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EFFECTS OF CONCENTRATION WATERMISCIBLE METALWORKING FLUIDS ON COOLING RATE

Abstract

Quenching is the most common procedure of metal heat treatment, which involves adequate cooling from given austenite temperature to achieve full transformation into martenzite structure. The cooling rate of quenching media mainly depends on thermal characteristics of the metals, section thickness of the workpieces, and the quenching medium heat-removal properties. Correct selection of adequate cooling media decreases risk of tension formation, possible cracking, and deformation of workpieces. The most commonly used cooling media for quenching steel are water, vegetable and mineral oils, polymer solutions, molten salts, fluidized baths, gases, and air. Water is a severe quenchant while oils cool more slowly than water but their main disadvantage is high fire hazard. Using watermiscible fluids combines positive properties of those two types of quenchant media, the water and the oils.

In this work are presented physical and chemical properties of watermiscible metalworking fluids as cooling media. Several fluid mixtures were prepared with water in different concentrations. Cooling curves for every concentration of test cooling fluids are plotted with determined cooling rates and H-values using ISO 9950 standard.

1. INTRODUCTION

Metal heat treatment includes a whole range of heating and cooling treatments which are applied in the construction of different tools and other machine parts in order to gain the desired mechanical properties of a specific workpiece. During these procedures the alloy is exposed to temperature changes in order to change its structure and to gain the desired properties. The basic parameters of every heat treatment are the temperature (T) and time (t). The heat treatment processes include hardening, annealing, stress relief, tempering and surface hardening [1]. Hardening is heat treatment of steel under the high temperature due to austenization and melting the sufficient quantity of carbon in austenite and sharp cooling which produces very hard, breakable and unstable martenzite structure. Hardening increases the hardness and the toughness of steel.

During the heat metal treatment many different cooling and quenching media can be used. According to ISO 6743-14 standard, Heat treatment-U [2], oils and similar products applied in the metal hardening process are divided into six groups:

>   H = oils
>   A = water and polymer fluids, emulsions
>   S = molten salts
>   G = gases
>   F = fluidized baths
>   K = other quenchants

These products are classified according to the phenomenon of tending to produce a steam layer at the beginning of the immersion of a hot workpiece, which is called the Leidenfrost phenomenon. The steam layer is created with quenching media which boiling point is under the austenization temperature such as water, oils, emulsions and polymers. The products without the Leidenfrost phenomenon are the media which boiling point is above the austenization temperature of steel such as molten salts and molten metals, gases and vacuum such as fluidized baths, technical gases - passive and compressed [3].

There are three stages of cooling process during the immersion of the hot workpiece into the quenching media which tends to produce a steam layer. They are: a) the steam layer stage, b) the boiling stage and c) the convection stage, as it's shown in Figure 1 [4].
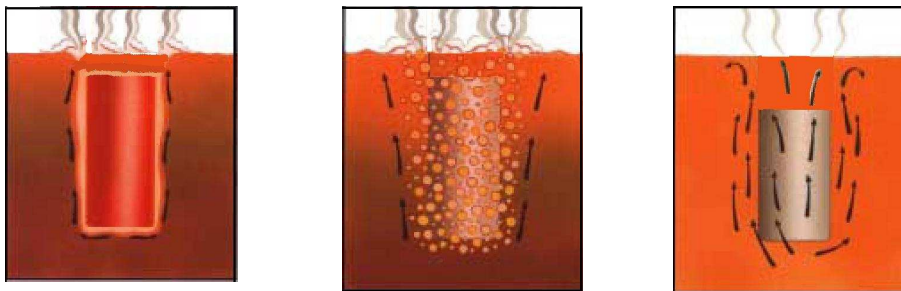
a – steam layer stage   b – boiling stage   c – convection stage

Figure 1: Stages of workpiece cooling in the quenching media with the steam layer

