Impact Mechanism of Interfacial Polymer Film Formation in Aqueous Quenchants

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Abstract: The results of studies of the cooling ability, rheological and surface-active properties of aqueous solutions of polyalkyleneglycol, sodium salt of carboxymethyl cellulose and polyacrylamide are presented. The choice of polymers is due to the problem of studying the mechanism of the cooling process in aqueous solutions of polymers. Comparison of the results of complex studies and video surveillance made it possible to propose a substantiated version of the mechanism of heat transfer during cooling of a metal sample in aqueous solutions of polymers. At the moment of shock boiling, a substance is formed in the wall layer, which is a nanosol (for PAG solutions) or a nanogassuspension (for Na-CMC and PAA). Under the action of a shock wave, it is directed from the heated metal surface to the interface between the polymer solution-vapor film, forming an interfacial polymer shock film. One of the stages of the shock mechanism of the formation of a polymer film is the adsorption increase in the polymer concentration on the surface of the bubbles formed during shock boiling; the next stage, the polymer shell of the bubbles, is spent on the formation of an interfacial polymer film. Heat fluxes and heat transfer coefficients are presented as a function of polymer concentration and surface temperature. The research results can be useful for assessing the effect of an interfacial polymer film on the ratio of the initial, first $q_{cr1}$ and second $q_{cr2}$ critical heat fluxes density, which determines the passage of heat transfer stages in water-polymer quenching media (WPQM).

Keywords: Aqueous Quenchants, Impact Mechanism, Interfacial Polymer Film, Chock Film Boiling

1. Introduction

The experience of scientific research of WPQM, the development of optimal compositions, pilot industrial tests and large-scale application in the processes of heat treatment of metals is more than 50 years old. However, at present, the study of the mechanism of the quenching process in WPQS continues, since the complex mechanism of the multistage cooling process in polymer solutions remains a subject of discussion [1-9]. Back in the 80s of the last century, a model of unsteady boiling was proposed, according to which the process of cooling a sample at $T>800^\circ C$ in water goes through five stages: shock boiling in the wall layer, film boiling (FB), transition boiling (TB), nucleate boiling (NB) and convective heat transfer (CONV) [10]. According to the calculations, the time of formation of a continuous vapor layer at the initial temperature of the surface of the part $T_s=840^\circ C$ for most steels is not more than $\tau_{fb}=2$ µs, and the decrease in the temperature of the metal surface is $\Delta T_s=10^\circ C$. Therefore, the authors of concluded that the short time of formation of the steam "blanket" and a slight decrease in the surface temperature $\Delta T_s$ give reason to believe that during quenching in water, the initial stage of shock boiling is replaced by the stage of film boiling. According to the authors, the simulation of the quenching cooling process taking into account 5 stages makes it possible to determine the moment, which is dangerous from the point of view of the strength of the part, when the surface cooling rate passes a critical value in the martensitic temperature range. According to [6], the use of water-polymer quenchants makes it possible to exclude such an
undesirable course of events, which is explained by the formation of a heat-insulating polymer film on the hot metal surface. As a result, the critical heat flux density increases, the film boiling regime is replaced by bubble boiling, after which the stage of convective heat transfer begins. It should be noted that the effect of a heat-insulating coating was first established by the authors of [11] upon cooling a nickel sample covered with a zirconium oxide film. According to the results presented in, the transition from film boiling to bubble boiling in the initial sample is observed at 215°C, while on the sample with a 200 mk thick zirconium oxide coating this transition occurs at 656°C. Calculations carried out in showed that the temperature gradient between the surface and the center of the coated and uncoated specimen is 320°C and 460°C, respectively, and this gradient is localized mainly in the coating. Apparently, the above results led the researchers to the idea of introducing target additives into water, for example, NaCl or polymers, which can form a heat-insulating coating on the metal surface that can intensify heat transfer during steel quenching [6, 7]. Since water-soluble polymers represent a whole class of high-molecular-weight compounds [12], dozens of works in this promising direction were soon published. A detailed analysis of these studies shows that in most of them [5, 6], a heat-insulating film (coating) is formed on the metal surface by itself, i.e. a priori it exists, and its effect on the heat transfer process is determined by the type of polymer, its concentration and the temperature of the solution. However, there is a science - adsorption of polymers [13], which studies the laws of interaction of macromolecules, i.e. polymers with a solid surface, and, as separate subsections, the interaction of macromolecules with the surface in concentrated and dilute solutions, the effect on the value of adsorption, i.e. film thickness, nature of surface and polymer. Particular attention is paid to the study of the properties of boundary layers, namely, the packing density and molecular mobility. The latter seems to be especially important, since these indicators mainly determine such thermophysical properties as thermal and thermal diffusivity [14]. Considering the above, it seems appropriate to focus on the very process of polymer film formation: factors that contribute to its appearance, location, lifetime and heat fluxes that determine its further transformation [15-17]. In the case of saline solutions, the change in the heat transfer mechanism is explained by the deposition of small salt crystals on the metal surface at the initial moments of the process. As the authors note, due to the high surface temperature, micro explosions of crystals occur, which destroy the vapor shell, thus accelerating the onset of the nucleate boiling process. The proposed scheme of heat transfer and wetting in saline solutions seems to be quite reasonable, taking into account that mineral salts of the NaCl type at the moment of adsorption and micro explosion do not pass the stage of thermal decomposition (Tm=801°C, Tb=1413°C) [18]. A different situation arises when organic polymers are used as additives, the temperature of thermal decomposition of which does not exceed 450°C [19]. Consequently, the question arises about the mechanism of the primary act of adsorption of macromolecules on the metal surface at Ts≥800°C, taking into account that the adsorption time does not exceed the duration of the shock boiling stage and is, according to various estimates, from 2 ms to 0.5 s and 1.5 s [10, 19]. Taking these circumstances into account, it is difficult to explain the formation mechanism of the nucleate boiling phase, the appearance of which is explained by the instantaneous formation of a polymer film on the metal surface [6, 15]. It should be noted that if in the early works on the WPQM the mechanism of the formation of the polymer film was given some attention, and the main emphasis was on the mechanism of heat transfer, assuming a priori the presence of a film on the metal surface, then recently this question has practically not been raised. Considering the above, the aim of this work is to study in detail the mechanism of formation of an interfacial polymer film and its role in the process of heat transfer on the surface of a sample heated to 810°C, taking into account that the interaction of a polymer solution with a metal begins from the moment of shock boiling [5].

