STUDIES ON THE KINETICS OF VERY RAPID COOLING IN DIFFERENT QUENCHING LIQUIDS—APPLICATION TO SOME ALLOYS OF IRON, NICKEL AND CARBON

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Introduction

ONE can set the problem of quenching metals and alloys in the following manner:

Let us consider a structural transformation arising in the metal or alloy within a certain interval of temperature θ_1, θ_2.

Let us suppose that this transformation, without induction period, has an initial speed characterized by finite values at all the temperatures within the interval θ_1, θ_2, and by negligible values at the boundaries θ_1 and θ_2 of this interval.

This speed of transformation can be measured for all the temperatures within the interval θ_1, θ_2 by recording, against time, the variations of a physical property of the sample in direct relation with its structure. With the well-known isothermal thermodilatometer of Prof. Chevenard, this physical property is the length of a cylindrical wire of some millimetres in diameter and 50 millimetres in length.

The speed of the reversible structural transformation:

$$\alpha \rightleftarrows \gamma$$

of ferrous alloys can be measured, at its initial stage, by this very simple process.

On the other side, the speed of cooling during quenching can be measured, in the same interval of temperature, by photographically recording the temperature-time curve with an electrostatic cathodic tube used, in connection with a suitable amplifier, as a without inertia recorder of the electromotive strength of a chromel-constantan thermocouple. If the thermocouple is built with very thin wires and solder, the response of this apparatus is practically an instantaneous one.

Now, if one gives the rate of transformation x_0 which must not be exceeded during the whole cooling, the speed of transformation

$$dx/dt = F(\theta) \quad [\text{Fig. 1(a)}]$$

as a function of θ in the interval θ_1, θ_2, the speed of cooling

$$d\theta/dt = \phi(\theta) \quad [\text{Fig. 1(b)}]$$

as a function of θ in the same interval.

The interval of time dt, during which the temperature stays within the interval of temperature $\theta, \theta + d\theta$ is:

$$dt = d\theta/\phi(\theta)$$

The very small rate of transformation attained during this time is:

$$dx = F(\theta) \ d\theta/\phi(\theta)$$

and the condition of quenching in the whole interval θ_1, θ_2:

$$\int_{\theta_1}^{\theta_2} \frac{F(\theta) \ d\theta}{\phi(\theta)} \leq x_0 \quad \dots \dots \quad (\text{I})$$

The problem of quenching in the interval θ_1, θ_2 can be solved by studying:

(1) The function $\phi(\theta) = d\theta/dt$, that is to say, the kinetics of cooling during quenching within the considered interval of temperature.

(2) The function $F(\theta) = dx/dt$, that is to say, the kinetics of the transformation in the same interval.

(3) By writing the inequality (I) and by solving it by a suitable graphical method.
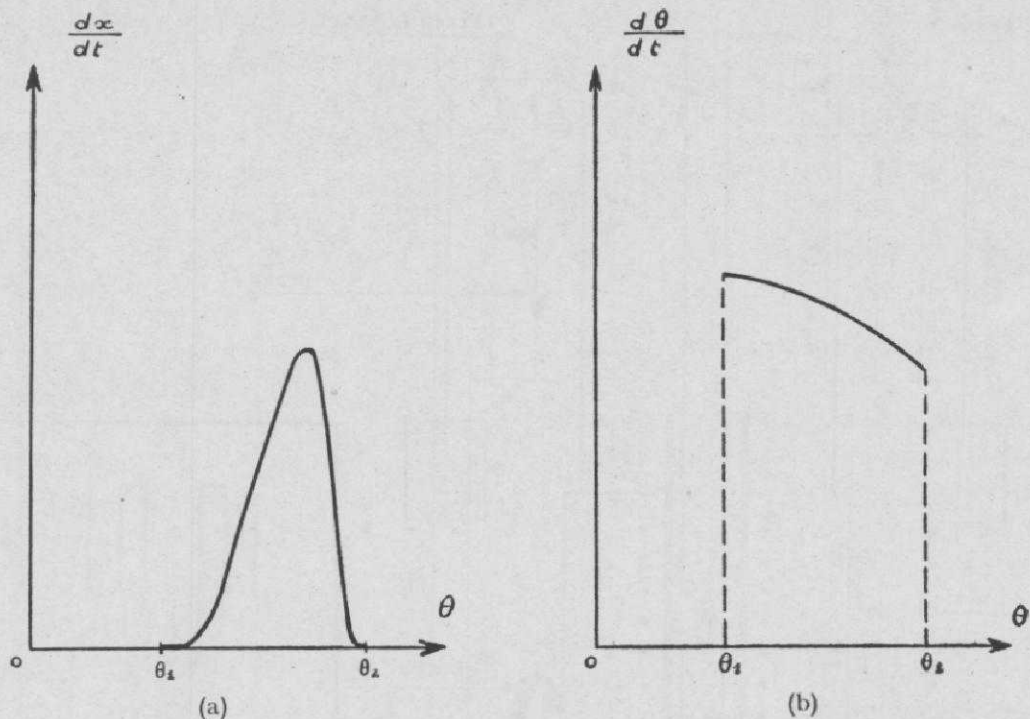
FIG. 1 — SCHEMATIC CURVES SHOWING THE VARIATIONS OF THE SPEED OF A HYPOTHETIC TRANSFORMATION AND OF THE SPEED OF COOLING DURING QUENCHING AGAINST TEMPERATURE

