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INFLUENCE OF TEMPERATURE ON PROPERTIES OF THE CARBOXYMETHYL CELLULOSE QUENCHING ENVIRONMENT

The carboxymethyl cellulose (CMC) dissolved in water in a percentage between 1 and 5 is used with good results for cooling of cast iron parts with ferritic-pearlitic matrix. The moderate cooling rate of this medium allows the structural transformation of austenite into martensite, but does not favour the increase of structural and thermal stresses dangerous for the integrity of the treated parts. The initial temperature of the cooling medium is an essential component for a correct heating result. In the paper the weldability characteristics of the solution at 20°C, 30°C, 40°C, 50°C, 60°C are studied, as well as the corrosion characteristics at the same temperatures for ferritic-pearlitic nodular cast iron samples. The effect of temperature on the surface properties (water contact angle and corrosion) was investigated. Cyclic and linear voltametry was carried out at the mentioned temperatures and SEM (Scanning Electron Microscopes) photographs and EDX (Energy Dispersive X-ray) analyses were made of nodular graphite cast iron samples corroded in 2% CMC solution in water. No substantial distinction was found regarding the wetting capacity of the carboxymethylcellulose solution and water.

Keywords: Carboxymethyl cellulose; pitting corrosion; wettability; heat transfer coefficient

1. Introduction

In the case of heat treatment technique of metallic materials an important component is the cooling technology. The cooling of the heat treated part either for annealing or for quenching must be carried out in an environment that ensures an adequate heat transfer. That is, ensuring the required structural transformation and the state of thermal, structural and working stresses that are established in the specimen during the cooling operation [1].

As quenching media for hardening we can mention classical media such as water, heat treatment oil, emulsions and also synthetic media such as polymer solutions, mineral solutions, etc. The quenching media used so far do not fully meet the requirements of modern treatment techniques which must ensure the widest possible range of physico-chemical properties of the heat treated parts. This is as a result of the continuous development of the machine-building industry, to have a low cost price, to be non-flammable, non-toxic and to keep their cooling properties constant over time. Therefore, as an alternative to classical quenching media, synthetic quenching media have been tested and used, usually chosen from waste substances obtained from the chemical industry of paper processing, petroleum products, etc. By mixing certain substances with water, gels are formed. Among these substances we mention carboxymethyl cellulose, which is the subject of this article [2-5].

These substances, which in most cases are surface active, form a large number of vaporization centers, accelerate vapor formation and reduce the rate of vapor condensation [6-8]. As a result, the resistance of the vapour layer is greatly increased, the critical boiling temperatures move into the low temperature range and the cooling capacity of the water is considerably reduced [9-12]. A product used in the heat treatment of large and very large parts requiring cooling baths with agitators and large recirculation systems is carboxymethyl cellulose.

It is a secondary product of the paper manufacturing process and has suitable properties to be used at 1-5% dissolved in water for heating [13]. As advantages we mention that it is not flammable like heat treatment oil and has good solubility in water.

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Cooling for the quenching process is carried out in the temperature range 800-50°C. The carboxymethyl cellulose (CMC) quenching environment in water shows chemical degradation and chemical decomposition reactions around 300°C, which modifies the cooling properties and also influences the corrosion characteristics of the environment.

Phenomena occurring at temperatures below 70°C have been studied since the immersion of the heat-treated sample (at temperatures higher than 800°C possibly for quenching). In the first instance particularly violent and rapid phenomena occur involving instantaneous heat transfer between the metal part and the cooling medium, followed by boiling, solvent evaporation and other related physicochemical phenomena such as cavitations, degradations and physicochemical transformations of the quenching medium.

Below 100°C we can consider that the heat treatment medium forms a continuous or interrupted boundary layer depending on the wettability of the solution on the surface of the metal part. With the decrease of the part-medium temperature difference, the adherent layer on the surface of the part acquires other characteristics that influence the heat transfer and implicitly the surface structural transformations as well as the corrosion characteristics of the elements in contact.

At temperatures higher than 70°C the liquid droplets (CMC solution) are highly unstable in that they quickly lose water from the structure. Despite previous research, the relationship between spreading phenomena and the contact angle of the liquid on a hot surface is still under debate [14-16]. One of the objectives of this study was to determine the contact angle of water or a carboxymethyl cellulose (CMC) solution on grey cast iron at different temperatures using the sessile drop method.