2. Materials, Devices and Experimental Technique

2.1. Polyalkylenglycol (PAG), Mm=35 · 10^3 (PAG-35)

Polyacrylamide (PAA), Mm=3 · 10^4
Sodium salt of carboxymethyl cellulose (Na-CMC), Mm=3 · 10^4

2.2. Installation and Technique

A description of the laboratory thermo-acoustic system for determining the cooling properties of quenching media is given in [20].

2.3. Investigation of the Rheological Properties of Water-polymer Quenching Media

The dynamic viscosity of the solutions was determined by the falling ball method (Lovis 2000M viscometer, Anton Paar, Austria) and a Reotest-2 rotational viscometer (Germany) with digital indication of the results.

3. Experimental Results

3.1. Rheological Properties of Polymer Solutions

The results of studies of the dynamic viscosity of aqueous solutions of polymers are shown in Figure 1 (a, c), Figure 2 and Figure 3.

According to the results shown in Figure 1, Figure 2, and Figure 3, in the area of low polymer concentrations, a close linear dependence of the shear stress τs on the shear rate Dr is observed, which makes it possible to classify such solutions as Newtonian liquids [21]. When the polymer content rises above a certain one, the so-called critical concentration (Ccr), which is determined by the
stereochemistry of macromolecules and Mm, the Newtonian nature of the solution flow is noticeably violated (Figure 2, b and Figure 3, b), which can be explained by the formation of a network of entanglements and/or structural units in solutions [22].

Figure 1. a) Dependence of dynamic viscosity η_D of PAG-35 solutions on concentration at T=20°C; b) Dependence of dynamic viscosity η_D and shear stress τ_r of PAG-35 solutions on shear rate Dr at T=20°C, C_PAG=2% wt.

Figure 2. a) Dependence of the dynamic viscosity η_D of Na-CMC solutions on concentration at T=20°C, Dr=1312 s^{-1}; b) Dependence of the shear stress τ_r on the shear rate Dr and the concentration of Na-CMC, %wt. at T=20°C.

Figure 3. a) Dependence of the dynamic viscosity η_D of PAA solutions on concentration at T=20°C, Dr=1312 s^{-1}; b) Dependence of the shear stress τ_r on the shear rate Dr and the concentration of PAA, %wt. at T=20°C.

3.2. Surface Tension of Polymer Solutions

According to [23], one of the quality criteria for quenching media is wettability; surface tension, which significantly affects the processes of nucleation, growth and detachment of bubbles during the period of nucleate boiling. To assess the wettability of polymer solutions, the surface tension (γ) was studied using the modified plate (platinum) Wilhelmy method [24].

As can be seen from the results shown in Figure 4, of the three polymers, only PAG-35 can be attributed to the surfactant class, since at a sufficiently low concentration (~0.1%wt.), the γ values decrease by almost 20 mN/m. The polyelectrolyte Na-CMC and the amine-containing PAA reduce the γ values by only 1.0-2.0 mN/m, which does not allow them to be classified as surfactants.