If the inequality (I) has a series of solutions of physical significance concerning the function $\phi(\theta) = d\theta/dt$ corresponding to different forms or sizes of sample and to one or several liquids, quenching is possible. All quenching liquids giving, for one sample of form and dimensions fixed, a cooling speed-temperature curve satisfying this condition can be considered as suitable quenching liquids.

The initial and fundamental idea of solving quenching problems by dividing them in two parts, first, cooling kinetics, second, transformation kinetics, was given by Prof. Albert Portevin[3,13] and his collaborators. Unfortunately in 1917 they were not convenient without inertia recorders and the consequences concerning rapid quenching according to Portevin's ideas could not be fully drawn.

In this paper, we are describing only the kinetics of cooling, and in some peculiar cases its consequences on structure. The kinetics of transformation will be studied later, when a suitable dilatometer with very little inertia will be constructed in our laboratory.

This problem of cooling during hard quenching was partially treated by some authors such as Levy[8], Gude[4], Tagaya and Tamura[19], Sakui and Sato[14,15].

Apparatus for Quenching Experiments

Quenching is realized by very quickly substituting the electrical furnace by the quenching bath (FIG. 2). This movement requires 0·6 second.

In some experiments, the sample was a cylinder of 8 millimetres in diameter and 10 millimetres in height. In others, it was a cylindrical wire of 3 millimetres in diameter and 50 millimetres in height. A coaxial hole of 1 millimetre in diameter permits the path of the thermocouple built with wires of 0·3 millimetre in diameter and having a solder of 1 milligram. A very thin tube, situated at the upper part of the cylinder,
