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RESEARCH ARTICLE

AUSTEMPERING PROCESSES VIA COLD LIQUIDS

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ABSTRACT

The paper discusses austempering process performed at the first step in cold environment friendly liquid and then, at the second step, quenched products go immediately for tempering at a temperature equal or higher of martensite start temperature Ms. The new technology is based on discovered new characteristics of transient nucleate boiling process where surface temperature maintains at the level of boiling point of a liquid relatively a long time. In the paper three variants of austempering processes are considered: austempering process with use of cold water salt solutions of high concentration; austempering process with use of cold water solutions of inverse solubility polymers; austempering process with use of cold plain water under pressure. It is shown that core cooling rates of austempered by new technology products are 2 – 3 times larger as compared with conventional austempering in melted salts and alkalis. The new technology has several advantages. It is possible governing austempering temperature within 100°C and 450°C to provide optimal condition for achieving fine microstructure of highly strengthened bainite. The aim of elaboration is extending significantly size of products suitable for austempering, increasing mechanical properties of a material and making technology green.

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INTRODUCTION

According to authors (Liscic *et al*, 2010), austempering is the isothermal transformation of a ferrous alloy at a temperature below that of pearlite formation and above that of martensite formation. Steel is austemepered by:

- Heating to temperature within the austenitizing range (usually 788°C – 871°C, or 1450°F – 1600°F);
- Quenching in a bath maintained at a constant temperature which is usually in a range of 260°C – 400°C (500°F – 750°F);
- Allowing to transform isothermally to bainite in this bath (usually in melted salt or alkali);
- Cooling to room temperature, usually in still air.

The process is described in detail by the inventors E.C. Bain and E.S. Davenport in US Patent 1,924,099 (Bain and Davenport, 1933). The maximum section thickness for 1080 steel that can be successfully austempered is 5 mm (0.2 in). In addition to indicated steel 1080, steels adaptable to austempering include (ASM Handbook, Vol. 4A, 2013):

- Plain carbon steels containing 0.50 to 1.00% C and minimum 0.60% Mn.
- Chromium-nickel-molybdenum steels such as 4340 and 4350. The hardenability of these steels is so great that they can be through hardened during austempering up to 50 mm (ASM Handbook, Vol. 4A, 2013; Heat Treater's Guide, 1995).
- Cast ductile irons.

Author (Bhadeshia, 2015) underlines that particular form of cast iron is where the matrix of spherical graphite is not pearlite, but bainite. This results in a major improvement in toughness and strength. The bainite is obtained by isothermal transformation of the austenite at temperatures below that at which pearlite forms and is known as austempered ductile cast iron. Comparison of the properties of austempered ductile iron (ADI) against ordinary steel and spherical graphite cast iron is shown in Table 1. Moreover, the Ductile Iron Casting (Ductile Iron Casting, 2018) offers designers versatility and higher performance at lower cost. It is underlined that this versatility is especially evident in the area of mechanical properties where ductile iron offers the designers the option of choosing high ductility, with grades guaranteeing more than 18% elongation, or high strength, with tensile strengths exceeding 120 ksi (825 MPa). Austempered Ductile Iron (ADI) offers even greater mechanical properties and wear resistance, providing tensile strengths exceeding 230 ksi or 1600 MPa (Ductile Iron Casting, 2018). Based on these achievements and wide use of

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austempered steel and cast iron in industry, there is a need to extend sizes of steels and castings at least for 2 – 3 times suitable for austempering processes.

Table 1. Comparison of the properties of austempered ductile iron (ADI) against ordinary steel and spherical graphite cast iron (Bhadeshia, 2015)

Properties	Steel	Spheroid graphite iron	ADI
Yield strength, MPa	740	540	830
Ultimate tensile strength, MPa	910	905	1085
Elongation in %	23	11	14
Charpy impact energy in J	325	75	140

It can be done by performing austempering process via cold liquids (UA Patent No. 109935, 2015). The selection of a quenching salt is governed primarily by the austenitizing temperature, austenitizing medium, and quenching temperature (Dubal, 2003). There are two main categories of quenching salts: nitrate-based and chloride-based, having working ranges of 150 to 595°C (300 to 1100°F) and 425 to 705°C (800 to 1300°F), respectively. Hydroxide- and carbonate - based salts are not recommended for quenching or austenitizing, because these materials adversely affect surface Chemistry. A nitrate-based salt is suitable for quenching from austenitizing temperatures up to 900°C (1650°F). Quenching from a higher temperature is not recommended unless parts are small and well separated. Even then, parts should first pass through a neutral salt bath maintained at a lower temperature. A chloride-based salt is recommended when quenching from high austenitizing temperatures like 980 to 1315°C (1800 to 2400°F), as are required for tool steels. Physical properties of nitrate – based quenching salt are discussed in Ref. (Dubal, 1999; 2003). More information on physical properties of melted salts one can find in literature (Foreman, 1993; Heat Treater's Guide, 1995; Hayrynen, *et.al.*, 2002). Some physical properties of nitrate – based melted salts are presented in Table 2.