Figure 4. Dependence of surface tension γ of aqueous solutions of PAG-35 (1), Na-CMC (2) and PAA (3) on the concentration of polymers at T=20°C.
3.3. Effect of Polymer Concentration on Cooling Curves (T, °C) and Cooling Rate of the Thermal Probe (dT, °C/s)

3.3.1. Cooling in Aqueous Solutions PAG-35

Figure 5 shows the curves of cooling and the cooling rate in PAG-35 solutions in a wide range of polymer concentrations in distilled water, in Table 1 indicators of the cooling process of the thermal probe in PAG-35 solutions.

![Figure 5. Curves of temperature and cooling rate of thermal probe in PAG35, concentration, %wt.: 1 – 0,0; 2 – 1,0; 3 – 2,0; 4 – 3,0; 5 – 5,0; 6 – 7,0; 7 – 10,0: a) T and dT; b) T and T*.](image-url)
Aqueous solutions of PAG have the property that the polymer loses its solubility during the so-called inversion temperature in the range of 65-80°C [5, 7, 15], and when cooled below, PAG again dissolves completely in water. According to [15], PAG solutions withstand such multiple cycles, which is confirmed by the long (up to 10 years) period of their operation under industrial conditions. Therefore, at present there are publications in which the subject of research is the detailed mechanism of the heat transfer process [25-27]. In this case, it is necessary to use a PAG with a known Mm, since it determines the optimal viscosity range in which the required temperature regime for metal cooling is realized.

According to the results of preliminary experiments, PAG additives with Mm ≥ 35·10^3 at a concentration of C ≥ 1.0%wt. have a noticeable effect on the cooling process. (Figure 5 a, b). In the concentration range from 2.0%wt. up to 10.0%wt. there is a significant decrease in the V_t^{max} and V_t^{TTP300} indicators by 40% and 60%, respectively, and for the T_{TP}^{Vmax} indicator - an increase by 65% (Table 1). A significant decrease (~3 times) in the cooling rate (V_t^{TTP300}) in the lower martensitic temperature range is a positive result, since this reduces the risk of residual stresses and cracks [28]. The transition of the T_{TP}^{Vmax} index to the high-temperature area (Figure 5, b, Table 1) indicates that the transition of film boiling to bubble boiling occurs in the area of higher temperatures beyond the boundary of the martensitic interval [10]. Considering that the dynamic viscosity of water and 1% PAG-35 solution differ by about 9% (Figure 1), and the surface tension of the (γ) PAG-35 solution is 20% lower than the γ values for water, therefore, PAG additives affect the nucleate boiling phase [23]. This is confirmed by the appearance of an inflection on the curves of the cooling rate dT6, T6* and a clear shoulder on the curves dT7, T7* when the thermal probe is cooled in PAG-35 solutions with a concentration of 7%wt. and 10%wt., respectively (Figure 5).

### 3.3.2. Cooling in Na-CMC Solutions

Na-CMC is a salt of a weak carboxylic acid and therefore behaves like a polyelectrolyte in aqueous solutions [17] and is easily combined with water-soluble products - starch, glycols, glycerol, corrosion inhibitors, and biocides. Due to this, solutions of Na-CMC are used as a base in the development of water-polymer quenching agents, which are used in the quenching of high-alloy and heat-resistant steels [29, 30]. Figure 6 shows the curves of cooling and the cooling rate, there are indicators of the cooling process of the thermal probe in Na-CMC solutions in Table 2.
A fairly low concentration of 0.25%wt. polymer in CMC significantly affects the course of the cooling curves and the cooling rate (Figure 6 (a, b), Table 2). On the cooling curve dТ2, a noticeable "shoulder" is observed at t=1.6 s, and the maximum of the dТ2 curve is located near t=3.3 s, while the maximum of the dТ1 curve of water is observed at t=2.2 s. It is interesting that such a separation of the position of the maximum of the cooling rate curve was established when small concentrations of carbon nanotubes (CNT) were added to water [31]. The possibility of the formation of nanoparticles in aqueous solutions of Na-CMC was established in [32], while their radius decreases with increasing temperature and solution concentration. The effect of small additives (0.25%wt.) is accompanied by a sharp decrease of V_t^max values compared to water: ΔV_t^max=49.4°C /s (Table 2), i.e. by almost 20%. With an increase in the concentration of Na-CMC to 0.5% weight an inflection is observed on the curves dТ3 and Т3*, while the value of ΔV_t^max=87.5°C /s, and an increase of the polymer content to 0.75%wt. is accompanied by a slowdown in the decrease in ΔV_t^max to 93.0°C /s. Analysis of the dynamics of the decrease of V_t^max values in the concentration range from 0.0% to 0.75% inclusive shows that it has a character close to exponential. Subsequent decrease in V_t^max values with increasing concentration in relation to V_t^max at C=0.75%wt. obeys a linear law, which gives grounds to assume the existence of two different heat transfer processes in Na-CMC solutions. The first one is in the area of low concentrations of 0.0% - 0.50%wt., in which the cooling proceeds sequentially through the stages: shock boiling, boiling of the shock film [33], nucleate boiling and convection, while the first stage ends with the formation of a polymer film. 