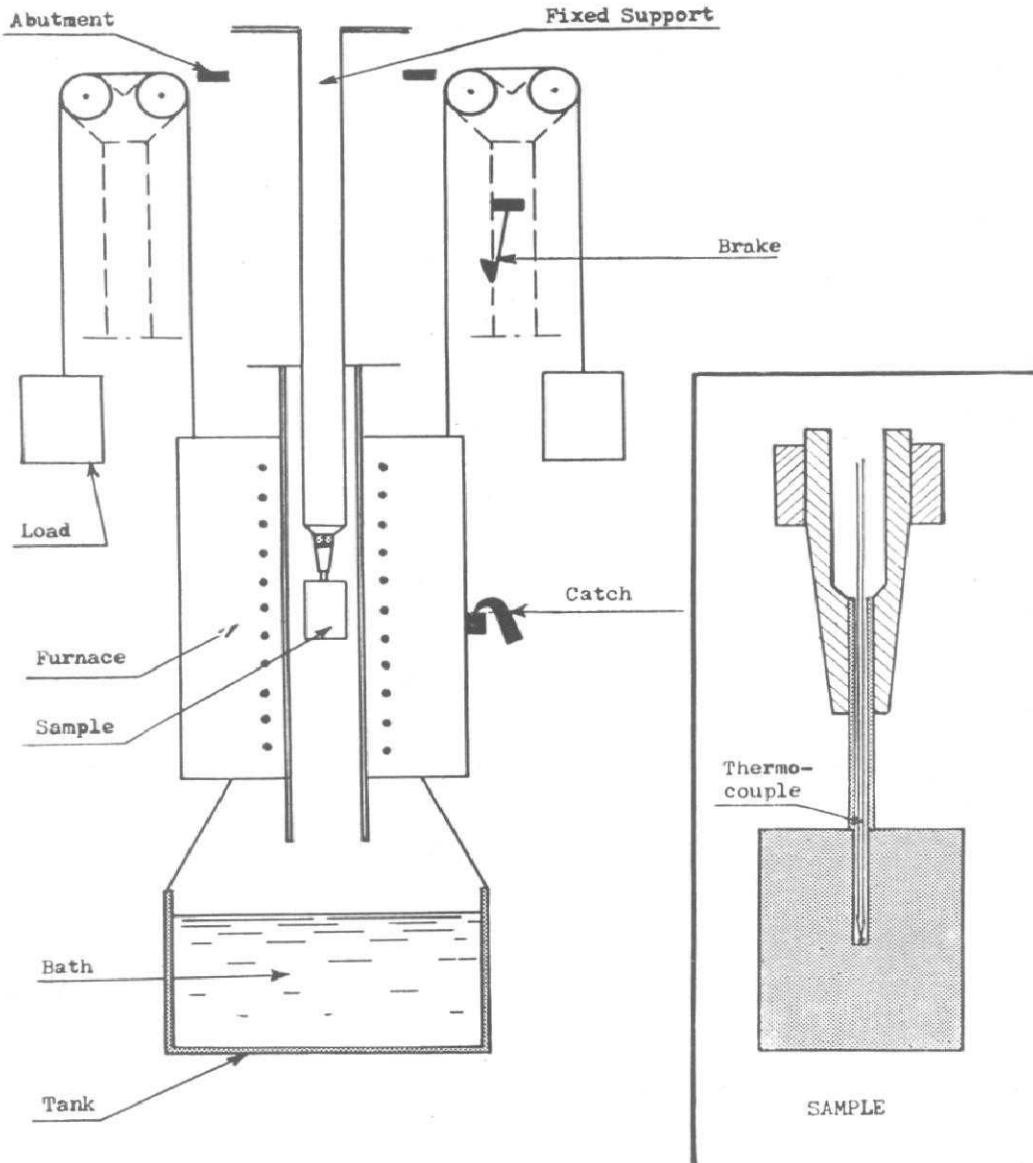
FIG. 2 — APPARATUS FOR QUENCHING EXPERIMENTS

prevents the penetration of liquid in the hole (FIG. 2).

The movement of the furnace and tank is ungeared by opening the electrically govern-ed catch. The electrical furnace goes up, carrying the tank and quenching bath which, at the end of its course, meets the specimen. Suitable brakes and shock-absorbers stop the movement when the whole specimen is immersed in the bath at the desired depth. Special vessels with electrically warming elements are used in the case of metallic baths. Another type of vessel with a special cover permitting to avoid creeping of vapours across the tube of the furnace and formation of explosive

mixtures with air is used when the quenching liquid is an inflammable one. In these vessels, an atmosphere of nitrogen and vapours is steadily maintained.

The recording cathodic tube is an electro-static one. An amplifier of suitable voltage can give a highest gain of 2000. A voltage of 0·008 volt provides a vertical deflection occupying 1 centimetre on the screen. A non-linear time base is realized by supplying the vertical plates of the tube with the increasing charging voltage of suitable condensers. The mean velocity of the spot can be fixed at the desired value. The lowest value attainable with our cathodic tube corresponds to a full-size pattern on the screen during 16 sec. Practically, it has no limit towards the highest values concerning our peculiar application.

Conditions of photographic recording and of visual observation are simultaneously realized.