Table 2. Physical properties of nitrate – based quenching salt (Dubal, 2003)

Property	Value
Thermal conductivity	0.571 W/mK
Heat transfer coefficient	4500 W/m^2K - 16500 W/m^2K
Drag out rate	50 – 100 g/m^2

Note that small addition of water to a salt bath produces a significant increase in its quench severity, as shown in Table 3. Combination of agitation (50 cm/s (100 ft/min]) and a water addition (~3%) to melted salt increases quench severity three-fold, compared with that of a no agitated, "dry" salt bath that significantly increases surface hardness and depth of hardness. Water content of the bath typically varies from 2 to 3% at 150°C (300°F) to about 0.5% at 315°C (600°F).

Table 3. Effect of increasing water content in % in melted salt on increase quench severity (agitation 6 ft/min)

Water content in %	$^oC/s$	$^oF/s$
1	53	95
2	61	109
3	72	128
5	77	134

Note that cooling rate at the core of standard cylindrical probe (12.5 mm in diameter) at the temperature 720^oC during quenching in cold water polymer solution is $168^oC/s$ which was calculated using equation (Kobasko, *et.al.*, 2010):

$$v = \frac{aKn}{K}\left(T - T_m\right) \qquad \text{…………………(1)}$$

Here v is cooling rate in $^oC/s$; Kn = 0.3; $K = 6.75 \times 10^{-6} m^2$; $T = 720^o C$; $T_m = 20^o C$.

Core cooling rate of standard probe in cold water salt and polymer solutions is 2 – 3 times larger as compared with melted salts containing water.

Self – regulated thermal process

The self – regulated thermal process was discussed many times in published literature (Kobasko, 1968; 1980; 1998; 2005; 2009; 2010; 2016). In this paragraph the main characteristics of the self- regulated process are provided. The self – regulated thermal process (SRTP) is transient nucleate boiling when film boiling is absent and surface temperature of steel parts maintains at the level of boiling point of a liquid relatively a long time and never can be below boiling point of liquid until inside temperature gradient satisfies convection mode (Kobasko, 1980; 2016). The self – regulated thermal process takes place when heat transfer coefficient (HTC) during transient nucleate boiling is very large and during convection is small (Kobasko, 2016). In this case, a big difference between HTCs acts as a relay, supporting surface temperature at the level of boiling point of a liquid. If one doesn't agree with such notion, he will be confused with the possibility of immediate dropping of surface temperature to bath temperature T_m when HTC is very large. Only considering both HTCs simultaneously, it is possible to explain correctly the formation of "a shoulder" on the surface cooling curve. As shown in a book (Kobasko, 1980), there is a possibility to control surface temperature of steel parts during self – regulated thermal process by adjusting pressure or concentration of water salt and polymer solutions. Within the short period of time (1 – 2 sec), the surface temperature of steel parts drops from T_0 to boiling point of a liquid and this short period of time, according to French (French, 1930), doesn't depend on size of steel part (see Table 4).

Table 4. Surface temperature of steel spheres of different diameters versus time in seconds when quenching from 875^oC in 5% NaOH water solution at 20^oC moving with 0.9 m/s (French, 1930)

Diameter, mm	700^oC	600^oC	400^oC	300^oC	150^oC
6.35	0.027	0.037	0.051	0.09	0.69
12.7	0.028	0.042	0.071	0.11	0.60
25.4	0.033	0.042	0.074	0.13	0.82
63.5	0.023	0.039	0.093	0.14	0.59

This important fact allows reconstruction temperature fields in simple steel parts during quenching. As mentioned above, the self –regulated thermal process takes place because a big difference between nucleate boiling heat transfer coefficient (HTC) and convective HTC. During nucleate boiling process the huge amount of thermal energy is taken from the surface of steel parts by growing vapor bubbles. Release frequency and diameter of bubbles for different heated materials are provided in Table 5.

Table 5. Effect of heated surface material on bubble departure diameter and release frequency in the case of boiling water at normal pressure (Tolubinsky, 1980)

Material	d_o (mm)	f(Hz)	$d_0 f(m/s)$
Permanite	2.5	61	0.153
Brass	2.3	67	0.157
Copper	2.8	56	0.157
Average	2.3	62	0.155