With an increase in the concentration of Na-CMC to 0.75%wt. (Figure 6, b, curve T4*) the second cooling mechanism is realized, as evidenced by a sharp 3-fold increase in the duration of film boiling. With a slight change of the parameters V_t^max, T_{TP}^{V_{max}} and V_{TIP\,300}^t, an
increase in the cooling kinetics indices $\tau_{600}$, $\tau_{400}$ and $\tau_{200}$ by 1.5, 1.8, and 1.6 times, respectively, is observed (Table 2). With a further increase in the content of Na-CMC in the solution, the cooling mode is retained, as evidenced by the congruence of the $T_4^*$. $T_7^*$ curves (Figure 6, b). A significant increase in the duration of the vapor phase can be explained by the formation at the interface between Na-CMC solution of a polymer film, the thickness and strength of which increases with the increase of concentration of Na-CMC. Such a film can form on the surface of the polymer solution almost instantly; at the end of the shock boiling stage, as a result of hydrodynamic shock. The strength of such a film will be determined not only by the concentration of the polymer, but also by its physical and mechanical properties. It can be assumed that the first variant of the heat transfer process is realized with the participation of individual isolated Na-CMC nanoparticles, and with an increase in the polymer concentration, associates of Na-CMC nanoparticles participate in the formation of an impact of polymer film. The analysis of the results from Figure 6, (a) shows that the threshold concentration at which a sufficiently stable polymer film is formed is about 0.4%wt.

### 3.3.3. Cooling in PAA Solutions

Polyacrylamide belongs to a series of linear water-soluble polymers that effectively reduce resistance in a turbulent flow of liquids [12]. This effect manifests itself at very low concentrations (~ $10^{-4}$% of high molecular weight PAA $(M_m=1\cdot10^6-7\cdot10^6$). In aqueous solutions, the PAA macromolecules have the form of a nanosized statistical coil, the dimensions of which are determined by $M_m$ and the temperature of the solution [12]. Figure 7 (a, b) shows the results of the study of the cooling curves, the cooling rate, the parameters of the cooling process in PAA solutions are listed in Table 3.

**Table 3. Cooling parameters obtained by IS09950 at 20°C bath temperature and with no agitation.**

| No. | Indicator (unit) | Cond. Design. | Concentration of PAG-35, %wt. | 0.0 | 0.0075 | 0.015 | 0.003 | 0.05 | 0.10 |
|-----|-----------------|---------------|--------------------------------|-----|-------|-------|-------|------|------|
| 1   | Probe Cooling Time from 850°C to 600°C, s | $\tau_{600}$ | 2.5 | 3.5 | 7.0 | 11.1 | 12.2 | 13.3 |
| 2   | Probe Cooling Time from 850°C to 400°C, s | $\tau_{400}$ | 3.9 | 5.1 | 8.7 | 14.2 | 20.0 | 26.7 |
| 3   | Probe Cooling Time from 850°C to 200°C, s | $\tau_{200}$ | 7.1 | 9.1 | 13.0 | 18.8 | 24.9 | 34.2 |
| 4   | Maximum cooling rate, °C/s | $V_{t_{\text{max}}}$ | 161.1 | 149.2 | 135.8 | 77.0 | 53.1 | 40.5 |
| 5   | Temperature TP at max. cooling rate, °C | $T_{TP_{\text{max}}}$ | 570 | 633 | 571 | 438 | 356 | 276 |
| 6   | Cooling rate, at temperature TP=300°C, °C/s | $V_{t_{TP_{300}}}$ | 69.3 | 57.3 | 52.4 | 48.5 | 46.2 | 37.6 |
A comparative analysis of the results shown in Figures 6 and 7 for aqueous solutions of Na-CMC and PAA indicates a significant similarity of the concentration dependences of the cooling curves, the cooling rate $dT$, and the cooling rate $T^*$ on temperature. Taking this into account, it seems possible that the above description of the results of studies of Na-CMC solutions can be attributed to PAA solutions. As in the case of Na-CMC solutions (Figure 6, b), the entire spectrum of cooling rate curves clearly divided into two families depending on the polymer concentration: 0.0% - 0.015%wt. and 0.03% - 0.10%wt., in which the corresponding cooling mechanism is realized: shock boiling → shock polymer film → film boiling → nucleate boiling → convection. In the formation of a shock polymer film, by analogy with the Na-CMC solution, both individual nanosized PAA coils and associates participate, and the threshold concentration of Na-CMC is about 0.015%wt.