The steam layer stage (a) begins immediately after the immersion of a hot workpiece into the media. The high temperature of the workpiece forms the steam layer which functions as an insulator preventing the contact between the quenchant and the metal surface. The steam layer has a low thermal conductivity which is the cause of the low cooling rate. The duration of this stage primarily depends on the quenchant. The temperature decrease of the workpiece, depending on the quenchant and the workpiece geometry, the steam layer becomes unstable and it disappears providing the contact between the quenchant and the workpiece surface. Severe boiling (b) rapidly releases the heat and the colder fluid comes to the

surface. The heat release occurs really fast from the surface. In this cooling stage the maximum quenching rate is achieved and the temperature decrease reduces boiling. In the last cooling stage (c) when the temperature of the workpiece decreases under the boiling point of the quenchant, the heat is released only by the convection on the quenchant. Therefore the cooling in this stage can be considerably increased by the circulation of the quenchant [5]. Figure 2 shows the cooling rate curve with the stages plotted for each quenchant. If the steam stage is short, fast homogeneous cooling of the whole workpiece surface occurs. If the boiling stage is long, the quenchant releases the heat well with bigger cuts.
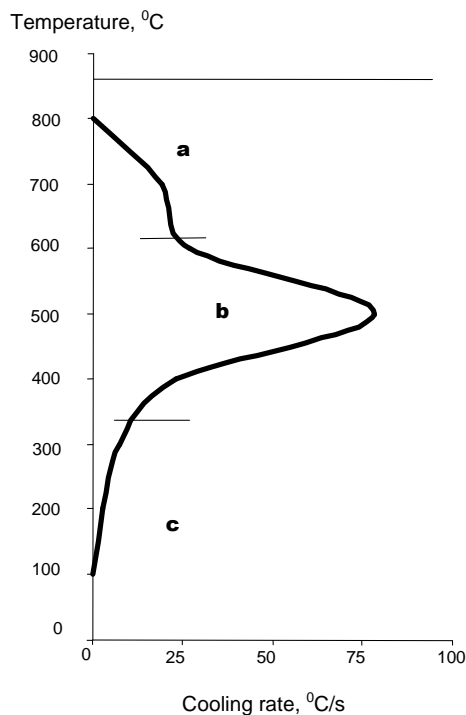

Figure 2. Cooling rate of quenching fluid

Among different kinds of metals and their alloys, steel is most commonly thermally treated. Depending on the steel quality, an appropriate quenching fluid needs to be chosen which will give the biggest share of martenzite, which reduces the possibility to produce tensions or cracks. To harden a given workpiece, it needs to be cooled fast enough from the austenitization temperature.

For the determination of an appropriate quenchant, we started with the TTT analysis (time-temperature-transformation) diagram for the continuous cooling, and upper and lower critical quenching rate already determined by it. The upper critical quenching rate is the lowest cooling rate used to produce the complete martenzite (M) microstructure, and the lower critical quenching rate is the lowest cooling rate needed in order to start the transformation into martenzite. From the continuous TTT diagram, Figure 3, one can see the critical temperature points (between 650 and 400 ^{0}C) around the incubation temperature where fast cooling is necessary in order to avoid the transformation of cooled austenite into pearlite or bainite [6].
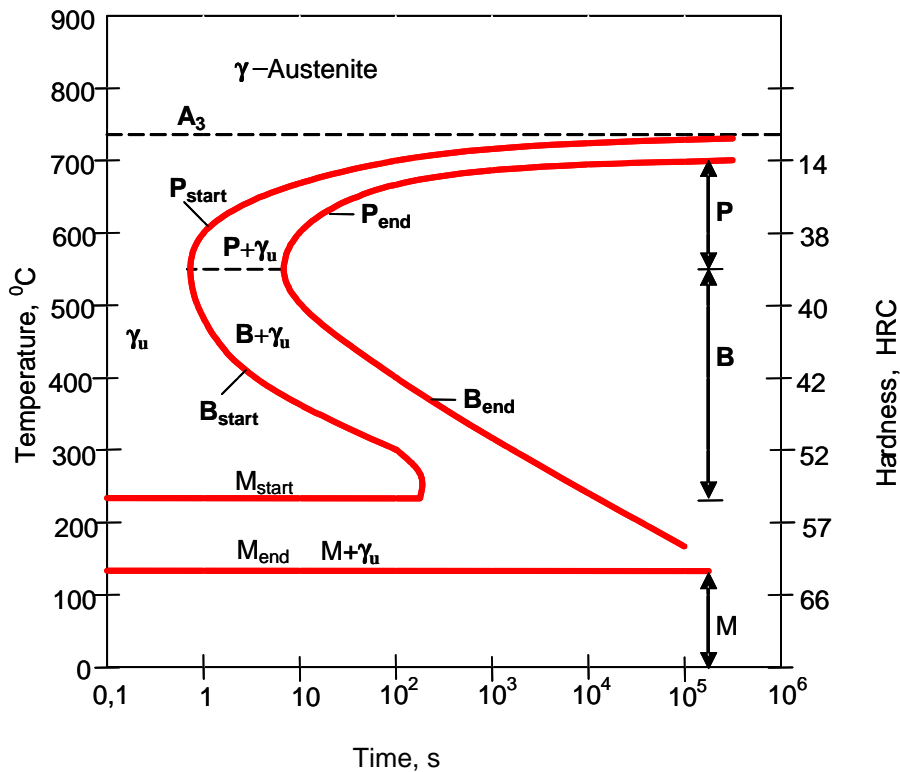
Marks of microstructural phases: γ, A - Austenite, P – Pearlite, B – Bainite, M – Martensite