2. Materials and methods

2.1. Materials used for the experiment

Analyses were performed on 10% CMC heating medium at 3 different temperatures, 20°C, 40°C and 60°C. In order to analyse the change of the cooling medium properties with temperature, for all experiments a cast iron was used. Samples of ferritic-pearlitic nodular cast iron were used, a material that has austenite to martensite transformation but is sensitive to cracking on heating and requires moderate heating rates over the range of structural transformation, presented in Fig. 1. The chemical composition of the metallic material has been mentioned in the TABLE 1.

2.2. Experimental methods

Experimental tracing of the cooling curves. In the paper the cooling curves of a standardized silver cylindrical specimen were plotted. The experiment was carried out using a set-up con-
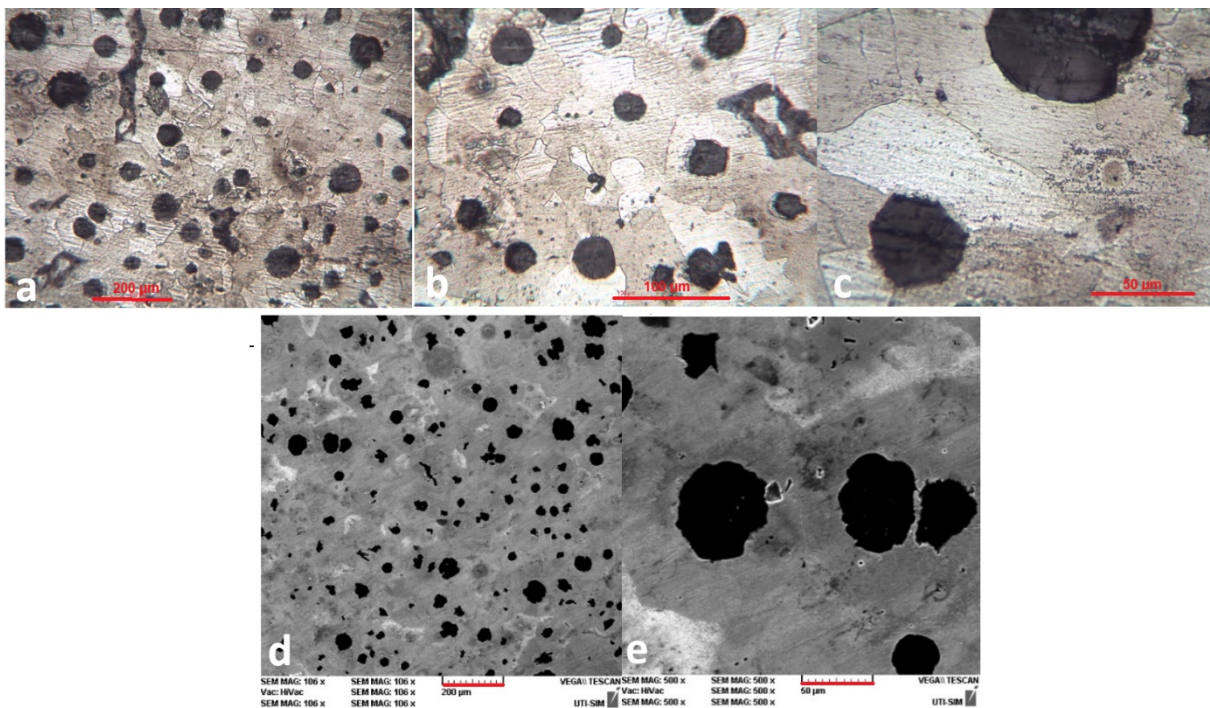

Fig. 1. Surface images of nodular cast iron sample obtained by OM: a) 100×, b) 200×, c) 600× and by SEM d) 100×, e) 500×

TABLE 1

Chemical compositon of cast iron

Element	Fe	C	Si	Ni	Mg	Mn	P	S	Cr	Ti	Al	Cu
%	balance	4.50	2.28	0.12	0.10	0.09	0.05	0.04	0.02	0.02	0.01	0.01

sisting of a furnace for heating the standardized silver specimen with embedded thermocouple, recorder and time base.

The specimen was heated to a temperature above 800°C and placed in the container with the quenching medium under analysis, the cooling curve was recorded with a "y-t recorder".