3.4. Video Surveillance of the Cooling Process in Polymer Solutions

3.4.1. PAG-35 Solutions

In the experiments, we used an ELP-USBFDHG-SFV USB webcam, 30 frames per second, connected to a PC via an X96Max attachment, for online observation, an installation and a technique for capturing a TP image in a hardening environment, allowing to record fast processes of phase transitions at unsteady boiling. The duration of shooting the process and fixing the fragments were chosen in accordance with the results shown in Figure 5, a, Figure 6, a and Figure 7, a. For comparison, Figure 8 shows the results of video surveillance of TP when cooled in distilled water.

![Figure 8. Formation of heat transfer stages during cooling in distilled water at $T=20^\circ$C.](image)
The boiling phase of the water vapor film occurs at the moment of shock boiling (arrow), and approximately 0.5 sec. from the lower end of the TP, its destruction begins, which ends by the end of the 2nd sec. of exposure. Then there is a repeated wetting, a transition to the NB phase, then to CONV.

Boiling of the film at the moment of shock boiling is clearly seen in Figure 9, but after 0.1 sec. cloudiness appears around the TP, which is accompanied by an explosion, rewetting and transition to the NB phase. Cloudiness is observed until the beginning of the 2nd sec., then it transforms, and after 2 sec. begins to disappear from the lower end of the TP. After the 10th sec., the cooling moves to the convection phase.

Figure 9. Formation of heat transfer stages in a PAG-35 solution in water, C=1.5%wt., T=20°C.

Figure 10. Formation of heat transfer stages in a PAG-35 solution in water, C=3.0%wt., T=20°C.

Figure 11. Formation of heat transfer stages during cooling of TZ in a PAG-35 solution in water, C=7.0%wt., T=20°C.

Boiling of the shock film continues until the 5th second (Figure 10), it completely covers the surface of the TP. Immediately after the 4th second, cloudiness appears, accompanied by an explosion, rewetting and transition to the NB phase. After 2 seconds, the cloud compresses, changes its shape and size, and after the 12th second, the NB phase moves to the convection phase.

The boiling phase of the shock film is observed up to the 5th second inclusively (Figure 11); it completely and evenly covers the surface of the TP. Immediately after the 5th second, cloudiness appears from the lower end of the TP, which takes 0.2 seconds, covers the entire surface, an explosion occurs, followed by rewetting and transition to the NB phase. Cloudiness is observed until the 6th second, then its shape and size change, remains on the surface of the TP in the form of a rather thick loose film, the NB phase lasts until the 10th sec. inclusively.
3.4.2. Video Surveillance of Na-CMC Solutions
The boiling phase of the shock film is observed up to the 9th second (Figure 12), the film completely covers the surface of the TP. At the 10th second, an explosion occurs, from the lower end of the TP the film begins to collapse. At the 11th second, the nucleate boiling phase NB is observed along the entire height of the TP, which lasts up to the 15th second, after which the cooling moves into the stage of convection. The experimental results presented in Figure 6 and Figure 12, obtained by two independent methods, show a good correlation.

3.4.3. Video Surveillance of PAA Solutions
The film boiling phase is observed up to the 15th second (Figure 13); it completely and evenly covers the surface of the TP up to the 17th second inclusively. At the 18th second, bubbles appear at the lower end of the TP, a "stocking" of the NB phase is formed, which slowly rises upward, displacing the film boiling phase. The process of "putting on the stocking" ends at the 39th second, and at the 41st second the convection stage starts.

3.5. Heat Fluxes and Heat Transfer Coefficients
3.5.1. Heat Fluxes and Heat Transfer Coefficients in PAG-35 Solutions
Using the data of cooling curves (Figure 5), presented in Table 1, by the method of IHC solution [34], the dependence of the value of heat fluxes $q(T_s)$ and the heat transfer coefficient $\alpha(T_s)$ on the surface temperature $T_s$ and the concentration of PAG-35 in water was calculated. Figure 14 shows the heat fluxes of PAG-35 solutions in the concentration range from zero to 10%wt. Heat fluxes quickly reach high values when the thermal probe is cooled to 700°C, then a fan-like divergence is observed, reaching the maximum values of $q(T_s)^{\text{max}}$, which are determined by the polymer concentration. An increase in the concentration of PAG-35 is accompanied by a shift in $q(T_s)^{\text{max}}$ towards high temperatures from 400°C in water to 575°C in a 10% solution of PAG-35, while the value of $q(T_s)^{\text{max}}$ decreases from 4.1 MW/m$^2$ to 2.2 MW/m$^2$ (Figure 14, curves 1 and 6). This character of the curves of the function $q(T_s)$ contributes to the homogeneity of the heat transfer process, homogeneous cooling of parts, minimization of residual stresses and the appearance of cracks [17].

