Evaluation of possibility of using polysiloxane water emulsion as quenching media for metal heat treatment

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Thermal effect, or heat treatment, as a part of each technological process for manufacture of metal constructions and components, is one of the most widely distributed methods for transformation and improvement of physical-chemical properties and structural features of metals and alloys. Several technological processes, such as quenching of metals, require cooling media. In comparison with conventional media (water and oil), which are characterized by essential ecological, technological and fire-proof technical restrictions, use of polymeric emulsions as quenching media is actual. This sort of quenching media has several advantages: it allows to control metal cooling rate and provides uniform cooling of product surface, what allows to prevent appearance of internal stresses, cracks, deformations and defects in material structure. To develop colloid-stable emulsion, using as cooling media in metal quenching, it is actual to apply polysiloxane resin as polymeric component, due to hydrophobic ability of emulsified polysiloxane. In this case, obtain of water emulsions of polysiloxane resins needs especial conditions of emulsification. The paper suggests use of polysiloxane water emulsion, which was obtained via the method of phase inversion at the optimal temperature conditions as cooling liquid in metal quenching; these optimal emulsification parameters include speed 9,500–10,000 min^{-1}, temperature 60 °C and time period 60 min. Obtained emulsion on the base of polysiloxane and polyvinyl alcohol is characterized by small size of particles (about 1–2 μm), low viscosity (0.2 Pa·s), owing to high shifting forces during emulsification and temperature procedure, while metal surface acquires hydrophobic effect after emulsification, with the value of wetting angle up to 146°. It is shown that consequent lowering of polysiloxane concentration in water emulsion provides low viscosity even during temperature rise. When polysiloxane concentration reaches 7.5 %, emulsion displays good heat-exchanging capacity, which provides quenching rates comparative with use of industrial oil and water-polymeric media. The structure with acicular troostite and cementite, which is typical for substantially lower cooling rate, are mainly forming as a result of polysiloxane water emulsion use during quenching of samples made of steel 35Kh.

Key words: polymeric emulsion, metal heat treatment, polysiloxane, quenching, cooling liquid, polysiloxane emulsion, chromium steel, 35Kh steel.
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Introduction

Development of compositions and methods for stabilization of water polymeric emulsions is one of the actual applied tasks of colloid chemistry. Such emulsions can be used in paint and varnish industry, in building, metallurgical, diamond mining, textile, leather and paper-and-pulp industries, as well as in medicine and cosmetic medicine.

From the other side, a row of technological processes, such as metal quenching, need a cooling media [1–5]. Water is traditionally used as the most cheap heat exchanging media; however it is characterized by high cooling ability within the wide range, what can be cause of increased internal stresses and crack forming. Cooling oils and solvents, from their side, have essential technological and fire hazard restrictions. Thus, use of emulsion as a quenching media is quite prospective from the point of view of combining the properties of so various media.

Depending on the processing aim, different technological requirements are formulated for emulsions [6–9], and they seem to be very contradictive at the first glance: dilution of siloxane hydrophobic agent in water; extraction of the substances using micellar solutions; emulsion polymerization between non-mixing phases with initiator, which is dissolved in water.

Composition and properties of initial components and the methods of their manufacture are the main factors influencing technological properties of emulsions. Analysis of the existing emulsification methods for dispersing systems

[10–12] displayed that obtaining of emulsions can be realized both by mechanical action and by varying of correlation between components and physical conditions. The method of temperature phase inversion is the most actual at present time. However, taking into account the results of previous researches [13–15], it is necessary t examine the factors impeding use if these emulsions for processing the components of various destination.

Surface processing of materials using emulsions allows to reach quality improvement of various functional coatings with minimal consumption of expensive polysiloxanes as a rule [16–18] and to create surfaces with unusual properties for initial materials.

Silicon organic oils are characterized by high temperature of inflammation, inactivity to the environment and slight volatility. They also have high viscosity, which impedes heat exchange, non-mixing ability and very high cost, which makes it difficult to use them as quenching media. However, it is possible to achieve a comparative technical effect by essential decrease of oil amount when using it as water emulsion.