For each cooling medium the cooling rate was calculated in intervals [°C/s]:

– The obtained results were tabulated and based on them were plotted: cooling curves $T = f(t)$, Fig. 2.
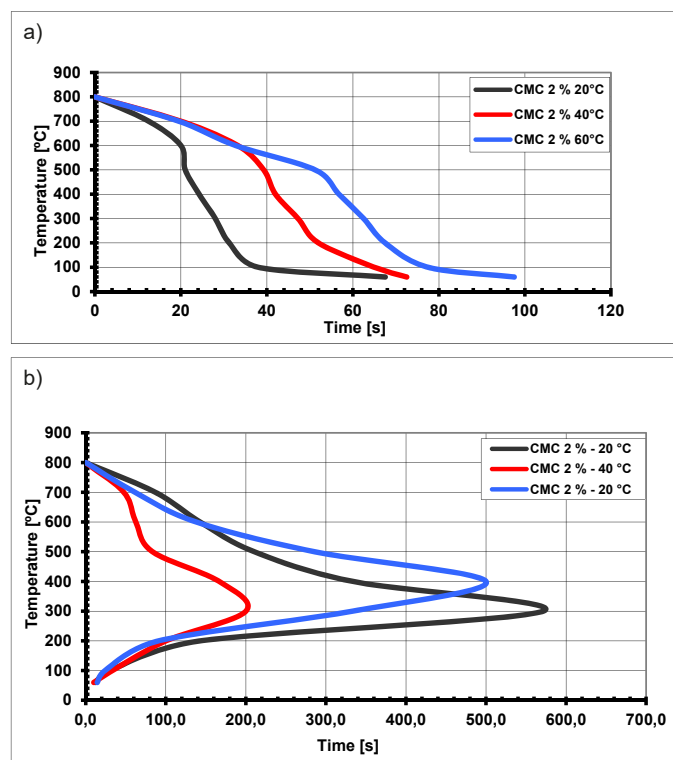– Variation of cooling rate with temperature $v_r = f(T)$.

Fig. 2. a) Cooling curves for CMC 2%, 20°C, 40°C, 60°C, b) Variation of cooling rates for CMC 2%, 20°C, 40°C, 60°C

Determination of corrosion characteristics. A potentiostat equipped with a three-electrode cell was used to analyse the influence of the heating medium on corrosion. A calomel satu-

ration electrode, a reference electrode and a working electrode incorporated in Teflon, with an exposed area of 0.6 cm^2. Linear and cyclic potentiometry measurements were performed and the Tafel method was used to evaluate the corrosion parameters for each medium at 20°C, 30°C, 40°C, 50°C and 60°C.

An Optical microscopy (OM), INSIZE, equipped with Moti-Cam camera (10+, 10.0 MP) specialized in microscopic analysis was used to analyze the surface modification of the sample before and after corrosion. For scanning electron microscopy (SEM) a VegaTescan LMH II microscope was used.

Characterization of contact angles. Since the roughness of the surface affects the contact angle, the sample's surface has been polished. After polishing the surface with sandpaper grits of 100, 400, 600 and 1000 to a mirror shine, the sample was immersed in ethanol and ultrasonic cleaned for fifteen minutes. The sample was placed inside the temperature chamber, and two microliters of test solution (deionized water, CMC solution, ethylene glycol and diiodomethane) were dropped onto it. The temperature of the samples was gradually increased from 20°C to 60°C. To check the surface temperature, an infrared thermometer was used. The experiments were carried out in an air atmosphere. An optical contact-angle meter system (Kruss Easy Drop goniometer, Germany) was used to measure the static contact angles. The reported results are the averages of a minimum of five measurements taken at different points on the surface. The recordings were started after the droplets were deposited on the surfaces and stopped after 30 seconds.

