International Journal of Physics and Applications
Online ISSN: 2664-7583; Print ISSN: 2664-7575; Impact Factor: RJIF 5.22
Received: 07-07-2020; Accepted: 22-07-2020; Published: 08-08-2020
www.physicsjournal.in
Volume 2; Issue 2; 2020; Page No. 06-12

Phenomena of physics taking place during hardening steel in water salt solutions of optimal concentration

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Abstract

In the paper the idea on forced heat transfer exchange is discussed and used for designing the new quenching technology which is less costly and can be implemented as a mass production in the heat treating industry. The new technology explores optimal hardenability steel resulting in creation surface compressive residual stresses followed by super strengthening effect that saves alloy elements and increases service life of products. It is shown that optimal quenched layer in steel can be achieved if cooling is interrupted at proper time. For this purpose a generalized equation is used and examples of calculations are provided. If mass production of new technology is achieved, it can reduce emission of CO_2 into atmosphere since long lasting and costly carburization processes can be eliminated via using optimal hardenability steels. The proposed new technology can be combined with exploring hydrodynamic emitters that produce resonance effect to destroy film boiling process. Obtained results are useful for the practice and are interesting for persons who are going to investigate carefully the unusual phenomenon on forced heat transfer exchange.

Keywords: phenomenon, periodical heat transfer exchange, new technology, interruption, environment

Introduction

In last decades more attention was paid to free electrons in metals, especially it was made during quench process investigation. As known, conventional Law of Fourier (1)

$$q = -\lambda \frac{dT}{dr} \quad (1)$$

Generates parabolic heat conductivity equation (2)

$$c\rho \frac{\partial T}{\partial \tau} = \lambda div\left(gradT\right) \quad (2)$$

While modified law of Fourier (3) that takes into account free electrons in metal [1]

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

Generates hyperbolic heat conductivity equation (4) considered and solved by many authors [1, 2, 3]:

$$c\rho \frac{\partial T}{\partial \tau} + \frac{1}{w_r^2} \frac{\partial^2 T}{\partial \tau^2} = \lambda div\left(gradT\right) \quad (4)$$

Here $w_r = \sqrt{\frac{a}{\tau_r}}$ is the speed of thermal wave distribution in metal during its cooling [1].

When any film boiling during quenching is completely absent and transient nucleate boiling takes place, the boundary condition (5) can be used during quenching steel in liquid media [4]:

$$\left[\frac{\partial T}{\partial r} + \frac{\beta^m}{\lambda}\left(T - T_s\right)^m\right]_{r=R} = 0 \quad (5)$$

In many cases initial condition for quench process is written as:

$$T\left(r,0\right) = T_o \quad (6)$$

Transition from nucleate boiling process to convection is evaluated from the equity of heat flux densities at the end of nucleate boiling and at the beginning of convection [4]:

$$q_{nb} \cong q_{conv} \quad (7)$$

After transition when convection starts the boundary condition (8) has a conventional form

$$\left[\frac{\partial T}{\partial r} + \frac{\alpha}{\lambda}\left(T - T_m\right)\right]_{r=R} = 0 \quad (8)$$

The analytical solution of equation (1) with the boundary condition (3) and boundary condition (6) was proposed by authors in 1979 [5]. The solution appeared to be very complicated; however, after its analyzing and numerous accurate experiments, it was reduced to rather simple form (9):

$$\tau_{nb} = \overline{\Omega} k_F \frac{D^2}{a} \tag{9}$$

The first experimental evidence that cooling in electrolytes of optimal concentration is intensive quenching was provided by French in 1930 (see Table 1) [6]. Independently on size of spherical steel samples, the duration of cooling time from 875 °C in 5% water solution of NaOH at 20 °C agitated with 0.914 m/s was very short and varied within 0.6 s – 2 s.

Table 1: Time required for the surface of steel spheres of different sizes to cool to different temperatures when quenched from 875 °C in 5% water solution of NaOH at 20 °C agitated with 0.914 m/s (French, 1930) [6].