Figure 3: Time-temperature transformation (TTT) diagram for eutectoid steel

TTT diagrams show the behaviour of certain kinds of steel as the cooled austenite. This diagram (also called the isothermal transformation diagram or C-curve) provides us to foresee the structures, properties and necessary thermal treatments for steel. The P_{start} curve shows the time of the beginning. The time when the transformation is completed the time is shown with the P_{end} curve. The maximum

transformation rate for the eutectoid steel occurs at the temperature of 550 ^{0}C. Two kinds of microconstituents are produced as the result of the transformation. Pearlite (P) is produced above 550 ^{0}C and bainite (B) is produced at lower temperatures.

2. Heat metalworking fluids

Heat metalworking fluids are hardening oils, emulsive and synthetic fluids and water. Water is a severe quenching media while the oils cool considerably slower than water. The main disadvantage of oil is the fire hazard and the main disadvantage of water is the poor corrosion protection. The positive properties of water and oil, as quenchants, are combined by the application of watermiscible fluids. Oil fluids and watermiscible fluids have their advantages and disadvantages, and some of their application properties (depending on their price) are shown in Table 1.

Table 1: Advantages and disadvantages of metalworking fluids application

COSTS/PROPERTIES	WATERMISCIBLE FLUIDS	OILS
Product price	+	-
Storing	-	+
Maintenance	-	+
Cleaning devices	+	-
Workpieces degreasing	+	-/+*
Work space degreasing	+	-/+*
Fire hazard	+	-

+ = advantage, - = disadvantage, * = advantage if the oil is water washable

When selecting the cooling agent or the raw material for the production, attention must be paid not only to the technical requirements, but also to the requirements of the environmental protection and human safety [7]. Hardening oils contain base oil and additives. The base oil can be mineral, synthetic or natural (vegetable or animal oil), but mostly mineral base oils are used. Additives function as the oxidation inhibitors, foam inhibitors, workpiece cleanness improvers, cooling rate improvers, etc. The basic physical and chemical properties of hardening oils are viscosity, boiling, fluidity, flash point, oxidation and thermal stability, volatility and washability. Viscosity as one of the most important lubricant characteristics present the internal friction criteria, which work as resistance to the molecule position change in the lubricant under the shear stress. The viscosity depends on the temperature and the pressure. The cooling rate depends on the viscosity. The contents of emulsive fluids or "soluble oils" are similar to oils when added a greater amount of surface-active substances in order to produce a stable emulsion which is an operating media and the corrosion protection is also needed due to high water content. The synthetic agents do not contain oil component but they contain surface-active substances, corrosion inhibitors, high molecular constituens – polymers and other substances. The emulsive fluids and synthetic agents are applied when water blended, forming emulsions or solutions in different concentrations depending on the desired

properties. In all these groups there are quenchants for slow, normal and quick quenchings. Table 2 shows the oil classification which is used in heat treatment according to ISO 6743-14 norm in relation to the quenching procedure. Table 3 shows the aqueous fluids classification [2].