The dependence of the heat transfer coefficient $\alpha(T_s)$ on the concentration of PAG-35 and the surface temperature $T_s$ is shown in Figure 15. Addition of 2%wt. PAG-35 reduces the values of $\alpha(T_s)^{\text{max}}$ by 2000 W/m$^2$ K, while the position of $\alpha(T_s)^{\text{max}}$ remains at about 200°C (Figure 15, curve 2). The decrease of $\alpha(T_s)^{\text{max}}$ value can be explained by the formation of a PAG-35 nanoemulsion as a result of the destruction of a shock polymer film, the thermal conductivity of which is lower than that of water. With an increase in the concentration of PAG-35 to 3%wt. position $\alpha(T_s)^{\text{max}}$ shifts to 320°C, while its value decreases by 6700 W/m$^2$ K (Figure 15, curve 3). Taking into account the results of video surveillance (Figure 10), such a significant decrease of $\alpha(T_s)^{\text{max}}$ value can be explained by the fact that the stage of film boiling prevails in the process of heat transfer with such
Consequently, PAG-35 additives smoothly affect the main parameters of the cooling process $q(\text{T}_s)$ and $\alpha(\text{T}_s)$, which makes it possible to select the composition of water-polymer quenching media in accordance with the requirements of the hardening technology in production conditions.

![Figure 14. Heat flux density $q(\text{T}_s)$ in PAG-35 solutions with concentration, %wt.: 1 - 0.0; 2 - 2.0; 3 - 3.0; 4 - 5.0; 5 - 7.0; 6 - 10.0, $\text{T}$=2°C.](image1)

![Figure 15. Heat transfer coefficient $\alpha(\text{T}_s)$ in PAG-35 solutions with concentration, %wt.: 1 - 0.0; 2 - 2.0; 3 - 3.0; 4 - 5.0; 5 - 7.0; 6 - 10.0, $\text{T}$=20°C.](image2)

### 3.5.2. Heat Fluxes and Heat Transfer Coefficients in Na-CMC Solutions

Figure 16 shows the results of calculations by the IHC method [34] of heat fluxes $q(\text{T}_s)$ in Na-CMC solutions and distilled water. On curve 1, Figure 16, there is a noticeable peak at about 775°C, which corresponds to boiling of the shock water film [33]. With a decrease of the cooling temperature, a rapid increase of the heat flux is observed, reaching $q(\text{T}_s)_{\text{max}}$ at 440°C and a gradual decrease of $q(\text{T}_s)$ values down to 200°C, after which a sharp drop occurs at a cooling temperature of 150°C (Figure 16, curve 1). Addition of 0.25%wt. Na-CMC into water radically changes the character of the $q(\text{T}_s)$ curve (Figure 16, curve 2): rather intense peaks appear at 740°C and 700°C, which should be attributed to the boiling of the shock film [33] and the polymer shock film, respectively, while a small maximum at 600°C corresponds to transition boiling [5]. A shift of $q(\text{T}_s)_{\text{max}}$ is observed in the polymer solution up to 300°C,
while $q(T_s)_{\text{max}}$ value decreases from 3.5 MW/m$^2$ in water to 2.75 MW/m$^2$ at 0.25%wt. Na-CMC solution. Increasing the polymer content to 0.75%wt., 1.5%wt. and 2.0%wt. is accompanied by a proportional decrease of $q(T_s)_{\text{max}}$ and its shift to 275°C, 240°C, and 180°C, respectively (Figure 16, curves 3, 4 and 5). The minimum $q(T_s)_{\text{max}}$ values are observed in the temperature range of 800°C - 530°C in 0.75%wt. solution, 800°C - 400°C in 1.5%wt. solution, and 800°C - 330°C in 2.0%wt. solution of Na-CMC and they correspond to film boiling in a polymer "shell".

The dependence of the heat transfer coefficient $\alpha(T_s)$ of Na-CMC solutions in water on the surface temperature $T_s$ is shown in Figure 17. Addition of 0.25%wt. Na-CMC into water is accompanied by a slight shift of $\alpha(T_s)_{\text{max}}$ from 175°C (Figure 17, curve 1) to 185°C (Figure 17, curve 2), while $\alpha(T_s)_{\text{max}}$ value decreases by 20%. Increasing the concentration of the polymer to 0.75%wt. shifts the position of $\alpha(T_s)_{\text{max}}$ from 185°C to 160°C, i.e. to the area of lower temperatures, which confirms the above assumption about two different heat transfer processes in Na-CMC solutions. With an increase of the polymer content to 1.5%wt. and 2.0%wt. the position and $\alpha(T_s)_{\text{max}}$ value practically do not change, however the $\alpha(T_s)_{\text{max}}$ value decreases by 32% in 0.75%wt. solution, 45% in 1.5%wt. solution and 60% in 2.0%wt. Na-CMC solution. Consequently, the addition of Na-CMC to water affects both the absolute values of $q(T_s)_{\text{max}}$ and $\alpha(T_s)_{\text{max}}$ and the position of their maxima, which makes it possible to regulate the properties of the CMC in accordance with the requirements of the technology of heat treatment of metals.