Size, Inches, (mm)				**Time, sec**				
	700 °C	**600 °C**	**500 °C**	**400 °C**	**300 °C**	**250 °C**	**200 °C**	**150 °C**
0.25” (6.35)	0.027	0.037	0.043	0.051	0.09	0.15	0.29	0.69
0.5” (12.7)	0.028	0.042	0.058	0.071	0.11	0.15	0.26	0.60
4.75” (120.6)	0.043	0.066	0.09	0.12	0.17	0.21	0.29	0.95
7.15” (181.6)	0.040	0.070	0.100	0.140	0.240	0.310	0.42	1.15
11.25” (285.8)	0.043	0.120	0.190	0.330	0.570	0.960	1.26	2.18

The initial process of cooling during quenching is not enough deeply investigated yet. The authors [7] in 1979 discovered the shock boiling process which is generated by tiny vapor bubbles oscillating with the high frequency. Fig. 1 shows possible ways of initial process of quenching in cold liquids where shock boiling impacts the first critical heat flux densities [7].

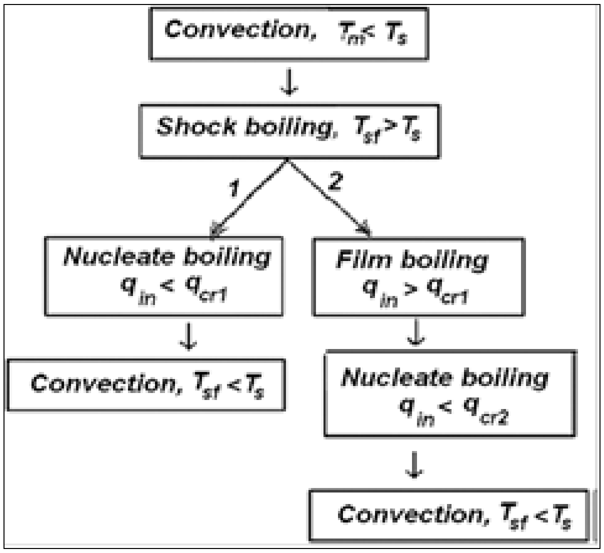

Fig. 1: Two possible boiling processes that may occur during quenching, depending on critical heat flux densities [7].

At the beginning, since the boundary layer is not heated to saturation temperature, natural convection takes place. The shock boiling starts. It should be noted here that Tolu bin sky [8] came to conclusion that during extremely high cooling the ratio q_{cr2}/q_{cr1} is equal to 0.05, *i.e.*

$$\frac{q_{cr2}}{q_{cr1}} = 0.05 \tag{10}$$

During slow cooling this ratio, as is well known [8, 9], is equal to 0.2, *i.e.*

$$\frac{q_{cr2}}{q_{cr1}} = 0.2 \tag{11}$$

It means that shock boiling increases the first critical heat flux density 4 times. That is why, in many cases the film boiling is absent and cooling process becomes intensive.

It was established also that during quenching the self - regulated thermal process takes place where surface temperature during nucleate boiling maintains relatively a long time at the level of saturation temperature T_s of a liquid [4, 10] that can be written as:

$$T_{sf} = T_s + \Delta\overline{\xi} \approx const \tag{12}$$

This period of time is evaluated by Eq. (9) [10, 11].

The value of Ω is a function of the convective Biot number (see Fig. 1). Note that the initial austenitizing temperature and bath temperature are fixed at 850 °C and 20 °C. When convective Biot number $Bi \to \infty$, the value of $\Omega \to 0$. These new processes were carefully investigated by authors [4, 10] and as a result it was established that heat transfer coefficient during nucleate boiling decreases versus time exponentially (see Table 2).

Table 2: Real heat transfer coefficients versus time during quenching spherical steel sample 38.1 mm in diameter in water 5% water solution of NaOH at 20 ºC

2 s	4 s	6 s	20 s
200,000	120,000	90, 000	30,000

For more information regarding heat transfer coefficients during nucleate boiling process see Ref. [4].

Phenomenon of forced heat transfer exchange and new technology

In contrast to results shown in Table 2, it was discovered that during quenching silver probes in electrolytes of optimal concentration heat transfer coefficient increases versus time that contradicts the theory of transient nucleate boiling process. It can be explained by such a way. The density of free electrons on the silver surface layer is larger as compared with steel and electrical forces in double electrical layer are larger. The observed unusual phenomenon consists in the following. When film boiling appears, electrical forces move charged liquid layer to metal surface. The shock boiling starts immediately that creates within the short time the the new film boiling layer process which becomes periodical. And such the periodical cooling process looks like: film boiling → shock boiling. → film boiling → shock boiling → film boiling → shock boiling and so on. Oscillating with the high frequency, shock boiling process generates the high HTCs. With time passing, the shock boiling prevails resulting in increasing average heat transfer coefficient (see Table 3) [12].