Table 2: Classification of oils for heat treatment according to ISO 6743-14

QUENCHING PROCEDURE	OIL TEMPERATURE ^{0}C	APPLICATION	SYMBOL
cold quenching	$\vartheta \leq 80$	oil for normal quenching	UHA
		oil for quick quenching	UHB
semi-hot quenching	$80 < \vartheta \leq 130$	oil for normal quenching	UHC
		oil for quick quenching	UHD
hot quenching	$130 < \vartheta \leq 200$	oil for normal quenching	UHE
		oil for quick quenching	UHF
extra hot quenching	$200 < \vartheta \leq 310$	oil for normal quenching	UHG
		oil for quick quenching	UHH
quenching in vacuum furnaces			UHV
other applications			UHK

Table 3: Classification of aqueous fluids for heat treatment according to ISO 6743-14

QUENCHING PROCEDURE	APPLICATION	SYMBOL
surface quenching	water	UAA
	aqueous fluid for slow quenching	UAB
	aqueous for quick quenching	UAC
deep quenching	water	UAA
	aqueous fluid for slow quenching	UAD
	aqueous fluid for quick quenching	UAE
other applications		UAK

The cooling rate and the operating temperature are important operating properties of the quenchant and therefore they need to be determined by some of the applicable methods [8]. Figure 2 shows that the cooling rate significantly effects the hardenability and material hardness after quenching.

3. Experimental part

3.1. Determining cooling capacities by ISO 9950 [9] method

The probe (diameter 12,5 mm and length 60 mm) is used for testing the cooling capacity by ISO 9950:1995 method, and it is made of Nickel alloy INCONEL 600

(Figure 4). In the centre of the probe is NiCr/ NiAl thermocouple. The thermocouple is connected to a PC or a printer in order to plot and register the needed values: temperature, time, cooling rate. The test probe warms up to $850 \pm 5\ ^0$C and stays in the furnace for 5 minutes. From the furnace the probe is put into the quenchant where the cooling capacity is measured. To determine the cooling rate two typical curves are plotted: the temperature change and the cooling rate in the centre of the probe with time as it's shown in Figure 5.
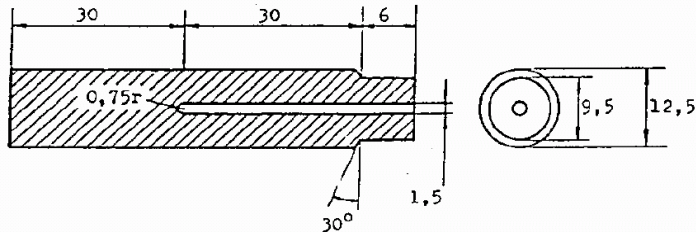

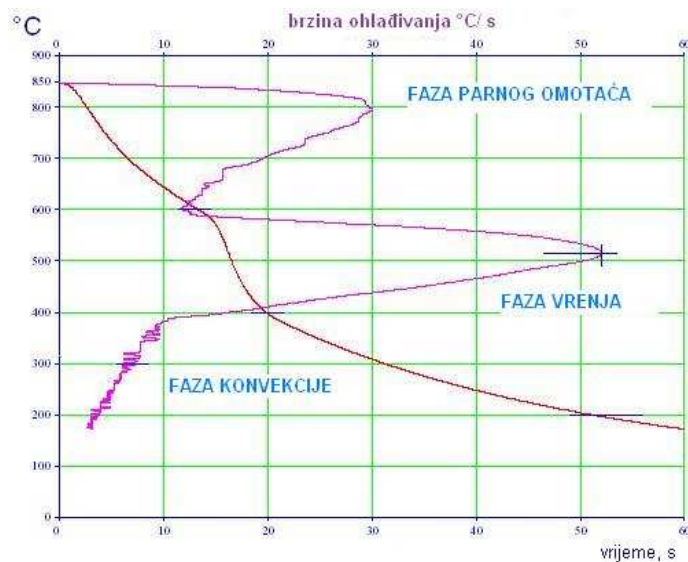Figure 4: Probe test method ISO 9950:1995