3. Results and discussions

3.1. Thermal transfer and cooling curves

Carboxymethyl cellulose (CMC) is very cheap and can be found in abundance because is a cellulose derivative found in the textile industry, paper industry, pharmaceutical industry, etc. The substance is organic in nature, having good ecological properties, non-toxic to living organisms. Carboxymethyl cellulose has a fibrous appearance, presented in Fig. 3, and a yellowish-white colour, a melting point of 274°C and a density of 1,6 g/cm^3.
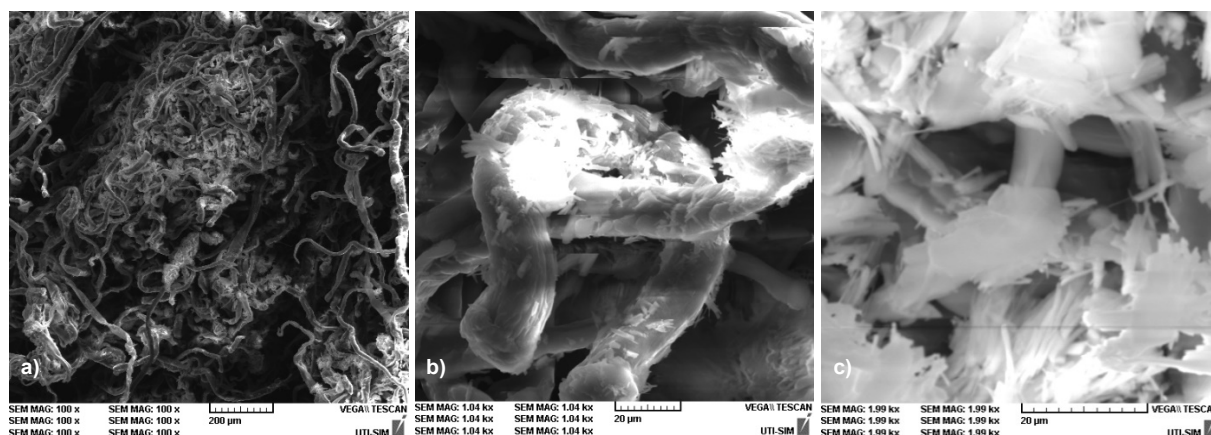

Fig. 3. Structural morfhology of CMC: a) 100×, b) 500×, c) 1000×

Carboxymethyl cellulose dissolves in water forming a colloidal solution and changing even at concentrations of 1-2% in water both the viscosity and cooling characteristics as well as the wettability towards metal surfaces. The pH of the 2% CMC solution in water is 10.19.

It can be observed from the graphs plotted that the initial temperature of the CMC 2% cooling solution in water is of great importance for the intensity and quality of cooling.

An environment with a carboxymethyl cellulose solution at 20°C cools the metal part in 67 seconds, while an environment with a carboxymethyl cellulose solution at 60°C cools in 97.5 seconds.

It is also noted that at the initial temperature of 40°C we have a change in the properties of the medium which is a solution of an organic polymer and has at that temperature a partial amorphization point which leads to a decrease in the maximum cooling rate and thus a change in the character of the cooling and the expected structural transformations. In terms of cooling uniformity, the 20°C curve is recommended.

3.2. Corrosion tests

From linear potentiometry tests, Fig. 4a) performed at 4 different temperatures to simulate the behaviour of the heating environment. The value of the E potential ($i = 0$) for the sample at 20 degrees is 817 mV, and for the CMC 30 and CMC 40 samples the tendency of corrosion decreases, probably due to the deposition of a layer of CMC solution, with a protective effect on the sample surface. For the CMC 50 sample the corrosion potential increases considerably, up to –1077 mV, which means that at a temperature of 50 degrees a protective layer is no longer formed, the electrolyte/calc medium deteriorates and the sample corrodes at a high rate. The variation of Rp also confirms the result, the lowest value was found in CMC 50, Fig. 4b).

From the cyclic diagram, Fig. 4c), a piting type of corrosion is observed in all tested samples over the whole potential range. This is due to the ferritic-pearlitic, heterogeneous structure of the nodular melt. The high degree of inhomogeneity given by the different phases interrupted by the graphite nodules gives the surface structure coming into contact with the carboxymethyl cellulose solution different electronegativity potentials. For this reason, localized corrosion occurs on the phases with more electronegative potential, becoming anode and the areas with less electronegative potential becomes cathode, the surface remaining intact.

At 50°C initial temperature the protective film is more easily destroyed, which leads to a more pronounced oxidation and at a higher speed than in the other cases.