Inertia of the whole recording apparatus is practically inertia of the thermocouple. When a solder of 1 milligram in weight is quenched, a cooling speed of 25,000°C. per second can be attained. In our own experiments, the hardest quenching liquid gives 500°C. per second as highest value. It is evident that in these conditions the thermocouple inertia is practically negligible.

Kinetics of Very Rapid Cooling during Hard Quenching

Fig. 3 shows different experimental curves directly obtained with the cathodic recording tube. For interpretation and for practical uses, it is better to transform, by a suitable differentiation, all these curves in curves of variations of the cooling speed against temperature or against time. The cooling speed-time curves must be chosen for detailed analysis of phenomena. The speed-temperature curves are permitting to set in clear terms the problem of quenching.

Figs. 4, 5 and 6 show speed-temperature curves for different quenching liquids.

The first and simplest case is that of quenching in undecomposable liquids or solutions, such as quicksilver (FIG. 4A) and other molten metals, of which both liquid and vapour phases are absolutely undecomposable, in the absence of dissolved gases, water and some aqueous solutions stable at 100°C. (FIG. 5A). In the last two cases, the liquid phase is strictly undecomposable and the gaseous phase practically undecomposable when temperature is not too high or when the time of staying at high temperatures is a very short one.

In all these cases we have between the specimen and the liquid an intermediate layer of metallic vapour or water vapour. This layer is always relatively thin, less than 0·1 millimetre in water and in aqueous solutions. A great temperature gradient is realized and a mechanism of permanent exchange of molecules between the liquid and the vapour phases assures a very quick transfer of heat.

Two very different laws of variation of speed against temperature are observed on both sides of the maximum.

From the characteristic temperature of the maximum, θ_M, down to the room temperature θ_1, the cooling speed decreases when temperature decreases according to the very simple approximative law:

$$d\theta/dt = - a(\theta - \theta_1)$$

where $-a$ is the negative slope measured on the curve. By integration, we have:

$$\theta = \theta_1 + (\theta_M - \theta_1) . \exp. (- at)$$

From the initial temperature θ_0, down to the value θ_M at the maximum, the law of increasing speed when temperature decreases is practically a linear one. The slope of the straight line is so great that the highest value of speed is attained at only 50°C. lower than θ_0 value. It is this part of the curve which
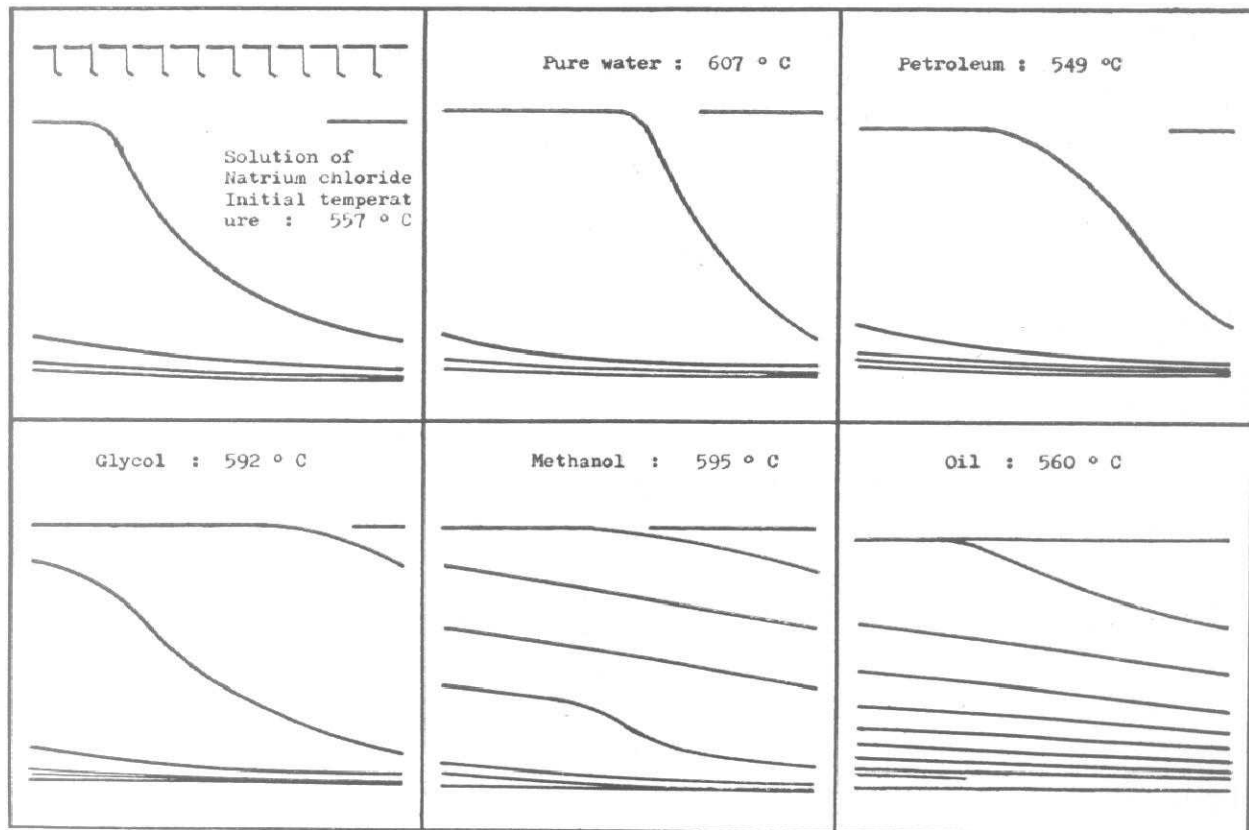
FIG. 3 — EXPERIMENTAL COOLING CURVES FOR A LITTLE CYLINDER OF NICKEL OF 4·53 GR. DURING QUENCHING AS RECORDED WITH AN ELECTROSTATIC CATHODE TUBE (Temperature is plotted against time. See in the left-hand upper edge of the figure a standard curve with a periodic signal of half a second)

