 0.7 MPa surface temperature maintains at the level approximately 200°C. According to the first law of transient nucleate boiling cooling surface curves are the same. However, developed nucleate boiling during quenching under pressure 0.7 MPa starts in 1 s while during quenching under pressure 0.1 MPa developed nucleate boiling starts in 1.5 s. The first law of transient nucleate boiling was observed by many investigators in different countries in different periods of time. In the USA, French performed its accurate experiments in 1930 which are of great value even today (see Table 1) [14]. According to accurate experiments of French, surface temperature of spherical samples 12.7 mm - 120 mm diameters during quenching in 5% NaOH - water solution drops from 875°C to 150°C within 0.6 s - 0.95 s (see Table 1). Similar results of experiments were observed in the USA, Ukraine, Japan, Former Soviet Union (FSU) and other countries [3, 14, and 15].

Table 1: Time required for the surface of steel spherical samples to cool to different temperatures when quenched from 875°C in 5 % NaOH-water solution at 20°C and moving at 3 feet per second (0.914 m/s) [14]

D, mm	Time, Sec								
	700°C	600°C	500°C	400°C	300°C	250°C	200	150°C	125°C
12.7	0.028	0.042	0.058	0.071	0.11	0.15	0.26	0.60	1.0
50	0.025	0.04	0.06	0.065	0.08	0.10	0.29	0.65	1.4
120	0.043	0.066	0.09	0.12	0.17	0.21	0.29	0.95	1.5

Table 1 shows that surface cooling curves are identic and differ insignificantly from each other and support the first principle of transient of nucleate boiling.

SCIENTIFIC EXPLANATION WHY PARADOX EXISTS

The behavior of surface cooling curve when temperature maintains at the level of boiling point of a vaporable liquid was called self - regulated thermal process [5]. The overheat, which is a difference between saturation temperature T_s and actual temperature that produces nucleate boiling is very small. It is so small that it can be considered as linear function between points A and B or even constant value (see Fig. 4, and Eq. (1)):

$$T_{sf} = T_s + \Delta \bar{\xi} \approx \text{const} \quad (1)$$

Here T_{sf} is surface temperature, T_s is saturation temperature, $\Delta \bar{\xi}$ is average overheat.

This is the second principle of transient nucleate boiling. For such boundary conditions there are analytical solutions for different forms of quenched steel parts [16]. According to Fourier law of heat conductivity (see Eq. (2), heat flux density is evaluated as:

$$q = -\lambda \frac{\partial T}{\partial r} \quad (2)$$

Vernotton and Lykov [16] proposed to use modified law of Fourier (3) which is written as::

$$q = -\lambda \frac{\partial T}{\partial r} - \tau_r \frac{\partial T}{\partial \tau} \quad (3)$$

Here λ is thermal conductivity of material in W/mK ; τ_r is relaxation time in s^{-1} . If relaxation time τ_r is extremely small value or tends to zero, we have conventional heat conductivity law of Fourier (2).

As known [16], modified law of Fourier generates hyperbolic heat conductivity equation which takes into account free electrons in metal. According to the statistical physics, the pressure created by free electrons in metal is directly proportional to the absolute temperature T (see Eq. (4) [17]):

$$P = nkT \quad (4)$$

Here n is a number of electrons in one sm^3 of metal; k is the Boltzmann constant which is equal to $k = 1,3806488(13) \times 10^{-23} [K^{-1}]$ [17].

Free electrons in metal are reason for absence of any film boiling during quenching in electrolytes and presence of double electrical layer [18, 19]. The high electrical forces in the electrical layer eliminate any film boiling process during quenching in electrolytes. Authors [20] formulated boundary condition for analytical investigations of quenching processes. The hyperbolic heat conductivity equation with non - linear boundary conditions were solved by authors [21, 22]. Obtained analytical solutions are rather complicated requiring costly work of programmers. Formulated laws of transient nucleate boiling simplify cardinally calculations and create express method for recipes development. When any film boiling is completely absent, three laws of transient nucleate boiling take place which during quenching under variable pressure are reason for existing the paradox. The practical use of the paradox for the heat treating and forging industries are considered below.