The electron scanning microscope microscopy, Fig. 5 show a surface with more pitting in the case of the sample corroded in carboxymethyl cellulose solution at 50°C compared to the sample corroded at 20°C, which means that the higher temperature favours corrosion, i.e. between the complex reactions on the surface of the liquid-foam contact which are oxidation and
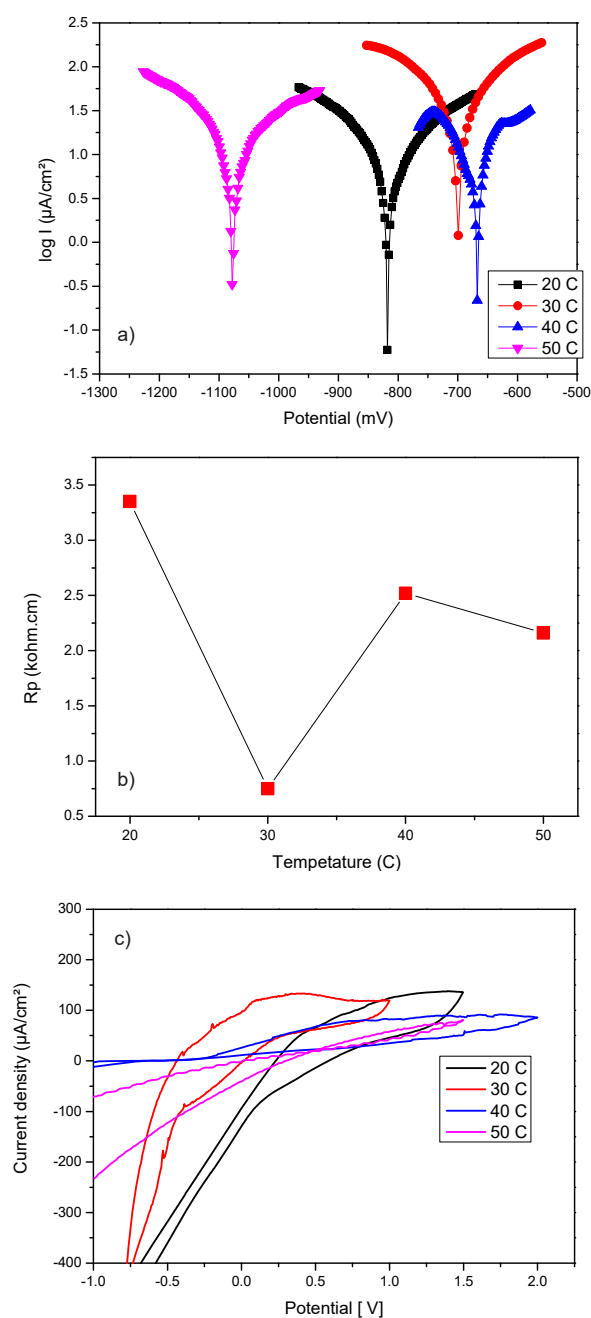

Fig. 4. Electrochimical results: a) Tafel plots, b) Rp variation, c) Cyclic voltammograms

repulsion the balance will be tilted towards oxidation, confirmed by EDX analysis, see in Fig. 6.