corresponds to the formation of the intermediate layer. The high cooling effect is chiefly due to the latent vaporization heat.

A very striking fact is that all curves obtained with different initial temperatures, 800°, 700°, 600°, 480°C., etc. (FIG. 4A) have, after their respective maxima, practically the same straight line as limit towards the low temperatures. This limit is attained about 50°C. below the temperature θ_M corresponding to the maximum, that is to say, 100°C. below the initial temperature θ_o.

If one desires to obtain the highest cooling speed attainable with a given liquid and a given sample in a given interval of temperature, for instance, between 500° and 400°C., it is quite useless to start from elevated temperatures, 900°C., for instance. It is sufficient to operate quenching from a temperature 100°C. higher than the upper limit of the interval, 600°C., for instance, for the upper limit of 500°C. in the previous example.

Quenching in decomposable liquids or solutions is a more complicated case. Figs. 4B, 4C, 4D, 5B and 6 are striking examples of this fact. In all these cases, the whole process of quenching from high temperatures, 800°C., for instance, is complex.

At high temperatures, the intermediate layer between liquid and sample is often formed of permanent gases proceeding from
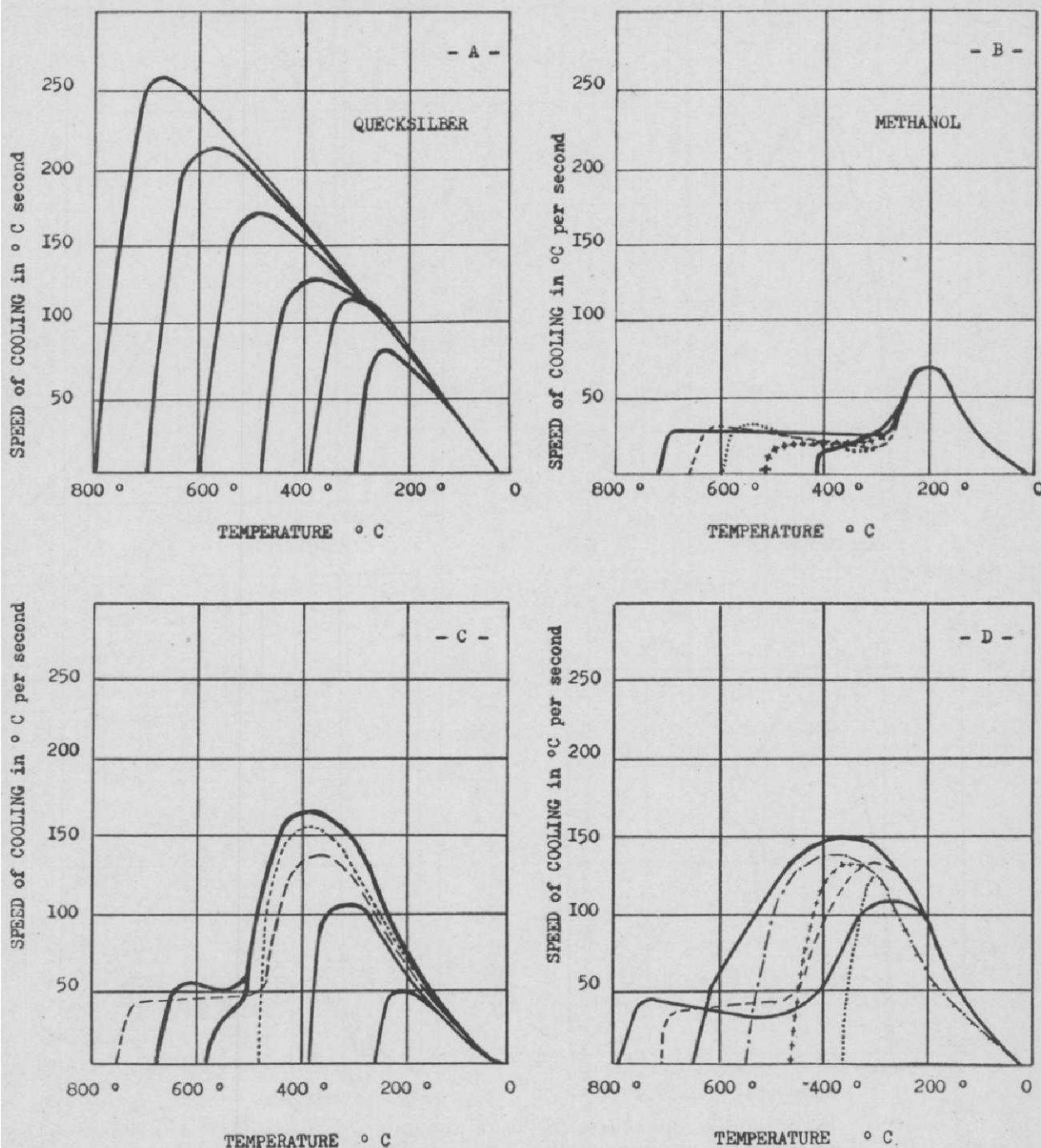
FIG. 4 — COOLING SPEED DURING QUENCHING IN: A — QUICKSILVER, B — METHANOL, C — GLYCOL, AND D — PETROLEUM

thermal decomposition or degasification. This layer, 1 millimetre thick, is a very poor heat conductor. No exchange of molecules between liquid and vapour is possible at their interface. The process of cooling at high temperatures is slow.