PARADOX AFFECTS PRACTICE

Fig. 5 presents the basic scheme of an automated process for steel heat treatment under controlled pressure. The quenching process is conducted as follows. When the piston is at starting position I, the part (5), which is austenitized, is delivered to the tray (1). At this time, the driving mechanism is turned on, and the piston occupies work position II, hermetically closing the top of the quench tank. Simultaneously, through an aperture (2), compressed air is introduced, creating the necessary pressure between the quenchant and the piston (cover). Pressure is delivered so that the quenchant saturation temperature approximates the M_s temperature. When quenching in water under pressure, during nucleate boiling there is a delay in the transformation of austenite into martensite; therefore, the effect of high thermal stresses consists of the supercooled austenite. Quench cracks under these conditions are not formed. After nucleate boiling is completed, the surface temperature decreases to quenchant temperature. The formation of the ferromagnetic martensitic phase is fixed by the solenoid (6). The signal from the solenoid is amplified (A) and triggers the relay (R) to actuate the driving mechanism (G), which moves the piston (3) to top starting position I. The part (5) is ejected from the tray (1) and delivered for tempering. It is replaced by the next part, and the cycle is repeated again [3]. This cooling process may be used for continuous automated industrial lines.

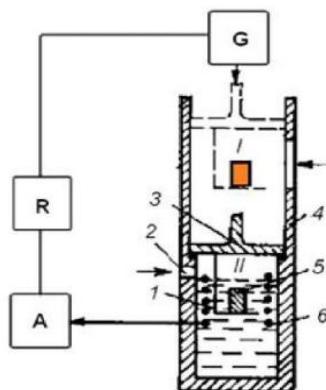


Fig. 5: Basic principal scheme of the automated process of steel quenching in water solutions under pressure: 1, tray; 2, aperture for pumping in compressed air; 3, mobile cover; 4, case of the quench tank; 5, the part to be quenched; 6, solenoid for fixing the initial time of transformation of austenite into martensite; A, the amplifier of a signal of the martensite start; R, relay of current; G, driving mechanism; I, starting position; II, work position.

It should be noted here that cooling is intensive when film boiling is absent even in motionless quenchants because vapor bubbles take from the surface of probe huge amount of thermal energy. That is why a serious and caring attention should be paid to investigations of crisis phenomena including evaluation the first critical heat flux densities taking place during quenching in liquid media to eliminate film boiling processes [23]. As known, intensive and uniform cooling creates surface compression residual stresses and makes steel super strengthened that increases service life of machine components [24, 25]. Very painstaking experiments and numerical calculations in this field were performed by scientists in Germany [26]. Similar approach in the future should be used for investigation

bainitic transformations. Contemporary codes for computer simulations of quenching processes were designed and used by authors [27, 28].

Considered paradox allows preventing martensitic transformations during direct quenching after forgings including low and high temperature thermomechanical treatment (see Fig.6). It has been shown by authors [29] that direct quenching after forging improves strength of material and eliminates some operations making technological process less costly. It means that thermomechanical treatment of bainite also improves its strength and plastic properties similar to martensitic transformations. The low and high temperature thermomechanical treatment can be combined as shown in Fig. 6.

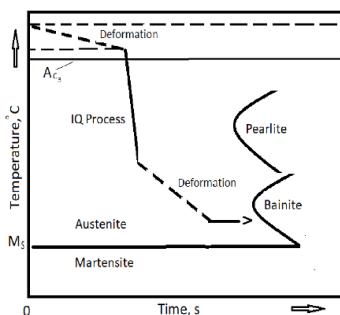


Fig. 6: Scheme of the high and low temperature thermomechanical treatment.

According to Prof. Bhadeshia [7, 8] , the strength of bainite can be factorized into components of the intrinsic strength of pure annealed iron (σ_{Fe}), substitutional solid solution strengthening contributions (σ_{ss}), strengthening due to carbon in solid solution (σ_c), and a variety of microstructural components including dislocation strengthening, particle effects and grain size effects (see Eq (5)):

$$\sigma = \sigma_{Fe} + \sum_i \sigma_{ss}^i + \sigma_c + k_e (\bar{L}_3)^{-1} + k_p \Delta^{-1} + C_{10} \rho_d^{0.5} \quad (5)$$

where ρ_d is the dislocation density and Δ the average distance between a cementite particle and its two or three neighbors. From measuring done on martensite, k_e is approximately equal to 115 MPa m. Assuming that the cementite particles are spherical and of uniform size, k_p is evaluated as $0.52 V_0$ MPa m, where V_0 is the volume fracture of cementite. Dislocation theory for body centered cubic metals gives $C_{10} \approx 7.34$ Pa m.