Figure 5: Diagram of temperature change – time (darker curve) and temperature – cooling rate

From the temperature change curve (T) with time (t) one can determine time needed for the appropriate temperature, for example 600 ^{0}C, 450 ^{0}C, 300 ^{0}C (Δt) or determine the average rate (v_{sr}) for the appropriate temperature interval ($\Delta T_{700\text{-}300}$), usually between 700 and 300 ^{0}C.

Average cooling rate (1):

$$v_{sr} = \frac{\Delta\vartheta}{\Delta t} = \frac{\Delta T_{700-300}}{\Delta t_{700-300}} \ [\,^0C/s\,] \qquad\qquad (1)$$

From the diagram of the cooling rate change with temperature, the temperature for any cooling rate can be determined as well as the stages of a particular quenchant with the steam layer. Apart from that, this diagram helps you to read the maximum cooling rate. If the cooling curve for calm water at 18 ^{0}C and a particular quenchant is plotted, within a particular temperature interval, then a quenching intensity or the H value according to the formula (2) can be determined:

$$H = \frac{\Delta t_{calm\ water18'C\ 700-300}}{\Delta t_{quenchant\ 700-300}} \qquad\qquad (2)$$

3.2. Test cooling fluids

For testing the cooling capacities and determining the effects of the concentration on the cooling ability by ISO 9950 method, two formulations of watermiscible cooling fluids were prepared: F-EM BU and F-SINT B. The F-SINT B formulation contains synthetic components and surface-active substances without aromatic rings, corrosion inhibitor which is a derivative of capronic acid, polymers and other necessary additives. The F-EM BU formulation contains mineral oil of a paraffin type with lower aromatic hydrocarbon content, surface-active substances which function as emulsifiers, corrosion protection and better adhesion and other additives.

Table 4: Marks of tested samples of watermiscible fluids and concentrations

SAMPLE NO.	COOLING AGENT	CONCENTRATION
41/07	synthetic fluid	10 % solution
42/07	″	20 % solution
43/07	″	30 % solution
44/07	emulsifying fluid	10 % emulsion
45/07	″	20 % emulsion
46/07	″	30 % emulsion
50/07	synthetic fluid	concentrate
51/07	emulsifying fluid	concentrate

These formulations are less harmful for the environment and human health since they do not contain for long time used additive based on barium which is considered harmful as well as the other components related to the latest trends in the development of lubricants for metal treatment [7]. These fluids which are produced as concentrates are mixed with water to produce working emulsions and solutions of different concentrations. Table 4 shows the provisional systems and the sample marks of tested fluids.

4. Test results and discussion

Table 5 shows physical and chemical properties of the concentrates and the appropriate standard test methods. These concentrates are applied when mixed with water: emulsions of the F-EM BU formulation and solutions of the S-SINT B formulation. The physical and chemical properties, foaming properties and corrosion protection properties have been tested. The test results show that both fluids have low foaming and excellent anticorrosive properties even at low concentrations (1,5 or 2 %).