The higher overheat of the boundary layer is the larger number N of growing bubbles appear. According to Tolubinsky (Tolubinsky, 1980), the value $d_0 f(m/s)$ doesn't depend on the boundary layer overheat. If so, the heat transfer coefficient during boiling is evaluated as a ratio of heat flux density produced by bubbles to overheat of the boundary layer and is very large, of course. Such approach is used by thermal scientists worldwide (Kutateladze, 1963; Tolubinsky, 1980). In heat treating industry, historically the heat transfer coefficient during boiling is related to bath temperature. The first is a real heat transfer coefficient while the second is an effective HTC which can be used mainly for core cooling time evaluation. The real HTC at the beginning of boiling is very large and can reach more than 200,000 W/m^{2}K. Convective HTC is rather small and for still water and water salt solutions is within 400 - 1200 W/m^{2}K. Convective HTC in average is 200 times smaller as compared with the nucleate boiling process. It means that $\alpha_{conv} << \alpha_{nb}$ or

$$Bi_V^{conv} << Bi_V^{nb} \qquad \text{………………..(2)}$$

Here Bi_V^{conv} is generalized Biot number during convection; Bi_V^{nb} is generalized Biot number during nucleate boiling process. To be more comfortable with the notion of self – regulated thermal process, let's consider well known universal correlation (Lykov, 1967) :

$$\frac{\overline{T}_{sf} - T_s}{\overline{T}_V - T_s} = \frac{1}{\sqrt{Bi_V^2 + 1.437 Bi_V + 1}}$$

…………………..(3)

Here $\overline{T}_{sf}$ is average surface temperature; $\overline{T}_V$ is average volume temperature.

Assume that surface temperature of steel part at the initial moment of time is below saturation temperature T$_s$ in the convection area. Taking into account Eq. (2), one can assume that $Bi_V \to 0$. In this case, according to Eq. (3), $\overline{T}_{sf} \to \overline{T}_V$. It means that surface temperature must increase immediately when it drops below T$_s$ and occurs in convection area. Assume now that overheat of boundary layer is rather large. In this case generalized Biot number Bi_V is very large also which tends to infinity, *i.e.* $Bi_V \to \infty$. According to Eq. (3), in this case $\overline{T}_{sf} \to T_s$ and it means no temperature overheat of a boundary layer and no nucleate boiling at all. Only one way is left. The surface temperature of steel part must be very close to boiling point of a liquid from the very beginning of cooling. The cooling system regulates overheat $\Delta\overline{\zeta}$ by itself which depends on size and form of a steel part. The overheat $\Delta\overline{\zeta}$ is small as compared with the initial temperature T$_0$. For practical use, one can formulate this behavior as:

$$T_{sf} = T_S + \Delta\overline{\zeta} \approx const \qquad \text{…………………………(4)}$$

Here T_{sf} is surface temperature during nucleate boiling process; $\Delta\overline{\zeta}$ is an average overheating responsible for boiling process. Such consideration is possible because $\Delta\overline{\zeta}$ is very small as compared with the initial temperature T_0. Self – regulated thermal process takes place also during quenching steel parts in water solutions of inverse solubility polymers. In this case steel parts are covered by insulating polymeric layer. Let's consider what is happening when cylindrical probe is covered by thin insulating layer. Temperature gradient in the insulating layer is many times larger as compared with the temperature gradient in the quenched probe (Kobasko, Liscic, 2017). Temperature gradient in the insulating layer and probe can be calculated from the conservation law of thermal energy on the boundary insulating layer – steel which can be written as $q_{in} = q_{sl}$ (5):

$$\lambda_{in} grad_{in} = \lambda_{sl} grad_{sl} \qquad \text{………………………(5)}$$

or

$$\frac{grad_{in}}{grad_{sl}} = \frac{\lambda_{sl}}{\lambda_{in}} \qquad \text{………………………(6)}$$

Here $grad_{in}$ is a temperature gradient in the insulating layer; $grad_{sl}$ is a temperature gradient in cylinder; λ_{in} is thermal conductivity of an insulating layer; λ_{sl} is thermal conductivity of steel.

Since surface temperature of insulated cylindrical probe during transient nucleate boiling maintains at the level of boiling point of a liquid (see Eq. (2)), surface temperature of steel must increase to satisfy ratio (6). This behavior of surface temperature of steel part one can use for performing austempering processes of steels with elevated martensite start temperature Ms. As known, thermal conductivity of insulating polymeric layer is very low and is equal approximately to 0.2 W/mK. The thermal conductivity of steel in average is 22 W/mK. It means that temperature gradient in the insulating layer is much larger as compared with temperature gradient in steel part or probe. It is possible if surface temperature of steel part is rather high. That is a reason for increasing surface temperature of steel during nucleate boiling process. This problem was discussed by authors (Kobasko, Liscic, 2017) and it was proved experimentally that surface temperature of Liscic/Petrofer probe during quenching in water polymer solution maintains at the level 400°C – 450°C (Liscic, 2016). This fact is very important and can be used for performing austempering processes in cold liquids. Moreover, it was noticed by mentioned authors that temperature in the surface layer of the probe was varying with passing of time. It can be easily explained by varying the thickness of the insulating layer during quenching. More information on contemporary quenching processes one can find in Ref. (Kobasko, Aronov *et. al.*, 2010). Authors (Kobasko and Zhovnir, 1979) received an analytical solution of parabolic heat conductivity equation with the non – linear boundary condition to calculate duration of transient nucleate boiling process when quenching steel parts in water and water salt solutions. It was assumed that film boiling was completely absent. As a result, simplified equations (7), (8), and (9) were constructed to calculate duration of transient nucleate mode or self – regulated thermal process (Kobasko, 1980):

$$\tau_{nb} = \left[0.24k + 3.21 \ln \frac{\vartheta_I}{\vartheta_{II}} \right] \frac{K}{a} \qquad \text{..........................(7)}$$

$$\vartheta_I = \frac{1}{\beta} \left[\frac{2\lambda(\vartheta_0 - \vartheta_I)}{R} \right]^{0.3} \qquad \text{..........................(8)}$$

$$\vartheta_{II} = \frac{1}{\beta} \left[\alpha_{conv} \left(\vartheta_{II} + \vartheta_{uh} \right) \right]^{0.3} \qquad \text{..........................(9)}$$