Table 3: Heat transfer coefficients (HTCs) taking place during quenching of silver and steel probes in water salt solutions [12].

Material	Probe, concentration and temperature	HTC at 600 ºC	HTC at 500 ºC	HTC at 400 ºC	HTC at 300 ºC
Silver	Spherical probe 20 mm in diameter cooled in 5% water solution of NaCl at 20 ºC	23380	41170	59800	78500
Silver	Spherical probe 20 mm in diameter cooled in 15% water solution of NaCl at 20 ºC	39380	66000	90650	100300
Silver	Spherical probe 20 mm in diameter cooled in 20% water solution of NaCl at 20 ºC	18460	23000	27400	89400
Stainless steel	Cylindrical probe 50 mm in diameter cooled in 1% water solution of UCON E at 23 ºC	4770	4590	2870	2600
Stainless steel	Cylindrical probe 50 mm in diameter cooled in 14% water solution of NaCl at 23 ºC	3550	2930	2326	1440
Stainless steel	Cylindrical probe 12 mm in diameter cooled in 6% water solution of Na_2CO_3 at 20 ºC	121430	-	-	8890

As seen from Table 3, HTCs related to steel probes 12 and 50 mm in diameters are in good agreement with the existing theory of transient nucleate boiling processes that take place during quenching in electrolytes. However, during quenching silver probes HTCs are so large that they cannot belong to film boiling process. Such huge HTCs can be generated only by periodical shock boiling process. The same periodical effect can be generated during quenching of steel parts if negative charge is connected to load (see Fig. 2).

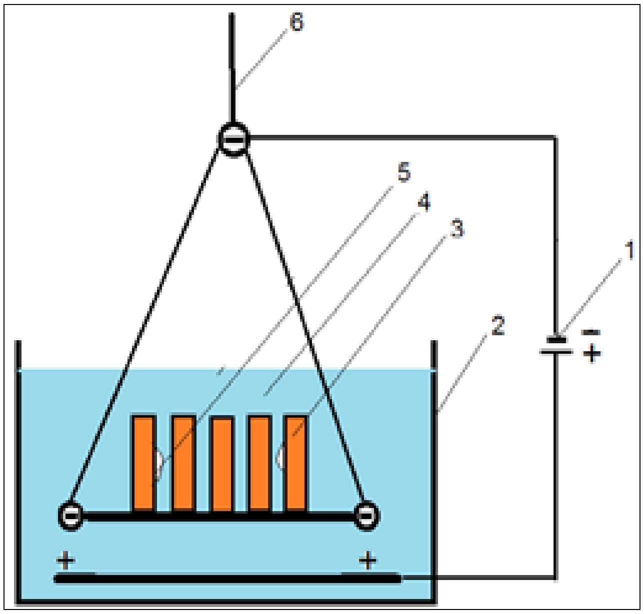

Fig 2: Schematic installation to provide intensive and uniform cooling by exploring external electrical forces: 1 is electrical accumulator; 2 is quench tank; 3 is steel part in a load; 4 is quenchant in quench tank; 5 is vapor bubble; 6 is element of moving system.

The procedure of batch quenching is very simple. Before immersion into electrolyte of optimal concentration the load is negatively charged to start forced heat transfer exchange by creating periodical process consisting in replacement of film boiling by shock boiling of high frequency. The innovation requires the further careful investigations to be widely used in the practice.

The discovered new phenomenon can be used in heat treating industry to make quenching technological process as a mass production. It can be combined with other achievements concerning strengthening of materials. They are as follows.

Compression surface residual stresses and super strengthened material

It was established in 1983 [13] that there is an optimal depth of hardened layer which provides formation of surface compression residual stresses in quenched steel parts. Later was established correlation between chemical composition of steel and size and form of steel part that provides maximal compression residual stresses after quenching (see Eq. (13)) [10, 14]:

$$\frac{DI \cdot Kn^{0.5}}{D_{opt}} = 0.35 \pm 0.095 \tag{13}$$

The developed technology is patented in Ukraine [14]

Here DI is critical diameter in m which depends on chemical composition of steel and is calculated using well known Grossmann’s equation [15]; D_{opt} is thickness of steel part in which optimal hardened layer is formed. More information is available in Refs [10, 14]. A procedure of its use is shown below:

- A steel grade with certain chemical composition is chosen.