Therefore, the aim of this work is examination of possibility and efficiency of using water emulsion of polysiloxane resin as a cooling media in the process of chromium steel quenching.

Description of materials and analytical methods

To fabricate and examine the properties of polysiloxane emulsion, silicon organic liquid 136–41 (GKZh-94, produced by "Khimprodukt" JSC) and polyvinyl alcohol (PVA) (SUNDY PVA 088-05, produced by "Sinopec Sichuan Vinylon Works") were used. The quenching media on the base of Fe polyacrylate (author's certificate No. 724581, MKI C21D 1/60, 1980) and industrial oil I-20A (according to the GOST 20799-88 "Industrial mask. Technical conditions") were chosen for comparison as a polymeric solution.

Obtaining of polysiloxane emulsion via the method of phase inversion was carried out according to the optimized procedure of high-speed emulsification [19], using laboratorial mixer Silverson with a sieve tip at the following emulsification parameters: speed 9,500–10,000 min^{-1}, temperature 60 °C and time period 60 min (consequently mentioned as the optimal technological procedure). The technology of emulsion preparation concluded in observation of sequential technological stages. Silicon organic liquid (GKZh-94) was placed in the jacket cup, which was previously switched to the thermostatic oven. Circulating thermostatic oven Huber MPC-202C was then switched on for the preset temperature 60 °C and then the mixer with dispersion speed 10,000 min^{-1} was initiated. Gradual introduction of water PVA solution (10 %) using an infusion pump Dixion Instilar 1428 was conducted at the following stage. Total introduction time was 90 min.

Study of hydrophobic efficiency of metal surface after its processing by water emulsion of polysiloxane resin was carried out by the sensor KRUSS DSA 30 via the sessile drop method, using ADVANCED software.

Possibility and efficiency of use of polysiloxane emulsion as a quenching media in the process of metal quenching were evaluated on the example of chromium construction alloy steel 35Kh, which is widely used in machine-building industry for fabrication of connecting details and components for machines and assemblies, for further operation with mechanical processing.

The cylinder samples (d = 46 mm, L = 100 mm) of rolled chromium steel 35Kh were used as the objects for examination of cooling ability. Chemical composition of the samples was determined via optical emission spectrometry (Foundry-Master, Oxford) and is presented in the **Table 1**. Quenching was conducted after heating of samples up to the temperature 860 °C.

Results and discussion

To decrease amount of surface-active substance (SAS), which is introduced in emulsion, and to increase the part of polysiloxane oil with preservation of low dimension degree, it was decided to obtain emulsion using the method of phases inversion at preset temperature [19]. Obtained emulsion can be characterized mainly as mono-dimensional, with size of particles at the level 1–2 μm. Final polysiloxane concentration made 40 %. Surface processing for the sample of steel 35Kh by modified emulsion leads to hydrophobization of metal surface: wetting angle was 146 °.

To assess physical-chemical dynamics of behaviour of obtained water emulsion on the base of polysiloxane oil during quenching, the dependence between efficient viscosity and temperature was determined (**Fig. 1**). In this case parameters of the developed emulsion with different concentration (25 % and 33 %) were compared with characteristics of industrial oil, water and quenching media.

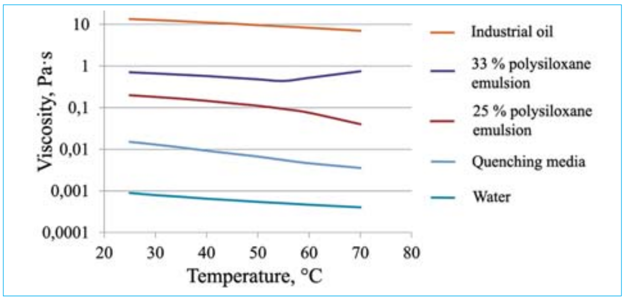

Fig. 1. Relationships between efficient viscosity and temperature of solutions

The typical dependence between lowering of efficient viscosity and temperature is observed for all fluids, but with various intensity degrees. In the case of emulsion with 25 % polysiloxane content, decrease of viscosity is noted, similar to its decrease in quenching solution. Increase of polysiloxane concentration in emulsion up to 33 % leads to non-linear thickening with temperature rise. It can testify on strong