3.3. Contact angle

The samples revealed a nonlinear wetting by applying a linear variation of temperature. The average values of the contact angles and the standard deviation are presented in TABLE 3. The metal surface can be characterized as hydrophilic, exhibiting a contact angle of around 60°. Pictures of water droplets on the grey cast iron surface taken during contact angle (CA) measurements can be seen in Fig. 7.
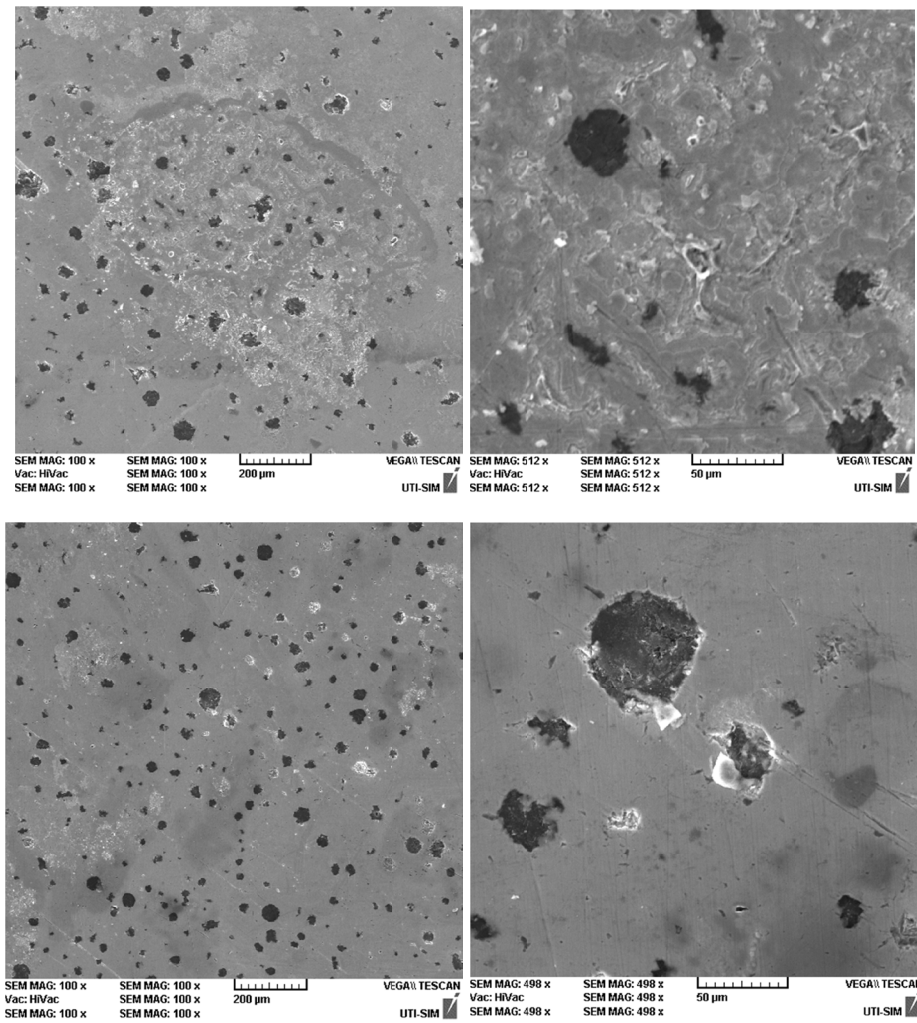
Fig. 5. Surface images of nodular cast iron sample corroded with CMC solution at 50°C obtained by scanning electron microscope at various magnifications: left) 100×, right) 500×
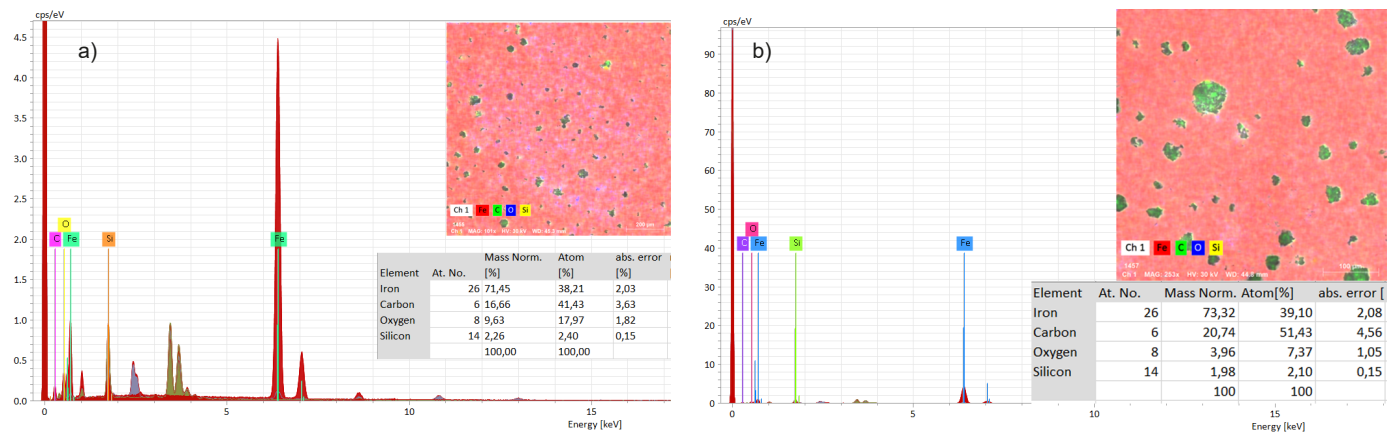

Fig. 6. EDX analysis of the surface of nodular cast iron sample corroded in CMC solution at (a) 20°C temperature (b) 50°C temperature

TABLE 2

Electrochemical corrosion parameters

Sample	E ($i = 0$), mV	i corrosion μA/cm	Rp kohm.cm	Beta a, mV	Beta c mV	Corrosion mm/Y
CMC 20	−817.30	12.58	3.35	249.30	−207.90	144.90
CMC 30	−699.80	35.77	0.75	145.30	−172.00	412.00
CMC 40	−668.10	3.28	2.52	47.10	−57.30	37.83
CMC 50	−1077.20	26.51	2.16	468.40	−290.10	305.30