Table 5: Physical and chemical properties of hardening fluids and test methods

FORMULATION	F-EM BU	F-SINT B
PROPERTIES	emulsifying fluid	synthetic fluid
CONCENTRATE		
Appearance and colour, visually	clear brown fluid	clear dark yellow fluid
Stabillity, 4, 20, 50^{0}C / 24 h, internal test 1	stable	stable
Viscosity, 40^{0}C, mm^2 s^{-1}, ISO 3104	62	60
WATER BLENDING, 5 % in softened water		
Appearance and colour, visually	white emulsion	transparent solution
pH-value, ASTM D 1287	9,1	8,8
Alcalic reserve, ASTM D 1221	1,8	9,2
Foaming, Internal test 2 Foam volume, ml Stability, after 5 min, ml	30 0	20 0
Corrosive properties Herbert test, 1,5 % conc., DIN 51360-01 Filter paper test, 2 % conc., DIN 51360-02	R0/S0 0	R0/S0 0
WATER BLENDING, 30 % in softened water		
Appearance and colour, visually	white emulsion	transparent solution

For testing the cooling properties of these watermiscible formulations the samples in three different concentrations were prepared with softened water. Figure 6 show their curves for observing the concentration and refractometer reading. Figures 7 and 8 show diagrams with test results of the temperature change with time for the tested samples. The diagrams demonstrated the average cooling rates for the temperature interval 700 to 300 ^{0}C, and the H value of particular test samples have been determined. The values are shown in Table 6.
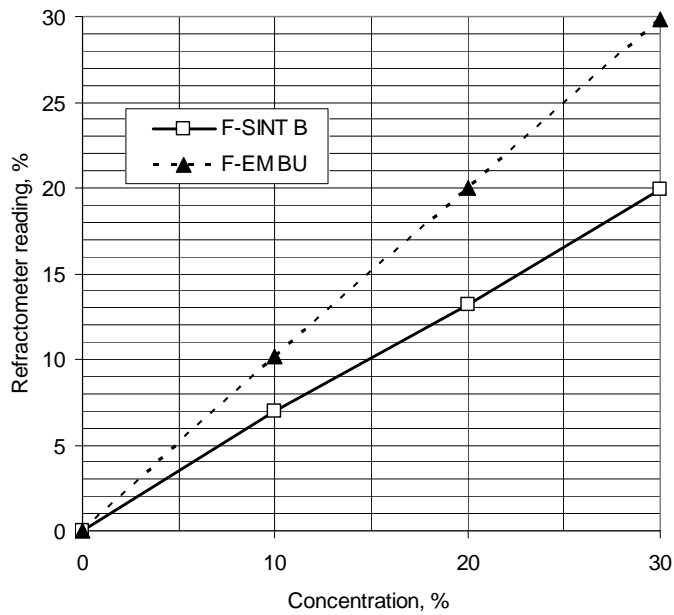
Figure 6: The relation of test fluids concentration and refractometer reading

Table 6: The cooling rates and H value test results of tested fluids

SAMPLE NO.	Δt, s	v_{sr}, ^{0}C/s	H
41/07	9	44	0,33
42/07	10	40	0,30
43/07	9	44	0,33
44/07	26,5	15	0,11
45/07	26,5	15	0,11
46/07	35,5	11	0,08
50/07	58	7	0,05
51/07	31	13	0,14