Table 1. Chemical composition of steel cylinder samples

Element	Fe	C	Si	Mn	Cr	P	S	N
Content, %	97.8 ± 0.1	0.36 ± 0.02	0.21 ± 0.01	0.7 ± 0.01	0.94 ± 0.02	<0.01	<0.01	<0.01

structural heterogeneity of these solutions, which appears owing to rebuilding of PVA conformation and variation of emulsion dimension degree with temperature rise. Thus, it is necessary to keep concentration not above 25 % in order to avoid forming of steric complications in emulsion operating during quenching.

Based on the above-described conclusions, emulsion was dissolved to the concentration 13.5 % and 7.5 % of polysiloxane and then tested in accordance with the requirements of ISO 9950 "Industrial quenching oils – Determination of cooling parameters – Non-destructive inspection using a probe of nickel alloy"; probe material was steel 12Kh18N10T (**Fig. 2**). The cylinder sample of steel 35Kh (d = 46 mm, L = 100 mm), with thermocouple located in the geometrical center, was heated up to the temperature 820 °C and dipped into one of the examined media. Both emulsion concentrations show lower speed of heat removal in comparison as with oil I-20A, which is usually used during quenching, as well with quenching media on the base of Fe polyacrylate.

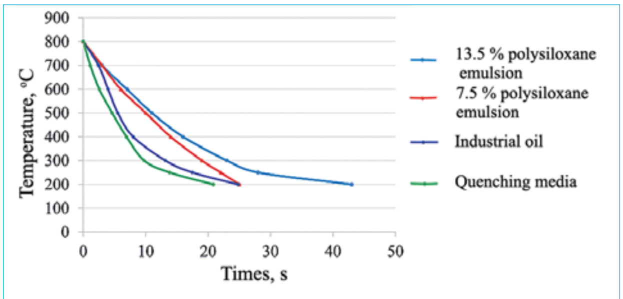

Fig. 2. Cooling speed of thermocouple in various media

To check cooling ability of emulsion in the real quenching conditions, each of cylinder samples of steel 35Kh was heated to 860 °C and held at this temperature during 60 min. Then each sample was dipped into examined liquid – developed emulsion with polysiloxane content 40 %, water and quenching media on the base of Fe polyacrylate. Liquid amount exceeded the mass of cooled sample by 7 times. Thereby and due to low values of inflammation temperatures (200 °C – for oil I-20A and 75 °C – for polysiloxane 136-41), heat removal ability of pure oils was not assessed. The sample was dipped in mixing liquid in vertical downward direction. After cooling to the room temperature, the sample was sawed by two equal parts along its length, and then metal hardness at the distance 3–27 mm from the edge was evaluated. Owing to high hardness (HRC>55) of the sample, which was quenched in water, its comparison was carried out with theoretical data (due to deformation and splitting of the sample) [20].

Emulsion and quenching media display similar influence on the properties of cooled metal (**Fig. 3**). Linear decrease of hardness occurs with increase of the distance from the dipped edge. For the case with the quenching solution, hardness near sample surface and on the depth 20 mm decrease from 48 to 43 HRC, and for the case with the developed emulsion – from 44 to 36 HRC. Water cooling theoretically displays decrease from 55 to 27 HRC, what can evidently finalize in creation of internal stresses.