$\vartheta_0 = T_0 - T_s$: $\vartheta_1 = T_1 - T_s$; $\vartheta_{II} = T_2 - T_s$; $\vartheta_{uh} = T_s - T_m$ T is temperature; T_o is initial temperature; T_m is bath temperature; T_s is saturation temperature; T_1 is start nucleate boiling temperature; T_2 is finish of nucleate boiling temperature; τ_{nb} is duration of transient nucleate boiling process in sec; R is radius in m; α is thermal diffusivity in m^2/s , λ is thermal conductivity of a material in $W/m\,K$; αconv is convective heat transfer coefficient in *W/m2K*; β =3.41; m= 10/3 k is Kondratjev (or Kondrat'ev) form factor in m2 (Kondratjev, 1952); *k =1,2,3* for plate, cylinder and sphere correspondently. In this paper, effect of β on duration of transient nucleate boiling process was investigated by author (see Table 6 below).

Table 6. Effect of value β on duration of transient nucleate boiling process τ_{nb} and overheat of a boundary layer ϑ_I and ϑ_{II} when quenching cylindrical probe 50 mm in diameter from 850°C in condition $\alpha_{conv} = 750 W/m^2K$

β	ϑ_I	ϑ_{II}	τ_{nb}
2	33.8	14.2	65.3
3.41	20	8.19	66.9
4	17	6.95	67
5	13.64	5.54	67.4

When initial austenitizing temperature is fixed at 850°C and bath temperature at 20°C, then results of calculations, based on equations (7), (8), and (9)), can be presented in a very simple form (10) (Kobasko, 2009):

$$\tau_{nb} = \Omega k_F \frac{D^2}{a} \; . \qquad \text{..................................(10)}$$

The value Ω is a function of convective Biot number and is provided in (Kobasko, 2016). Here k_F is form coefficient ; D is thickness (diameter for Liscic/Petrofer probe); α is thermal diffusivity of a material.

Coefficients k_7 for different shapes of steel parts are presented in Table 7.

Table 7. Coefficients k_7 for steel parts of different shapes

Shape of steel part	k_7
Plate	0.1013
Cylinder	0.0432
Sphere	0.0253
Cube	0.0338
Round plate with a diameter D and height Z = D/n	0.0303
n = 1	0.0639
n = 2	0.0926
n = 5	
Cylinder with a diameter D and height Z = nD	0.0303
n = 1	0.0391
n = 2	0.0425
n = 5	

Transient nucleate boiling processes during quenching steel parts in water and water salt solutions were investigated by authors (French, 1930; Kobasko, 1980; 2016). However, they are not investigated yet properly when steel parts or probes are covered by insulating layer. Authors (Kobasko and Liscic, 2017) started such investigations using Liscic/Petrofer probes. Note that temperature of covered by insulating layer surface of steel parts during transient nucleate boiling (self – regulated) process maintains at the level of boiling point of a liquid that follows the Eq. (4). It was used for:

- Developing IQ – 2 processes (Kobasko, Aronov, *et.al.*, 2010);
- Austempering via cold liquids (UA Patent No. 109935, 2015);
- Improvement of low temperature thermo – mechanical treatment.

Austemering process via cold water salt solutions of high concentration

High concentration of water salt solution increases its boiling point as shown in Fig. 1. By elevating boiling point of a salt solution, it is possible to delay completely martensite transformation if martensite start temperature Ms and boiling point of liquid coincide. For example, it can be observed in products made of ductile iron during their hardening. Moreover, high concentration of salt in water decreases convective heat transfer coefficient (see Table 8). Also, elevated concentration salts in water increases Prandtl number that, according to equation (11), decreases β value. The lesser is β value, the larger is overheat of a boundary layer (see Tables 6 and 9). As known, surface temperatures of product during transient nucleate boiling process maintains at the level boiling point of water salt solution that follows Eq. (4). The results of painstaking experiments (see Table 9), connected with measuring diameters of vapor bubbles and their frequency of departure in salt solutions NaCl and Na_2CO_3 at normal pressure, are presented in a book of the author (Tolubinsky, 1980). As one can see from Table 9, during boiling of high-concentration water solutions of NaCl and Na_2CO_3, their bubble growth rates are the same as for water. Author (Tolubinsky, 1980) noted that the steam bubble growth rate for boiling aqueous solutions is determined by properties of the