The temperature-dependence of the contact angle of water and CMC solution onto the grey cast iron sample

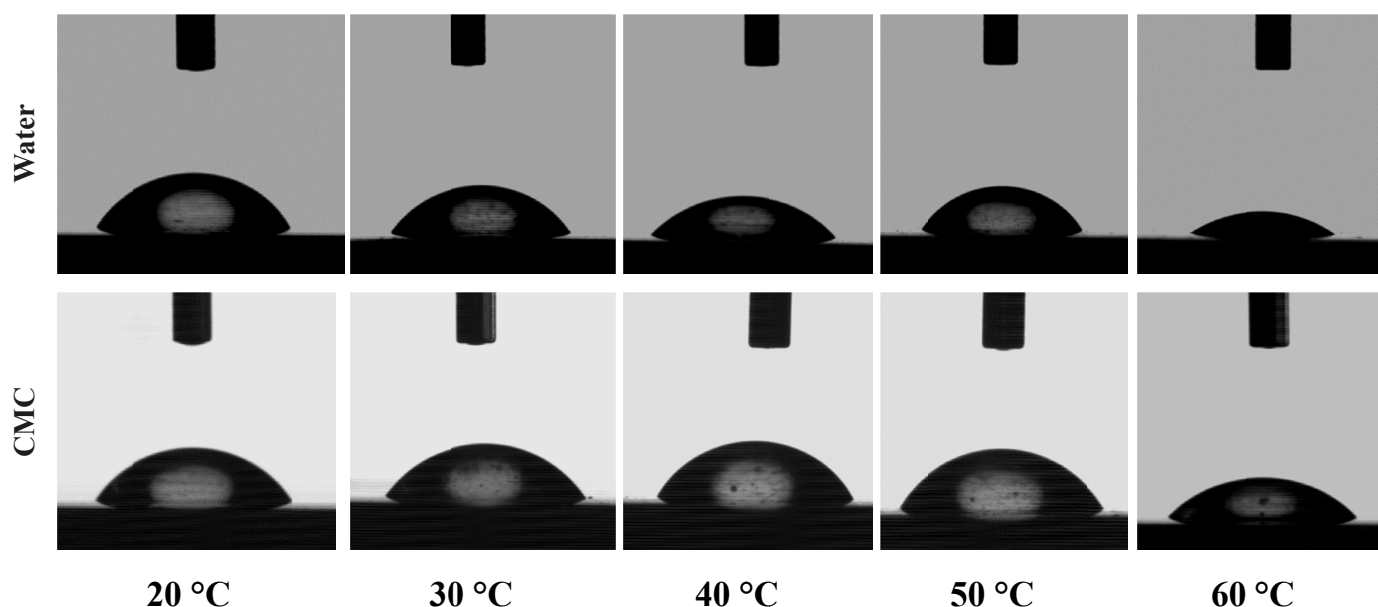| Temperature	20°C	30°C	40°C	50°C	60°C
Water	62.3° ± 1.0°	59.4° ± 1.8°	58.9° ± 2.3°	61.3° ± 3.7°	63.3° ± 0.5°
CMC solution	59.07° ± 3.7°	60.6° ± 1.9°	66.1° ± 0.3°	60.7° ± 1.7°	62.04° ± 2.0°

Fig. 7. Images of water and CMC solution contact angles taken at 20 seconds after deposition on the sample surface at different temperatures

Because of their high surface energy, metals typically have hydrophilic surfaces. The surface energies of the sample at different temperatures were evaluated utilizing the OWRK (Owens, Wendt, Rabel and Kaelble) method using three different fluids (water, ethylene glycol and diiodomethane). The total surface energy of a solid is divided into two components: polar and dispersive (TABLE 4). The polar component represents the energy associated with polar interactions (such as hydrogen bonding or dipole-dipole interactions). In contrast, the dispersive component represents the energy associated with non-polar interactions (such as van der Waals forces).