At low temperatures, the intermediate layer is formed of vapour alone. This less than 0·1 millimetre thick layer assuring heat transfer by permanent exchange of molecules at the vapour-liquid interface is a better heat conductor.
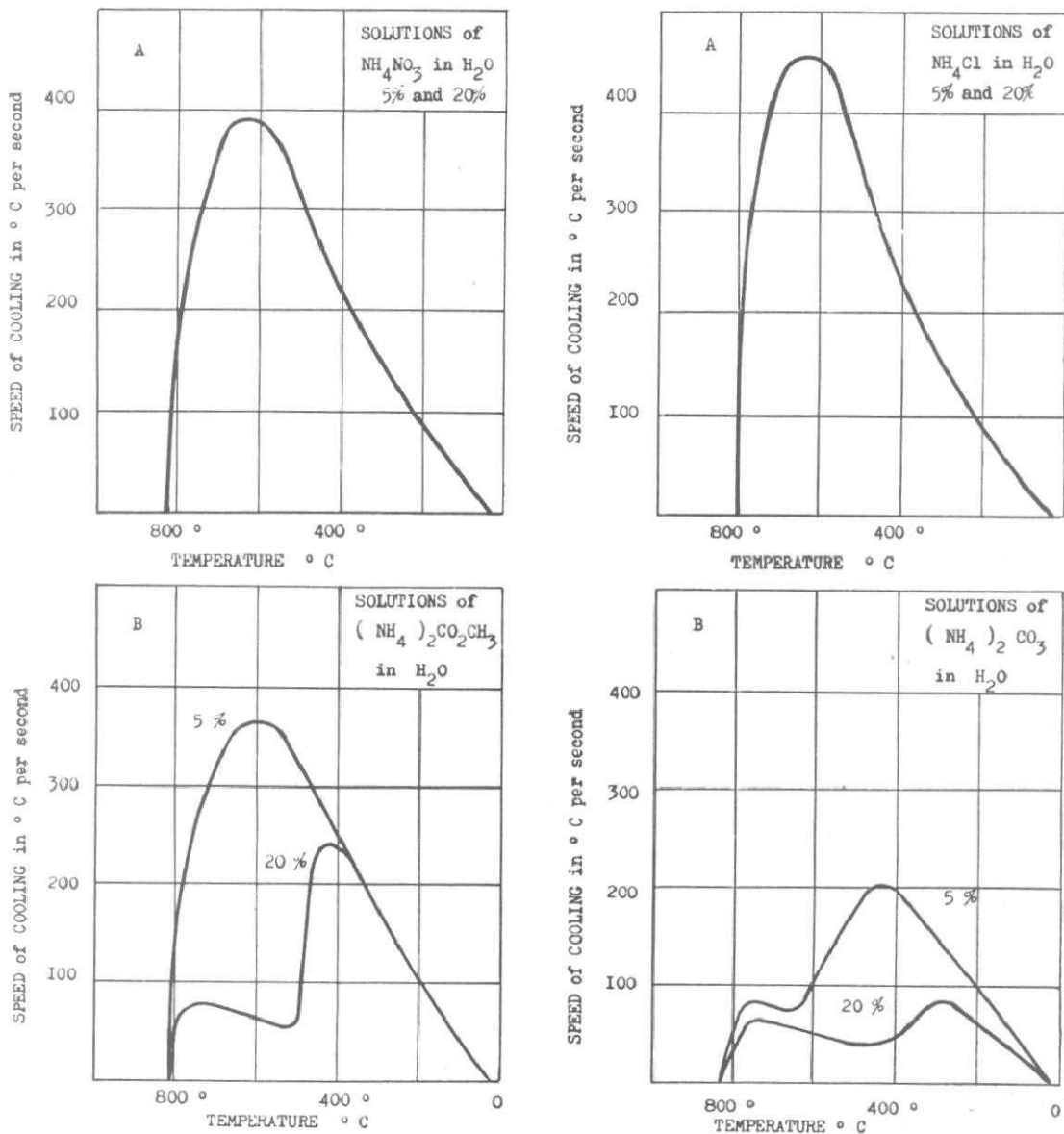
FIG. 5 — COOLING SPEED DURING QUENCHING IN SOME AQUEOUS SOLUTIONS: A — THE SOLUTION IS STABLE AT $100°C$.: SOLUTIONS OF AMMONIUM NITRATE AND AMMONIUM CHLORIDE. B — THE SOLUTION IS UNSTABLE AT $100°C$.: SOLUTIONS OF AMMONIUM ACETATE AND OF AMMONIUM CARBONATE