- The ideal critical size for this steel is determined.
- The ratio DI/D $_{opt}$ for specific steel part is evaluated and alloy elements are reduced two or three times to satisfy the ratio (13) which must be in a range of 0.2 – 0.5.
- The part is quenched in condition $0.8 \le Kn \le 1$.
- Intensive quenching is interrupted to provide self – tempering.
- The part is tempered at the temperature Ms or higher.

If a ratio (13) is satisfied, residual hoop stress distribution in steel component is optimal. More information related to optimal hardenability steel is available in the book [10] issued by Lambert Academic Publishing in 2018.

Patented technology allows decrease alloy elements in steel, increase service life of machine components and tools, make environment green and significantly reduce cost of technological process. Optimal hardenability steel (OH) differs from low hardenability (LH) steel [16, 17, 18] by its application to any size and form of steel part. Conventional steel can be used as an optimal hardenability steel if correlation (13) is satisfied. Some differences between LH, OH, and high alloy steel are shown schematically in Fig 3.

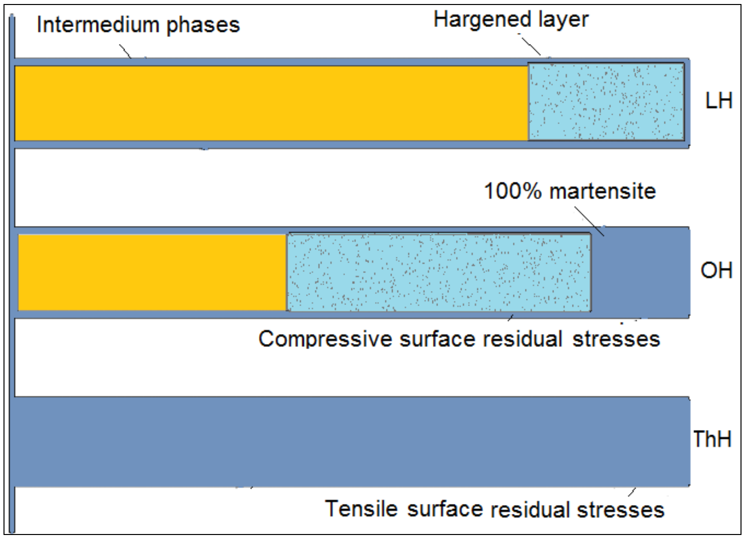

Fig 3: Optimal depth of hardened layer corresponding to the maximum surface compressive residual stresses: LH, low hardenability steel; OH, optimal hardenability; ThH, through hardening [10].

Fig. 4 explains mechanism of super strengthening phenomenon taking place in surface hardened layer [3]. The plates of martensite deform the supercooled austenite that is between them, creating high density of dislocations that are responsible for high strength of material.

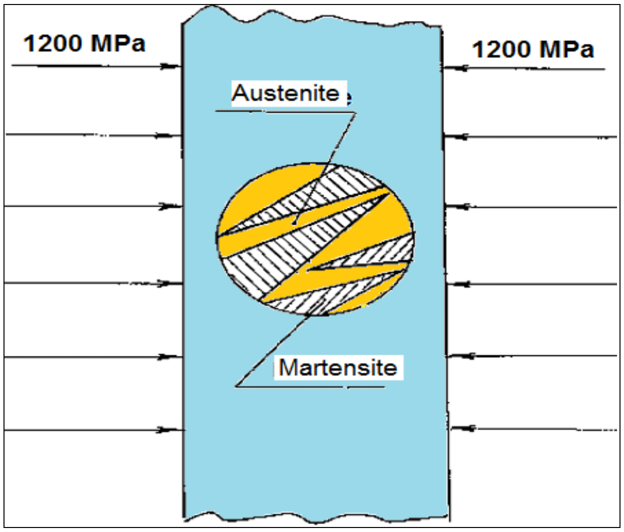

Fig 4: The transformation scheme of austenite into martensite in the compressed layer, illustrating the effect of additional strengthening (super-strengthening) of the material [10].

More information regarding residual stresses validation is available in Refs. [19, 20, 21]. Intensive quenching of optimal hardenability steel should be interrupted to provide self – tempering and provide fine and nano – bainitic microstructure at the core of steel parts. Generalized equation for designing of such process is provided below.

Generalized equation for interruption cooping time at proper time

As it was mentioned above, the accelerated cooling should be interrupted at proper time to avoid quench crack formation and decrease distortion [4]. For this purpose the generalized Eq. (14) is used (see example of calculation below) [22].

$$\tau_{eq} = E_{eq} \frac{K}{aKn} \qquad (14)$$

It is based on heat conduction theory and numerous accurate experiments [1, 4, 22]. Some calculated data are provided in Table 4.