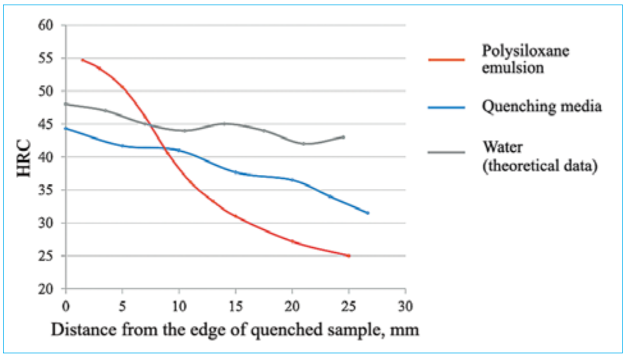

Fig. 3. Hardness variation in the sample cross section after quenching

The samples of metal microsection, which was cooled in the quenching solution, were characterized by homogenous structure, presented mainly by martensite (**Fig. 4*a***). However, metal cooling in emulsion, despite similar homogenous hardness, displays the mechanism of microstructure forming, which differs from water cooling. The structure of acicular troostite (> 80 %) and martensite (< 20 %) is forming mainly near the surface of quenched edge (**Fig. 4*b***), owing to higher cooling speed values. But at the depth 20 mm (**Fig. 4*c***), cooling occurs not so intensively, thereby the structure becomes mainly pearlitic one, with impregnations of cementite and formed net.

Based on the presented data, it can be concluded that the mechanism of cooling ability of polysiloxane emulsions differs from that of polymeric solution of quenching media. Cementite forming in the structure of quenched steel

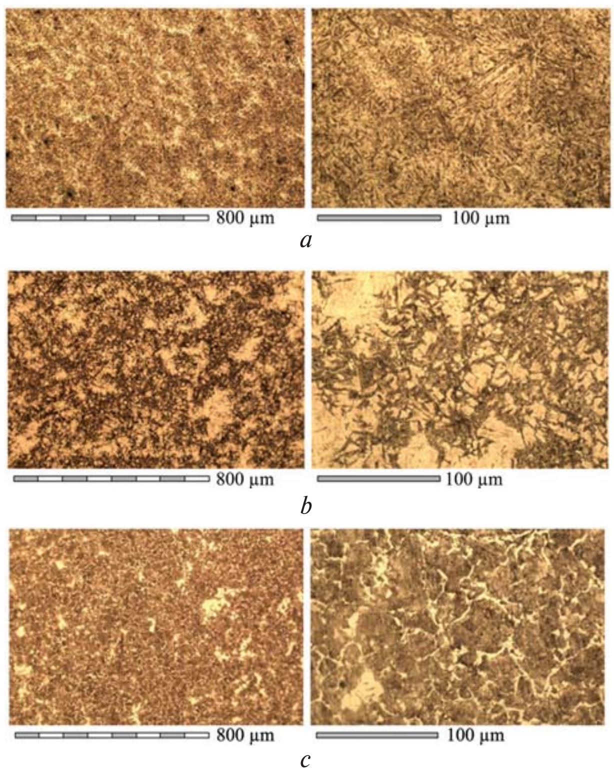

Fig. 4. Microstructure of the metal sample:
a – cooled in quenching solution; *b* – cooled in emulsion; *c* – cooled in emulsion at the depth 20 mm

at the lowered cooling speed can testify on decreased temperature gradient through volume of the sample. Generalized effect is summarized from local concentration and thickening of emulsion near the surface (film creation) and variation of enthalpy during destruction reactions for silicon organic liquid and crystallization of quartzite, which is presented in composition of this liquid, at the increased temperature (> 600 °C) during metal quenching.

Conclusion

Possibility of use of water emulsion on the base of polysiloxane and polyvinyl alcohol as a quenching media for heat treatment of structural alloy steel 35Kh is substantiated and confirmed.

It is shown that water emulsion, which was obtained via the method of phases inversion at the optimal technological conditions, is characterized by small size of particles (about 1–2 μm), low viscosity (0.2 Pa·s), owing to high shifting forces during emulsification and temperature procedure (60 °C). Due to high polysiloxane wetting ability, the developed emulsion forms hydrophobic layer on the metal surface with the value of wetting angle up to 146°.

It was established that heat-exchanging capacity of dissolved water emulsions (emulsion dilution in water to 7.5 %) allows to increase cooling time within the wide temperature range (from 200 to 800 °C) in comparison with quenching solutions and oil. The structure with acicular troostite and cementite, which is typical for substantially lower cooling rate, are mainly forming as a result of polysiloxane water emulsion use during quenching of samples made of steel 35Kh. Based on the results of implemented research, chromium steel, which was subjected to heat treatment in the developed emulsion of polysiloxane resin, is recommended to use in the process of fabrication of connecting details and components for machines and assemblies, for further operation with mechanical processing.

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