To establish mass production, the technology must be simple to implement, understandable to wide audience, highly attractive in terms of revenue growth. A technology for producing ultra-strong bainitic microstructures, including thermomechanical processing, could be such a technology. As compared to martensitic transformations, bainitic processing carries a lower risk of unwanted quench cracking and deformation, and offers greater advantages in terms of increased strength and ductility of materials (see Eq. (5)). In our case, simplicity is achieved by the discovered paradox which allows simultaneously immersing the part into the quenching bath and sealing the quenching chamber to establish the required pressure. This creates the possibility for production of

the bainitic microstructure and also for high-temperature and low-temperature thermomechanical processing to produce high-strength materials.

The duration of transient nucleate boiling is directly proportional to squared thickness of steel part, inversely proportional to thermal diffusivity of material, depends on form of steel part, and convective Biot number Bi. The generalized equation for such statement mathematically is formulated as:

$$\tau_{nb} = \Omega k_F \frac{D^2}{a} \quad (6)$$

Here τ_{nb} is duration of transient nucleate boiling measured in seconds; Ω is dimensionless parameter depending on convective HTC; k_F is dimensionless form coefficient; D is thickness of steel part in m; a is thermal diffusivity of material in m^2s^{-1} . Parameter Ω as a function of convective Biot number when initial temperatures T_m and T_o are fixed at 20°C and 850°C are provided in Table 2.

Table 2: Parameter Ω as a function of convective Biot number when initial temperatures T_m and T_o are fixed at 20°C and 850°C .

Bi	Ω	Bi	Ω
0.1	5.40	2	2.41
0.2	4.72	3	1.98
0.3	4.32	4	1.69
0.4	4.02	5	1.46
0.5	3.79	6	1.27
0.6	3.63	7	1.12
0.7	3.47	8	0.98
0.8	3.33	9	0.86
0.9	3.21	10	0.75
1.0	3.11	12	0.56

Table 3 provides coefficients k_F depending on forms of different steel parts.

Table 3: Coefficients k_F depending on forms of steel parts.

Shape of a body	k_F
Plate	0.1013
Cylinder	0.0432
Sphere	0.0253

Since parameter Ω is the function of convective Biot number when initial temperatures T_m and T_o are fixed at 20°C and 850°C , it is important to know convective heat

transfer coefficients versus temperature of water and pressure in chamber with water and conventional bath filled with low concentration of UCON A or UCON E. Real convective heat transfer coefficients (HTCs) versus time and pressure are provided in Table 4. Real convective HTC for (1%) low concentration of polymers at temperature 20°C is equal to 700 $\text{Wm}^{-2}\text{K}^{-1}$.

Table 4: Convective HTCs in $\text{W/m}^2\text{K}$ versus pressure and temperature of water.

P, Mpa	Water 10°C	Water 20°C	Water 30°C
0.1	548	640	1015
0.2	586	690	1105
0.3	609	719	1156
0.4	625	740	1196
0.5	638	756	1223
0.6	648	769	1246
0.7	657	780	1265
0.8	664	790	1280
0.9	670	798	1295
1.0	677	806	1310

UNIVERSAL CORRELATION FOR RECIPES DEVELOPMENT

There is the American patent 6,364,974 BI with intensity of quenching within $0.8 \leq \text{Kn} \leq 1$ where intensive cooling is interrupted at a time when compressive surface residual stresses reach their maximum value [24]. The core temperature for cylindrical samples at the moment of intense cooling interruption is within 400°C - 500°C. At this time the optimal hardened surface layer is already formed while in the core supercooled austenite still exists. In the next step of cooling the fine bainitic microstructure can be achieved via choosing proper tempering temperature. In this case quenched sample consists of martensitic hardened surface layer and bainitic fine or nano microstructure at the core. Surface compressive residual stresses combined with the bainite at the core of machine components increase of their service life. However, machine components have more complicated form that requires computer modelling and help of smart programmers. The author [30] proposed the universal correlation (7) which can be used for cooling time calculation and is written as:

$$\tau_{eq} = E_{eq} \frac{K}{aKn} \quad (7)$$

Here τ_{eq} is time in seconds, E_{eq} is parameter depending on how much dimensionless temperature $N = \frac{T_o - T_m}{T - T_m}$ of different forms decreases, T_o is initial temperature, T_m is bath temperature, T is current temperature, K is Kondratiev form coefficient in m^2 , a is average value of thermal diffusivity of steel in m^2s^{-1} , Kn is dimensionless Kondratiev number.

Equation (7) is used as an express method for heating and cooling time calculation when average values of thermal diffusivity of material and Kn dimensionless number are known. To see how it works, let's calculate cooling time of cylindrical sample 50 mm diameter quenched in low concentration (1%) of UCON E polymer solution from the initial temperature 850°C to 450°C where, as a rule, compressive stresses become maximum using the data presented in Table 5.