Table 4: Coefficients E_{eq} depending on dimensionless value θ which was decreased from 1.5 to 1000 times for different generalized Biot numbers Bi_V [22].

						$Bi_V = 0.1$ E_{eq}					
N	1.5	2	2.5	3	3.5	4	4.5	5	10	100	1000
Plate	0.44	0.73	0.96	1.14	1.29	1.43	1.54	1.65	2.38	4.64	6.95
Cylinder	0.49	0.77	1.00	1.18	1.33	1.47	1.58	1.69	2.42	4.68	6.99
Sphere	0.55	0.81	1.04	1.22	1.37	1.51	1.62	1.73	2.46	4.72	7.02
						$Bi_V = 0.5$ E_{eq}					
N	1.5	2	2.5	3	3.5	4	4.5	5	10	100	1000
Plate	0.53	0.817	1.04	1.22	1.38	1.51	1.63	1.73	2.43	4.73	7.03
Cylinder	0.65	0.94	1.16	1.35	1.50	1.63	1.75	1.86	2.55	4.85	7.16
Sphere	0.78	1.07	1.29	1.47	1.62	1.76	1.88	1.98	2.67	4.98	7.28
						$Bi_V = 1$ E_{eq}					
N	1.5	2	2.5	3	3.5	4	4.5	5	10	100	1000
Plate	0.57	0.86	1.08	1.27	1.42	1.55	1.67	1.78	2.47	4.77	7.07
Cylinder	0.74	1.03	1.25	1.44	1.59	1.72	1.84	1.94	2.64	4.94	7.24
Sphere	0.91	1.20	1.42	1.60	1.76	1.89	2.01	2.11	2.80	5.11	7.41
						$Bi_V = 2$ E_{eq}					
N	1.5	2	2.5	3	3.5	4	4.5	5	10	100	1000
Plate	0.61	0.90	1.12	1.30	1.46	1.59	1.71	1.81	2.51	4.81	7.11
Cylinder	0.81	1.1	1.32	1.50	1.66	1.79	1.91	2.02	2.71	5.01	7.33
Sphere	1.01	1.30	1.52	1.71	1.86	1.99	2.11	2.22	2.91	5.21	7.51
						$Bi_V = 5$ E_{eq}					
N	1.5	2	2.5	3	3.5	4	4.5	5	10	100	1000
Plate	0.63	0.92	1.14	1.32	1.48	1.61	1.73	1.83	2.53	4.83	7.13
Cylinder	0.86	1.15	1.37	1.55	1.71	1.84	1.96	2.07	2.76	5.06	7.36
Sphere	1.10	1.38	1.61	1.80	1.94	2.08	2.20	2.30	3.00	5.29	7.58
						$Bi_V = \infty$ E_{eq}					
N	1.5	2	2.5	3	3.5	4	4.5	5	10	100	1000
Plate	0.64	0.93	1.15	1.33	1.49	1.62	1.74	1.84	2.54	4.84	7.15
Cylinder	0.87	1.16	1.38	1.56	1.72	1.85	1.97	2.08	2.77	5.07	7.38
Sphere	1.11	1.39	1.62	1.80	1.95	2.09	2.20	2.31	3.00	5.30	7.60

Example: Calculate cooling time for cylindrical sample 20 mm diameter when quenching in water salt solution of optimal concentration at 20 °C where convective HTC is 750 W/m²K.

Value E_{eq} for given condition is: $N = \frac{850^o C - 20^o C}{450^o C - 20^o C} = 1.93$ or $E_{eq} \approx 1.16$ (see Table 4 when Bi $\rightarrow \infty$). Kondrat'ev form coefficient K for given sample is: K = R^2/5.783 = 17.3×10^{-6} m². Kondrat'ev number Kn = 0.55 (see Fig. 4). Average thermal diffusivity of steel within interval of temperatures 450 °C – 850 °C is $a = 5.75 \times 10^{-6} m^2 / s$. According to equation (14), cooling time from 850 °C to 450 °C is 6.3 sec (see Table 5).