Figure 16. Heat flux density $q(T_s)$ in solutions of Na-CMC (Na-CMC) with concentration, %wt.: 1 - 0.00; 2 - 0.25; 3 - 0.75; 4 - 1.50; 5 - 2.0 at $T=20°C$.

Figure 17. Heat transfer coefficient $\alpha(T_s)$ in solutions of Na-CMC (Na-CMC) with concentration, %wt.: 1 - 0.00; 2 - 0.25; 3 - 0.75; 4 - 1.50; 5 - 2.0 at $T=20°C$.
3.5.3. Heat Fluxes and Heat Transfer Coefficients in Polyacrylamide Solutions

Figure 18 shows heat fluxes $q(T_s)$ in PAA solutions in the concentration range from zero to 0.1%wt. On curve 1, Figure 18, there is a small but clear peak at about 785°C, corresponding to boiling of the shock film of water [33]. Addition of 0.0075%wt. PAA is accompanied by a noticeable decrease of $q(T_s)_{\text{max}}$ values, while its position shifts from 500°C to 550°C, and a noticeable inflection is observed around 770°C area, which is apparently due to the presence of a powerful shoulder on the curve of the temperature versus cooling rate (Figure 7, c, curve 2). The presence on curve 2, Figure 18 of noticeable inflections at 400°C and 300°C can be explained by the presence of a transition boiling regime in this temperature range [5]. Increasing the concentration of PAA to 0.015%wt. is accompanied by a return of $q(T_s)_{\text{max}}$ to 500°C, decrease of its value by 18% and the appearance of a "shelf" in the range of 720-800°C is explained by the formation of a shock polymer film. The subsequent increase in the concentration of PAA to 0.03%wt., 0.05%wt. and 0.10%wt. accompanied by a synchronous decrease of $q(T_s)_{\text{max}}$ by 60%, 72%, 79% and their shift to 430°C, 350°C and 220°C, respectively. The above changes of the $q(T_s)$ behavior with an increase of the PAA concentration occur...
symbatically with the expansion of the temperature and time range of the film boiling phase (Figure 7 (a, b)), (Figure 18, curves 4, 5 and 6).

The dependence of the heat transfer coefficient \( \alpha (T_s) \) on the PAA concentration and surface temperature is shown in Figure 19. Addition of 0.0075%wt. polymer radically changes the \( \alpha (T_s) \) curve: it contains three distinct intense maxima at 580°C, 400°C and 315°C, the presence of which can be explained by the metastable character of the FB phase at ultralow PAA concentrations. Two maxima at 400°C and 315°C probably correspond to the transition boiling regime in this temperature range [5], followed by a transition to the NB phase. The increase in the concentration of PAA to 0.015%wt. accompanied by a slight shift of \( \alpha (T_s) \) from 420°C, while the \( \alpha (T_s) \) value decreases by 22% in relation to \( \alpha (T_s) \) max in water. The subsequent increase of concentration to 0.03%wt., 0.05%wt. and 0.10%wt. accompanied by a synchronous decrease of \( \alpha (T_s) \) max value by 53%, 62% and 63% and a shift of their maxima to the range of lower temperatures up to 350°C, 280°C and 225°C, respectively. Analysis of changes in the behavior of \( \alpha (T_s) \) shows that there is a symbatic relationship between the decrease of \( \alpha (T_s) \) max and the shift of \( \Delta T_{max} \) from the PAA concentration. The results presented can be useful in the development of new WPQM for heat treatment of metals.

4. Discussion

When analyzing the results obtained, it should be taken into account that of the three selected polymers, only PAG has the property of reversible solubility and belongs to the class of nonionic high molecular weight surfactants [35]. Therefore, these two factors can explain the significant differences in the nature of the concentration dependences of the cooling curves and the cooling rate in PAG-35 solutions (Figure 5 (a, b)) in comparison with Na-CMC solutions (Figure 6 (a, b)) and PAA (Figure 7 (a, b)).