Table 5: Parameter E_{eq} as a function of N and Kn [30].

N	Kn = 0.7			Kn = 0.8			Kn = 0.9		
	E_{pl}	E_{cl}	E_{sph}	E_{pl}	E_{cl}	E_{sph}	E_{pl}	E_{cl}	E_{sph}
1.50	0.606	0.807	1.008	0.625	0.845	1.065	0.644	0.883	1.122
2.00	0.894	1.095	1,296	0.913	1,133	1.353	0.932	1.171	1.410
2.50	1.117	1.318	1.519	1.136	1.356	1.576	1.155	1.394	1.633
3.00	1.300	1.500	1.702	1.319	1.539	1.759	1.338	1.577	1.816
4.0	1.587	1.788	1.989	1.606	1.826	2.046	1.625	1.864	2.103
5.0	1.810	2.011	2.212	1.829	2.049	2.269	1.848	2.087	2.326
10	2.504	2.705	2.906	2.523	2.743	2.964	2.542	2.781	3.020
100	4.806	5.001	5.202	4.825	5.045	5.265	4.844	5.083	5.322
1000	7.109	7.310	7.511	7,128	7.348	7.568	7.147	7.386	7.625

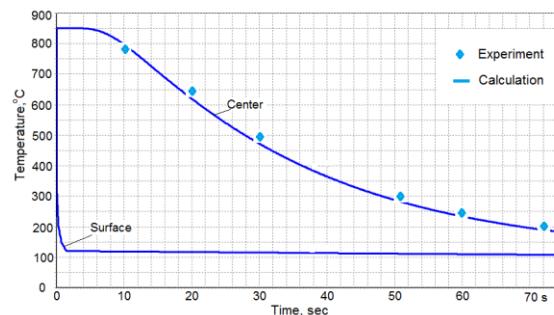


Fig. 7: Surface and core cooling curves when quenching cylindrical sample 50 mm diameter in low concentration of water polymer solution UCON E at 20°C.

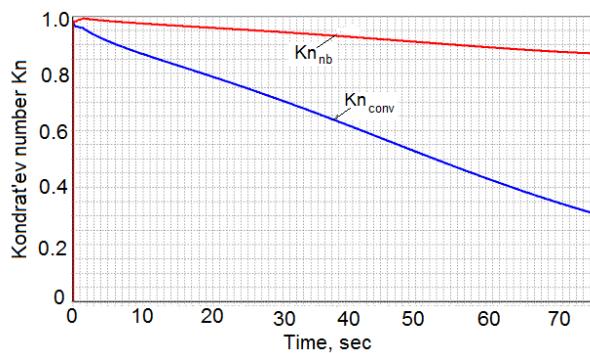


Fig. 8: Real and effective Kondrat'ev numbers Kn versus time when quenching cylindrical sample 50 mm diameter in low concentration of water polymer solution UCON E at 20°C.

For this purpose, one should calculate first the number $N = (850^\circ\text{C} - 20^\circ\text{C})/(450^\circ\text{C} - 20^\circ\text{C}) = 2$. When $N = 2$, the value $E_{eq} = 1.095$ (see Table 5). Kondratiev effective number $Kn = 0.7$ (see Fig. 8). Kondratiev form factor $K = 107.07 \times 10^{-6}\text{m}^2$ and average thermal diffusivity of steel within 100°C and 850°C is $5.36 \times 10^{-6}\text{ m}^2\text{s}^{-1}$. Substituting these data into generalized equation (7), we get 31.54 seconds while real time recorded by experiment is 32 s (see Fig.7). Obtained results of calculations are the same because error is 1.4%. Engineers can use their pocket phones to do such simple and quick calculations.

Thus, the two types of bainitic microstructure distribution inside of the quenched machine components are possible: bainitic fine or nano microstructure is formed throughout all volume of the machine component or bainitic microstructure is formed only at the core of machine component while its surface consists of super strengthened martensite with high compressive residual stresses. In both cases bainitic microstructure improves durability of machine components.

CONCLUSIONS

1. The Kobasko paradox consists in simultaneous heating of the probe surface and rapid cooling of the probe core during intensive quenching.
2. It is used for obtaining bainitic microstructures, as well as to carry out low-temperature and high-temperature thermomechanical processing in order to yield ultra-strong materials.
3. Compared to existing procedures, the proposed new technology is environmentally friendly and accessible for mass production. It can be used in heat treating and forging workshops.
4. The simple method of express cooling time calculation is proposed to provide super strengthened martensitic surface layer of optimal depth and fine or nano bainitic microstructure at the core of machine components.

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