Table 8. Convective heat transfer coefficient vs. concentration of $CaCl_2$ in water (Kobasko, 1980)

Concentration, %	5	12	25	37
Convective HTC in W/m^{2}K	700	600	500	450

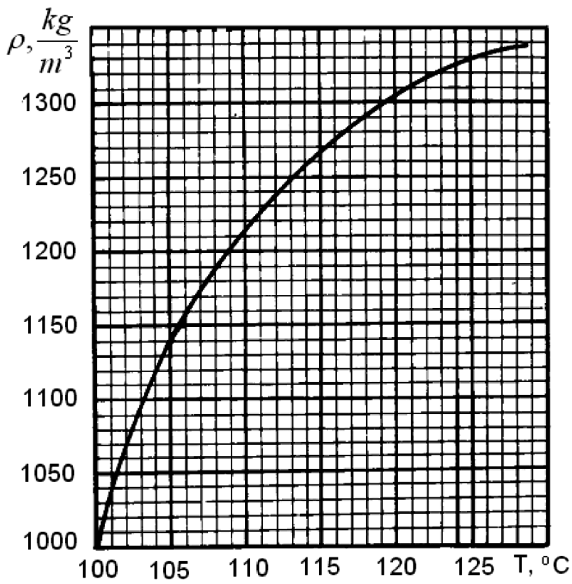

Fig. 1. Saturation temperature vs. concentration for an aqueous solution of $CaCl_2$

Table 9. Comparison of parameters of boiling process for water and aqueous salt solutions at normal pressure (Tolubinsky, 1980)

Substance	Bubble diameter d_0 , mm	Frequency $f, 1/s$	Growth rate $W'', mm/s$
Water	2.5	62	155
25% NaCl water solution	2.4	64.5	155
29% Na_2CO_3 water solution	2.4	65	156

solvent (water) and its steam, and is very weekly affected by properties of solved substances, viscosity and Prandtle number of a solution. Therefore, value of W'' at boiling aqueous solutions can be considered in practice to be equal to W'' at water boiling. Value β can be calculated as (Tolubinsky, 1980; Kobasko, 1980).

$$\beta = \frac{75\lambda'(\rho' - \rho'')^{0.5} g^{0.5}}{\sigma^{0.5} (\rho'' r^* \overline{w}'')^{0.7} \, \Pr^{0.2}} \qquad \text{..............................(11)}$$

where :

$\Pr = \frac{v}{a}$ is Prandtl criterion (number);

α is heat transfer coefficient at nucleate boiling ($W/_{m^2K}$);

λ is thermal conductivity of liquid ($\frac{W}{mK}$);

σ is surface tension ($N/_{m}$);

g is a gravity acceleration ($m/_{s^2}$);

ρ' is liquid density ($kg/_{m^3}$);

ρ'' is steam density ($kg/_{m^3}$);

q is heat flux density (W/m^2);

W'' is vapor bubble growth rate (m/s);

v is kinematic viscosity (m^2/s);

a^* is thermal diffusivity of liquid (m^2/s).

As seen from Eq. (11), the main effect on β value has Prandtl number Pr. It increases significantly with increasing concentration of salts and decreasing bath temperature (see Table 10). Taking into account Table 4 and Eq. (4) and also increased overheat of a boundary layer, it is possible to reconstruct surface temperature of plate like, cylindrical and spherical like samples to calculate temperature field during transient nucleate boiling process. Such approach is shown in Fig. 2. Duration of transient nucleate boiling is calculated using equations (7), (8), and (9). During reconstructing temperature field in cylindrical probe, it was supposed that any film boiling was absent (see Fig. 2). By quenching steel parts in water solutions of elevated concentration, it is possible to maintain their surface temperature at the level of 150°C or higher. As known (see Fig. 3), martensite start temperature Ms for this plain high carbon steel, beginning from 1.25 %C, is equal or below 150°C. It means that austempering process for this steel one can perform using cold water salt solutions. Cooling in water salt solutions should be interrupted at the end of transient nucleate boiling process and steel parts should go immediately for tempering at a temperature higher than martensite start temperature Ms. Note that martensite start temperature and martensite finish temperature can be affected by alloy elements in steel.