Comparison of the results obtained by measuring the temperature and cooling rate and video surveillance shows that the process of nonstationary boiling during cooling of TP in PAG solutions is multistage, and the number and sequence of the vapor-liquid phases is determined by the concentration and, consequently, the viscosity of the solutions. In the area of low concentrations (up to 2%wt.), the cooling process begins at the moment of shock boiling, which ends with the formation of a polymer shock film at the solution-vapor interface. Due to the low concentration of PAG, the thickness, and, consequently, the strength of the film is low, as a result of which it rapidly collapses, rewetting and transition to the NB phase occurs, then cooling moves to the convection phase. With an increase of PAG concentration up to 3%wt. and 7%wt. the duration of the boiling stage of the film increases to 4 s and 5 s, respectively, which can be explained by an increase of the thickness and, consequently, the strength of the polymer film. Comparing the corresponding kinetic curves of the cooling rate (Figure 5, a) for PAG-35 solutions with a concentration of 3%wt. and 7%wt. with the results of video surveillance, we can conclude that in the area of average concentrations (3.0 - 7.0)%wt. heat transfer occurs mainly in the boiling phase of a film in a polymer shell. This conclusion contradicts the results of a number of studies [4, 36-41], according to which the heat transfer coefficients increase in the following order: 100-250 W/m² · K (FB) < 700-1000 W/m² · K (CONV) < 10²-10³ W/m² · K (NB). Therefore, a version is proposed, according to which, after the formation of a polymer shock film, the bulk of the thermal energy from the heated metal is spent on breaking the H-bonds between the hydrogen of water molecules and the etheric oxygen of PAG macromolecules, i.e. for "dehydration" of polymer chains. Since visually no noticeable turbidity is observed inside the boiling film before the explosion (Figure 8 - Figure 10), therefore, its components are water vapor and individual nanosized PAG macromolecules. According to [37], such systems belong to nanosols (gas + liquid nanoparticles), which obey the corresponding laws of heat and mass transfer. It is possible that under conditions of high temperatures and shear hydrodynamic loads [8], the PAG solution turns into a kind of accumulator of thermal energy. When the inversion temperature in the boundary with the vapor film layer of the solution reached, the PAG loses its solubility and is released from the solution, while the integrity of the phase boundary is violated, the polymer film breaks through and rewetting occurs, i.e. transition to the nucleate boiling phase.

Studies of the cooling and technological properties of water-polymer quenchants based on Na-CMC and PAA have shown [29, 30] that an increase in the concentration of these polymers is accompanied by a noticeable decrease in the cooling capacity of solutions in the upper temperature range; the FB stage becomes more prolonged and stable. Therefore, detailed studies of the cooling capacity of aqueous solutions of Na-CMC and PAA with a known Mm were carried out in a wide range of concentrations. This task is urgent, because WPQM based on these polymers give positive results in the quenching of high-alloy and heat-resistant steels [29, 30, 44]. Despite the large volume of publications on WPQM, there is currently some uncertainty in the cooling mechanism in aqueous solutions of polymers, contradictions in the conclusions when comparing the results of studies of solutions of polymers of different chemical nature [6, 7, 42-44].

The above results allow us to propose a substantiated version of the cooling mechanism of the WPQM. The starting point of our research is the detection of a small peak (1692 W/m² · K) of \( \alpha (T_s) \) values when the unique Petrofer / Liscic thermal probe is cooled in distilled water, which the author attributed to the stage of shock film "boiling " [33]. When a polymer is added to water, a solution is obtained in which the high-molecular component is, depending on the stereochemistry of macromolecules, a network of entanglements, intermolecular bonds - from hydrogen to ionic, a composition of structural units (Na-CMC nanoparticles) [21, 22, 32], i.e. a kind of frame. At the moment of shock boiling, it takes on a significant proportion of hydrodynamic and thermal shocks. The substance formed...
at this moment, which is a nanosol (for PAG solutions) or a nanogas suspension (for Na-CMC and PAA solutions) [37], under the action of a shock wave is directed from the hot metal surface to the interface between the phases of a vapor-polymer solution, thus forming polymer impact film.

5. Conclusion

Taking into account the presented research results and presented in [9, 45], it can be assumed that one of the stages of the impact mechanism of the formation of a polymer film is the adsorption increase in the polymer concentration on the surface of bubbles formed during impact boiling. During the next stage the polymer shell of the bubbles is spent on the formation of an interfacial polymer film. Depending on the chemical nature, physicomechanical properties, and polymer content, the boiling phase of such a bilayer film can be short- or long-term, because its duration increases with an increase of the strength properties of polymers: PAA>Na-CMC>PAG-35. An analysis of the concentration and kinetic curves of TP cooling shows that the threshold concentrations at which an impact polymer film is formed is increased in the following order: 0.015% (PAA)<0.4% (Na-CMC)<2.0% (PAG) with practically the same viscosity of polymer solutions.

The proposed mechanism for the formation of an interfacial heat-insulating film (HIF) allows us to resolve the contradiction arising in the case of accepting the option of forming a HIF on the surface of a hot metal [7, 38-41]. In this case, the initial heat flux q_{up} immediately decreases, it becomes less than q_{up}^{1}, and then the immediate destruction of the FB phase follows. Since, according to the above results, the FB phase is sufficiently stable in solutions of Na-CMC and PAA, and in PAG solutions with a concentration of less than 2%wt. its rapid destruction occurs due to the manifestation of the effect of reversible solubility, therefore, HIF, i.e. polymer film, formed at the interface between the phases, a polymer solution-vapor film by an impact mechanism.

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