The test fluids F-EM BU and their curves do not show any important mutual differences. In addition it can be concluded that its application should be considered with caution since it was readily inflammable during the immersion of a test probe and it also produced a lot of foam.
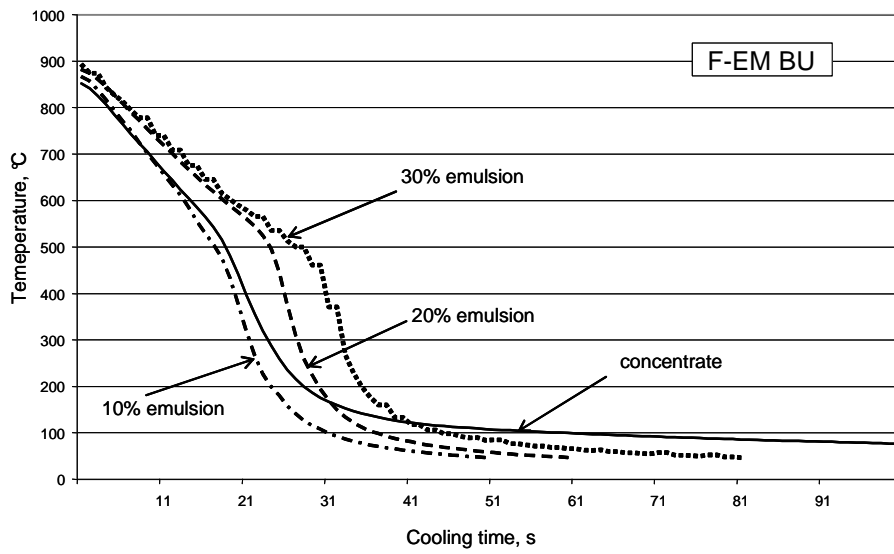
Figure 7: The measurement report of temperature change with time of test fluid F-EM-BU
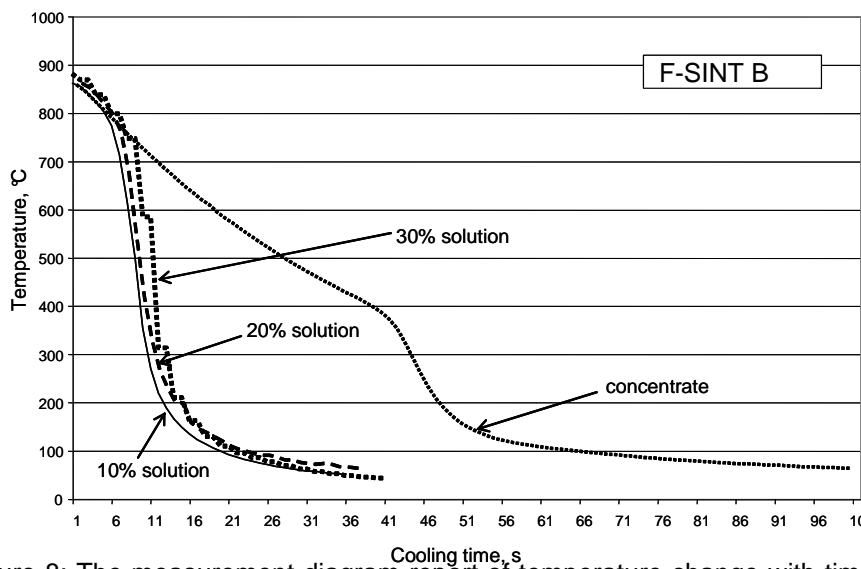

Figure 8: The measurement diagram report of temperature change with time of test fluid F-SINT B

Figure 8 shows that the sample with the lowest concentration, presents the steepest descent curve or the biggest cooling rate while the sample with 30 % concentration shows the smallest cooling rate.

The cooling rate of F-SINT B fluid with the solution concentration of up to 30 % is insignificantly influenced by the concentration. It has also been noticed that the solution concentration effects the time of cooling up to 700 ^{0}C. Even more intense effect could be gained by increasing the concentration.

5. Conclusion

Two kinds of watermiscible fluids for cooling have been tested: the emulsive fluid F-EM BU and the synthetic fluid F-SINT B. Concentrates and waterblends (emulsions and solutions) were prepared in different concentrations.

The average cooling rates and the H values according to ISO 9950 method are determined for all the samples out from the cooling curves. The results of the tested samples show that fluids of different concentrations and compositions significantly change the characteristics which are important for the cooling capacity. The F-EM BU fluid did not show acceptable results due to flammability.

Based on the produced properties, certain cooling fluids concentrations of F-SINT B can be used with different kinds of steel depending on their properties and specific requirements of the desired workpiece quality. Additionally this product has a considerable advantage because the parts are cleaner and more easily washable after treatment, and they also present lower fire hazard.

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621.785.56.065	emulzije za kaljenje uranjanjem	emulsions for immersion hardening
621.785.616	kaljenje čelika radi postizanja martenzitne strukture	martensitic quench hardening of steel
665.7.032.52	naftni i slični produkti sintetskog porijekla	petroleum and related products of synthetic base
.001.37	gledište komparativne evaluacije	comparative evaluation viewpoint

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