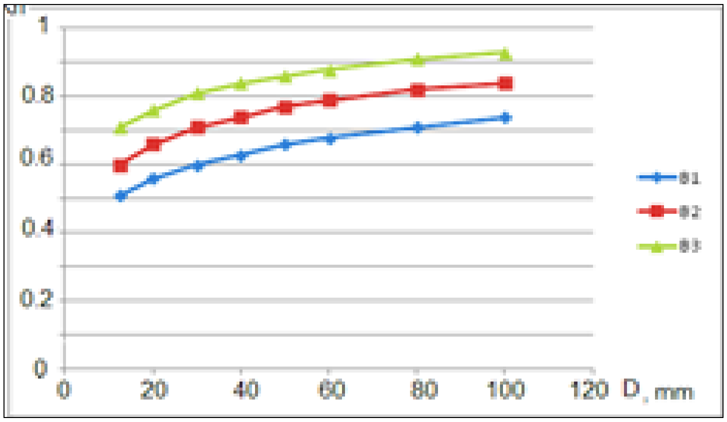

Fig 4: Effective number Kn versus size of cylinders for different convective heat transfer coefficients [23]: B1 is 750W/ m2K; B2 is 1500 W/ m2K; B3 is 4000 W/ m2K

Table 5: Core cooling time for cylindrical specimens of different diameters when quenching from 850 °C to 450 °C in water salt solution at 20 °C with convective HTC equal to 750 W/m²K).

D, mm	**K, m²**	**Kn**	τ_{opt}**, sec**
20	17.3×10^{-6}	0.55	6.3
30	38.9×10^{-6}	0.61	12.9
40	69.17×10^{-6}	0.63	22.1
50	108.08×10^{-6}	0.66	33

For cylindrical steel parts made of medium carbon steels optimal distribution of residual stresses through their section and super strengthening phenomenon takes place when during cooling time interruption core temperature is 450 °C [4]. When quenching steel parts from 850 °C in water salt solutions of optimal concentration at a temperature 20 °C, the value E_{eq} is

5. Discussion

As is well known, low hardenability steels are used for manufacturing relatively small steel parts like different kinds of gears, leaf springs, small rollers and so on (see Table 6) [17, 18] that are quenched intensively in water flow.

Table 6: Production application of intensive-quenched limited hardenability steels [17, 18].

Application	Former steel and process	New steel	Advantages
Gears, modulus m = 5 – 8 mm	18 KhGT, Carburized	58 (55PP)	No carburizing, steel and part costs decrease, durability increases
Large- modulus gears, m = 10 – 14	12KhN3A Carburized	ShKh4	No carburizing, durability increases 2 times, steel cost decreases 1.5 times.
Truck leaf springs	60C2KhG	45S	Weight decreases 15 – 20%, durability decreases 3 times.
Rings and rollers of bearings thicker than 12 mm	ShKh15G (AISI 52100) and 20Kh2N4A	ShKh4	No sudden brittle fracture in service; durability increases 2 times; high production rate.

Low hardenability steels cannot be used for large steel parts because they cannot provide enough thick hardened layer and large steel parts cannot be quenched in water flow in special fixtures. However, the same benefits, which are shown in Table 3, can be achieved if correlation (13) is satisfied. Note that correlation (13) is currently used to optimize quench process of low hardenability steels too. It is suitable for any condition of cooling and optimizing process is corrected by chemical composition of steel. It means that new technology based on phenomenon of forced heat transfer exchange can be a mass production.

Leading experts who are involved in developing new technologies for heat treating industry often underline that effect of global warming can be reduced if green technologies, based on achievements of science, are used. It makes sense to organize special scientific centers working on reducing of CO_2 to make technologies green. There are too many slogans saying that we need to fight global warming, but not many specific suggestions how one should fight global warming, effectively and quickly. Elimination of carburizing processes via using green technologies combined with the optimal hardenability steels is useful in CO_2 emission into atmosphere.

6. Conclusions

1. A new forced heat transfer phenomenon is considered in this paper. Its essence consists in periodical replacement with high frequency of film boiling by shock boiling that considerably increases heat exchange process during quenching of metal components in water salt solutions of optimal concentration. Its specific characteristic consists in increasing heat transfer coefficient versus time and process of quenching is intensive from the very beginning of cooling.
2. Phenomenon of forced neat transfer exchange can be used for developing less costly and less complicated new quenching technology for hardening metals. If further investigated, it can be a basis for organizing a mass production in heat treating industry.
3. The proposed technology is easily combined with the use of hydrodynamic emitters and optimal hardenability steels

that reduces emission of CO_2 into atmosphere via elimination of carburization processes.

4. Accelerated cooling of metals should be interrupted at proper time. It is shown that the generalized equation can be used for this purpose.

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