Table 10. Prandtl number versus temperature of water

T, ºC	0	10	20	30	40	50	60	70	80	100
Pr	1 3.5	9.45	7.03	5.45	4.36	3.59	3.03	2.58	2.23	1.60

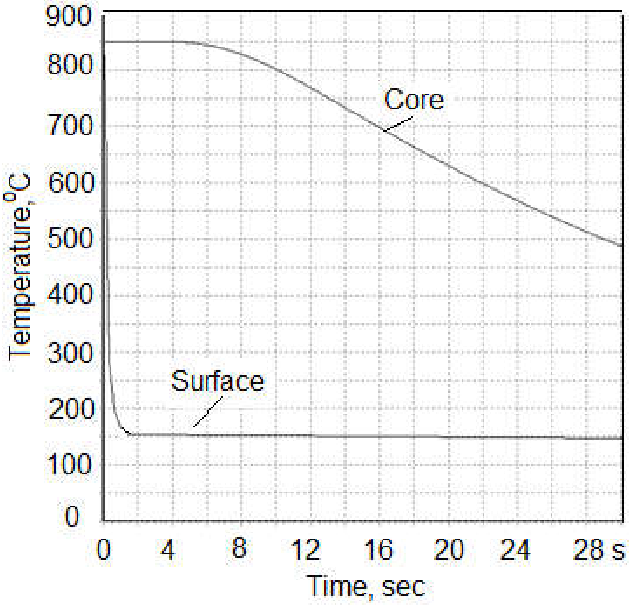

Fig. 2. Core and surface temperature versus time for cylindrical specimen 50 mm in diameter quenched in elevated concentration of $CaCl_2$ in water (see Fig. 1)

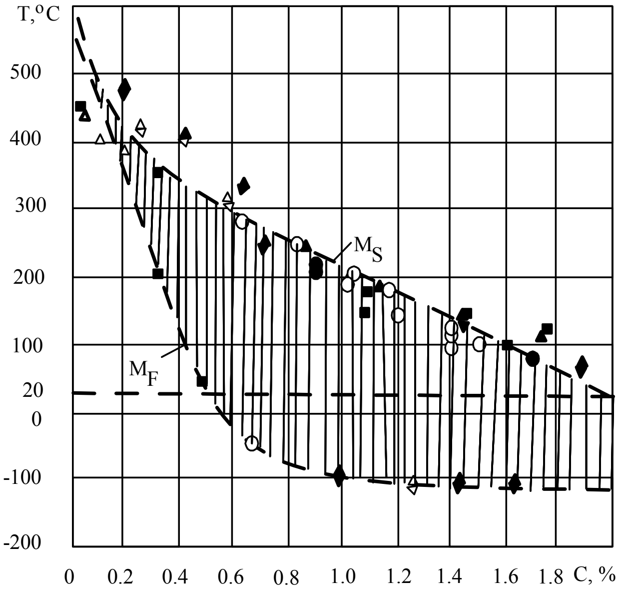

Fig. 3. Martensite start temperature M_S and martensite finish temperature M_F versus content of carbon in steel

Table 11. Saturation temperature in ° C of water versus pressure P in MPa

P, MPa	0.1	0.2	0.4	0.6	0.8	1.0
T_S, ºC	99.64	120.23	143.62	158.64	170.42	179.88

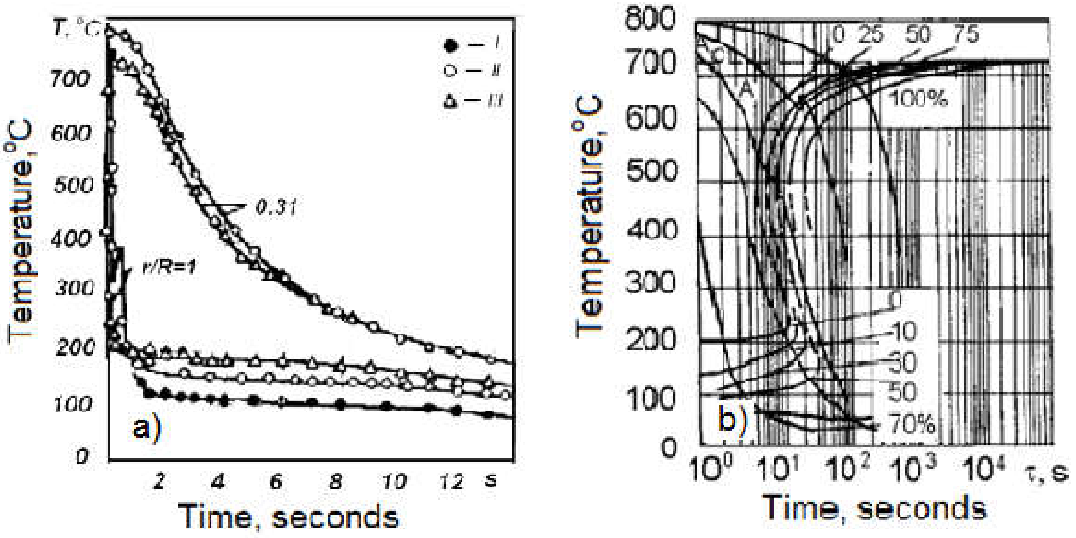

Fig. 4. Effect of pressure (experimental data) on the temperature curves of a cylindrical specimen of 20-mm diameter made of steel AISI 304 (a) and CCT diagram of AISI W1 steel (b): I, 0.1 MPa; II, 0.4 MPa; III, 0.7 MPa (R is the radius of the cylinder, r is the coordinate or distance from the core (Kobasko, 1980).