The polar component of the solid surface energies for the grey cast iron sample is almost half of the dispersive value, implying a low affinity and a higher contact angle for polar liquids. The water contact angle rises as the polar component's value falls (TABLES 3 and 4). Even though the aqueous carboxymethyl cellulose solution may display polar characteristics due to ionized carboxymethyl groups, van der Waals forces between the macromolecular chains are predominant interactions in the current situation. Considering the previously revealed, the contact angle of the carboxymethyl cellulose aqueous solution

and the dispersive component of the metal surface exhibit a proper inverse-proportional relationship. Fig. 8 illustrates the relationship between temperature and the contact angles of water and carboxymethyl cellulose solution. In addition, it highlights the polar and dispersive components of solid surface energy as a function of sample temperature.

The wetting capabilities can be affected by the emergence of oxides on the metal surface and contamination by organic molecules from the surrounding environment. The stability of the CMC solution changes at high temperatures. Initially, the intermolecular connections that hold CMC molecules together will break down, and then macromolecule thermal degradation could happen.

4. Conclusions

The following conclusions can be drawn from the present research:

1. Analysing the quenching cooling curves shows that the initial temperature of the cooling media leads to a longer

The dispersive and polar components of surface energy (mN/m) of the grey cast iron sample and their temperature-dependence

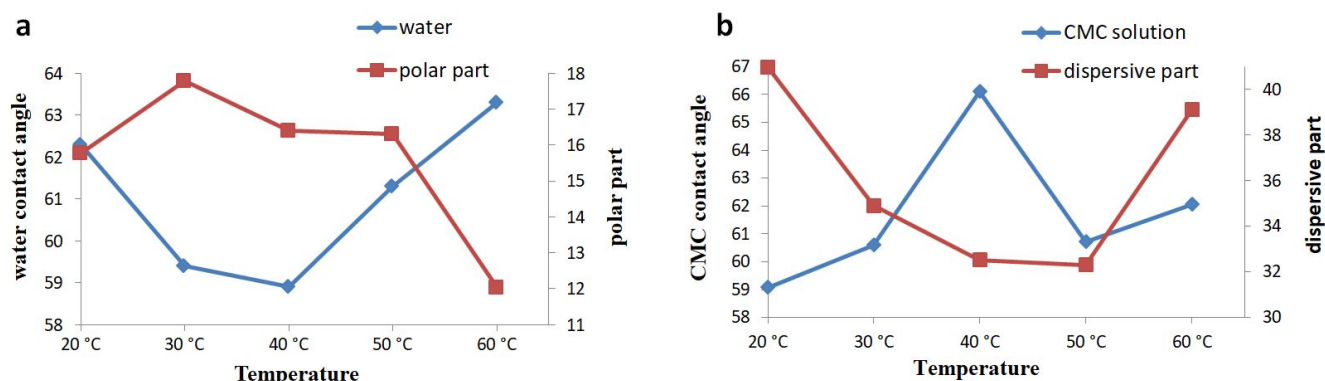| Temperature	20°C	30°C	40°C	50°C	60°C
Surface energy	56.73	52.75	48.91	48.64	51.12
Dispersive/polar part	40.95 / 015.78	34.9 / 17.80	32.50 /16.40	32.30 /16.30	39.09 /12.03

Fig. 8. The evolution of the water contact angle and the polar component of the surface energy (a), respectively the contact angle of the CMC solution and the dispersive component of the surface energy (b)

cooling time. Since carboxymethyl cellulose is a polymer and has a crystalline-amorphous transition point at 49°C a strong decrease of the maximum cooling rate is observed for the curve of 40°C initial temperature of the medium.

2. The cooling curve of the carboxymethyl cellulose solution at 20°C has an aliphaticity corresponding to the optimal quenching transformations and corresponds better than the other curves to the technological requirements of the quenching operation.

3. Analyzing the Tafel curves (linear voltammograms), it is observed that at temperatures of 50°C carboxymethyl cellulose has a structure that favors rapid corrosion of the surface of the nodular ferrite-pearlite cast iron.

4. At temperatures of 20°C, 30°C and 40°C the carboxymethyl cellulose solution forms a protective polymer layer on the metal sample so that oxidation and repassivation reactions lead to a delay in destructive corrosion.

5. Studying the cyclic voltammograms, it can be seen that all the samples show corrosion at points with the exception that pitting is more pronounced at 50°C, which is possible due to the presence of galvanic corrosion because the metal matrix and the graphite are at a distance on the chemical potential scale forming a galvanic pile.

6. Similar contact angle values were observed for water and carboxymethyl cellulose solution. With a linear variation of the metal surface temperature, a non-linear behaviour of the wetting values for water and carboxymethyl cellulose solution was observed.

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