Along with performing austempering process, cold high concentration water salt solutions can be used for performing martempering processes too.

Austempering process via cold liquids under pressure: The most promising implementation is austempering process via cold water or cold water salt solutions of optimal concentration under pressure.

Elevated pressure and optimal concentration of salts in water miximize critical heat flux densities and it means absence of any film boiling during quenching. Pressure increases boiling point of a liquid which can be equal to martensite start temperature Ms (see Table 11). Fig. 4 presents the experimental data concerning elevation surface temperature (a) during transient nucleate boiling process to martensite start temperature Ms of AISI W1 steel (b) by increasing pressure

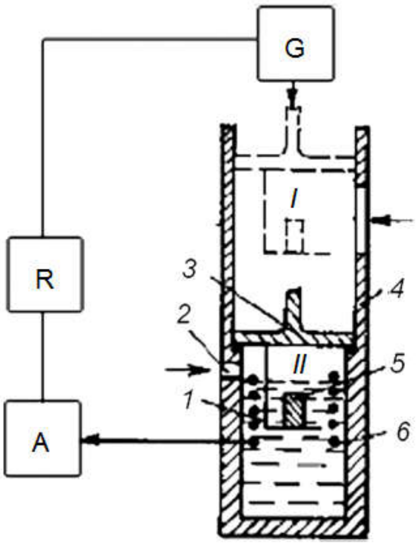

Fig. 5. Basic scheme of the automated process of steel quenching in water and aqueous solutions under pressure (Kobasko, 1980): 1, tray; 2, aperture for pumping in compressed air; 3, mobile cover; 4, case of the quench tank; 5, the part to be quenched; 6, solenoid for fixing the initial time of transformation 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

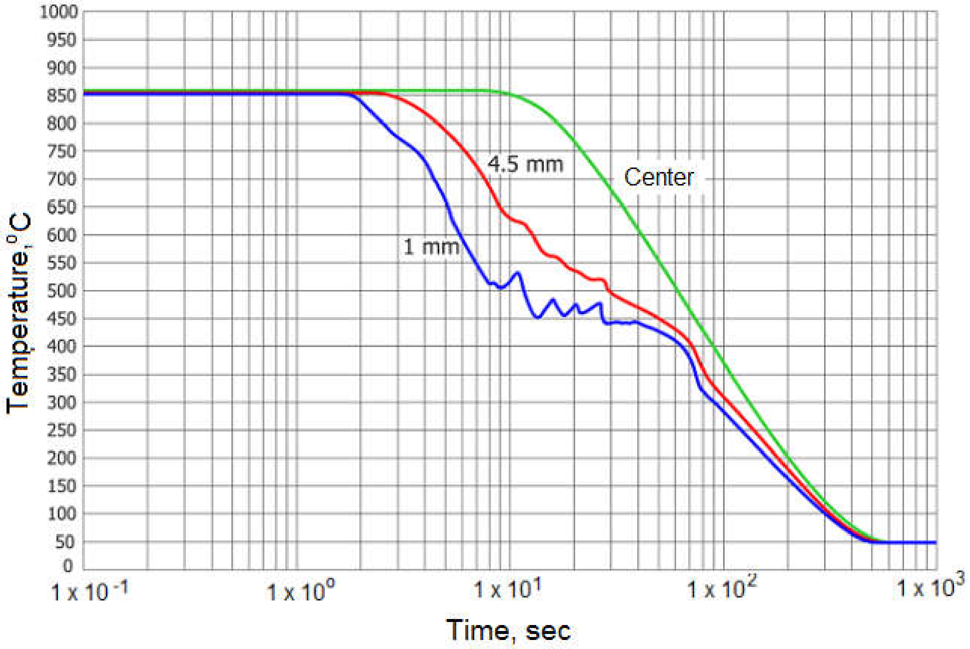

Fig. 6. Cooling temperature curves vs. time measured by the Liscic/Petrofer probe (50 mm in diameter) quenched in a polymer solution of 35°C, with agitation (Liscic, 2016)

Table 12. Cooling rate at the core of Liscic/Petrofer probe within 700°C – 720°C during cooling in different quenching media

Quenchant	Cooling rate, °C/s	Comments
Melted salt at 150°C	9.5	HTC is 4500 W/m^{2}K
Melted salt at 450°C when water is added.	11.5	HTC is 16500 W/m^{2}K
Melted salt at 450°C	4.8	HTC is 4500 W/m^{2}K
Water polymer solution at 35°C	9.5	See Fig.
Water salt solution of $CaCl_2$	17	Saturation temperature is 150°C
Cold water under pressure	25	Saturation temperature is 200°C
Cold water under pressure	27.5	Saturation temperature is 150°C

to 0.7 MPa (Kobasko, 1980). According to obtained data, cylindrical steel parts 20 mm in diameter after quenching in water under pressure should go after 9 seconds of cooling to immediate tempering at 200°C to provide correct austempering process as discussed. The possible installation for performing austempering process via cold water under pressure is shown in Fig. 5.

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 mobile cover 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 cover 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 cover. Pressure is delivered so that the quenchant saturation temperature becomes equal to martensite start temperature Ms. After nucleate boiling is completed, the surface temperature decreases to bath temperature. The formation of the ferromagnetic martensitic phase is fixed by the solenoid (6). The signal from the solenoid is amplified by (A) and triggers the relay (R) to activate the driving mechanism (G), which moves the cover (3) to top starting position I. The part (5) is driven out from the tray (1) and delivered for immediate tempering at a temperature which exceeds Ms. A system shown in Fig. 5 can be installed in forging shops to perform direct quenching processes right after forging. They include:

- Direct quenching after forging to perform high temperature thermo – mechanical treatment with and without austempering process;
- Direct quenching after forging with interruption cooling process to perform low temperature thermo – mechanical treatment;
- Special direct quenching after forging of optimal hardenability steels (Kobasko, 2018) to provide in surface layers of steel parts fine or nano – bainitic microstructure.

Mentioned above technologies allow obtaining super strengthened materials using plain carbon steels because cooling rate of steel parts is several times larger as compared with cooling in melted salts.

Austempering process via cold water polymer solutions of inverse solubility

Water salt solutions and quenching liquid media under pressure can be used successfully for oustempering processes when martensite start temperature Ms is equal or below 200°C. For medium carbon steel, where Ms is 350 °C, can be used water solution of inverse solubility polymers which increase surface temperature of steel parts during self – regulated thermal process up to 450°C. This problem was discussed by authors (Kobasko and Liscic, 2017) using experimental data of Prof. Liscic (Liscic, 2016). Some results of testing Liscic/Petrofer probe in water solution of polymers are presented in Fig. 6. As one can see from Fig. 6, during quenching in polymer solution temperature in surface layers of Liscic/Petrofer probe drops approximately to 450°C and maintains at this level relatively a long time slightly oscillating. Author (Kobasko, Liscic, 2017) explained such behavior of temperature by existing self- regulated process on the insulated surface. If so, oscillation is explained by varying depth of insulating layer during quenching. According to Fig. 6, process of cooling of cylindrical steel parts 50 mm in diameter in agitated polymer at 35°C should be interrupted within 60 sec when temperature in surface layer is 400°C and put immediately for tempering at 400°C if steel parts are made of medium carbon steel. In this case, austempering process will be fulfilled for medium carbon steels. Table 12 provides core cooling rates of Liscic/Petrofer probe within 700°C – 720°C for different austempering processes. Table 12 shows that core cooling rate of Liscic/Petrofer probe is two time larger during quenching in polymer solution as compared with melted salt at 450°C. Austempering processes via cold water under pressure provide three times larger cooling rate as compared with melted salt at 150°C (see Table 12).

DISCUSSION

Austempering process via cold liquids was patented for the first time in Ukraine (UA Patent No. 109935, 2015). The paper discusses physics of austempering processes based on established new characteristics of transient nucleate boiling process presented by Eq. (4) and Eq. (10). Austempering process via cold liquids has several advantages and some disadvantages. The first includes:

- Increased cooling rate during austempering;
- Possibility governing austempering process within larger range of temperatures;
- Provide green technology and simplify austemering processes to make them possible to install in forging shops.

The main disadvantage of proposed invention is overcooling thin elements of complicated steel parts below saturation temperature caused by shorter self – regulated thermal process in thin elements. Until this problem is not completely solved, austempering process via cold liquids will perfectly work for simple forms. Author believes that proposed invention has a great future. To make progress in this new direction, further experimental and theoretical investigations are needed. An excellent tool for further investigations of austempering processes via cold liquids is Liscic/Petrofer probe (Liscic, 2016). Currently, the mentioned problem is under investigations. At present time, self – regulated thermal process is successfully used for performing IQ- 2 processes of simple and complicated steel parts. including martempering. Authors (Aronov and Powell, 2016) received very important and promising results using direct quenching after forging.

Conclusions

- Austempering in cold liquids become possible due to discovered self – regulated thermal process which states that surface temperature of product during transient nucleate boiling process maintains on the level of boiling point of a liquid and never can be below it if $Bi_V^{conv} << Bi_V^{nb}$.
- New austempering technology in cold liquids, patented in Ukraine (UA Patent No. 109935, (2015)), is proposed which explores water salt solutions of high concentration, water polymer solution of inverse solubility and plain cold water under pressure.
- The essence of new technology consists as following. Heated to austenitizing temperature a product is immersed into cold liquid with a boiling point equal or little bit higher martensite start temperature Ms. The product is hold in a liquid until transient nucleate boiling is finished. After that the product is taken out from the liquid and put immediately for tempering at a temperature equal Ms or higher.
- New austempering technology extends sizes of products suitable for austempering, increases mechanical properties of material and makes environment cleaner.
- Along with austempering process, self – regulated thermal process makes possible martempering process

in cold liquids too and extends possibility of low temperature thermo – mechanical treatment.

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