Transition between these two processes can be visually observed during quenching from high initial temperatures θ_o. When the gaseous thick layer is progressively rubbed out from the bottom to the top of the sample, liquid falls on the metal and is very quickly vaporized. This phenomenon is quite responsible for the very great slopes of cooling speed-temperature curves between their approximately constant levels and their maximum (FIGS. 4B, 4C, 4D, 5B, 6A and 6B). Detailed form of each cooling speed-temperature curve is a very important fact. It is evident that, if one desires to solve a
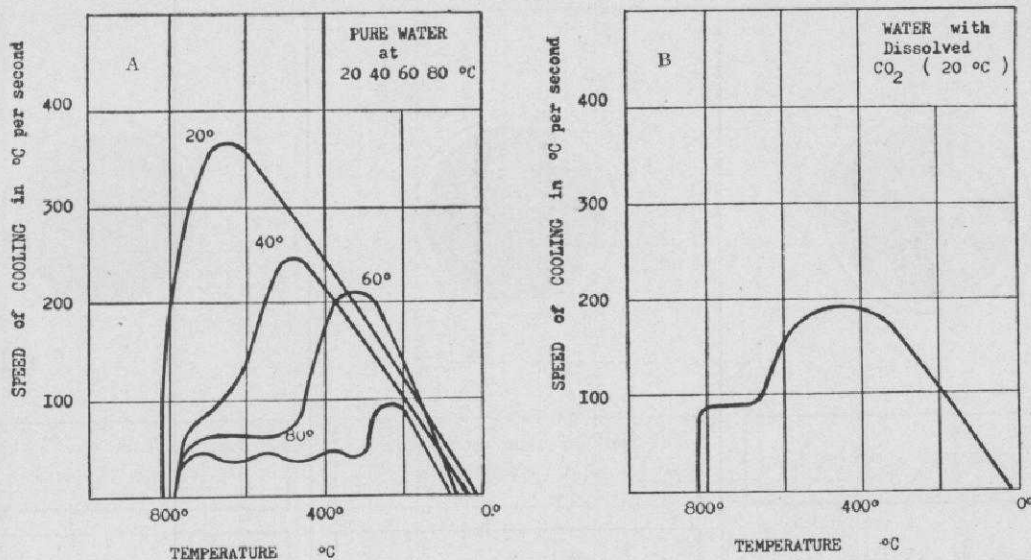
FIG. 6 — COOLING SPEED DURING QUENCHING IN: A — PURE WATER MAINTAINED AT DIFFERENT
TEMPERATURES; B — A SOLUTION OF CARBON DIOXIDE IN WATER

peculiar quenching problem, the mean cooling speed, which is usually defined by the whole time of cooling from high to low temperatures, is of very little significance.

It is absolutely necessary to consider the actual cooling speed $d\theta/dt$ at each temperature of the interval of transformation. Our curves show that some liquids such as oil, petroleum, warm water, generally considered as soft quenching agents, have actually this quality at high temperatures but not during cooling at low temperatures. One liquid is not a hard or a soft quenching medium in absolute manner, but only relatively to a given transformation arising in a given interval of temperature.

Three other interesting facts are in evidence on our cooling speed-temperature curves.

(1) *The influence of dissolved stable salts* on quenching in water (FIG. 5A) is quantitatively analysed. A maximum speed of 500°C. per second can be attained by quenching from 800°C. in a solution of NH_4Cl or $NaCl$ in water. In the same conditions, pure water gives a maximum of 350°C. per second.

The Zavarine's concept[22], according to which the very small crystals formed at the interface vapour-liquid by sudden vaporization break the vapour layer, is corroborated by the fact that the increase of the cooling effect is, in a large interval, practically independent of the concentration (FIG. 5A).

(2) *From comparison between the cases* of NH_4Cl or NH_4NO_3 solutions (FIG. 5A) and of $(NH_4)_2CO_2CH_3$ solutions (FIG. 5B), one can deduce that the effect of slow cooling by formation of a thick gaseous layer has its origin in the decomposition of the liquid phase alone. On the other hand, in quenching in organic unstable liquids such as methanol, ethanol, hexane, glycol, petroleum (kerosene), oil, etc. (FIGS. 4B, 4C, 4D), it is the vapour phase itself which is decomposed.

(3) *The very cause of the slow cooling process in warm water* is clearly explained. The intense degasification of water at the vapour-liquid interface, arising when all the water of the quenching bath is maintained at 80°C., is responsible for the very long, almost horizontal, level of the corresponding
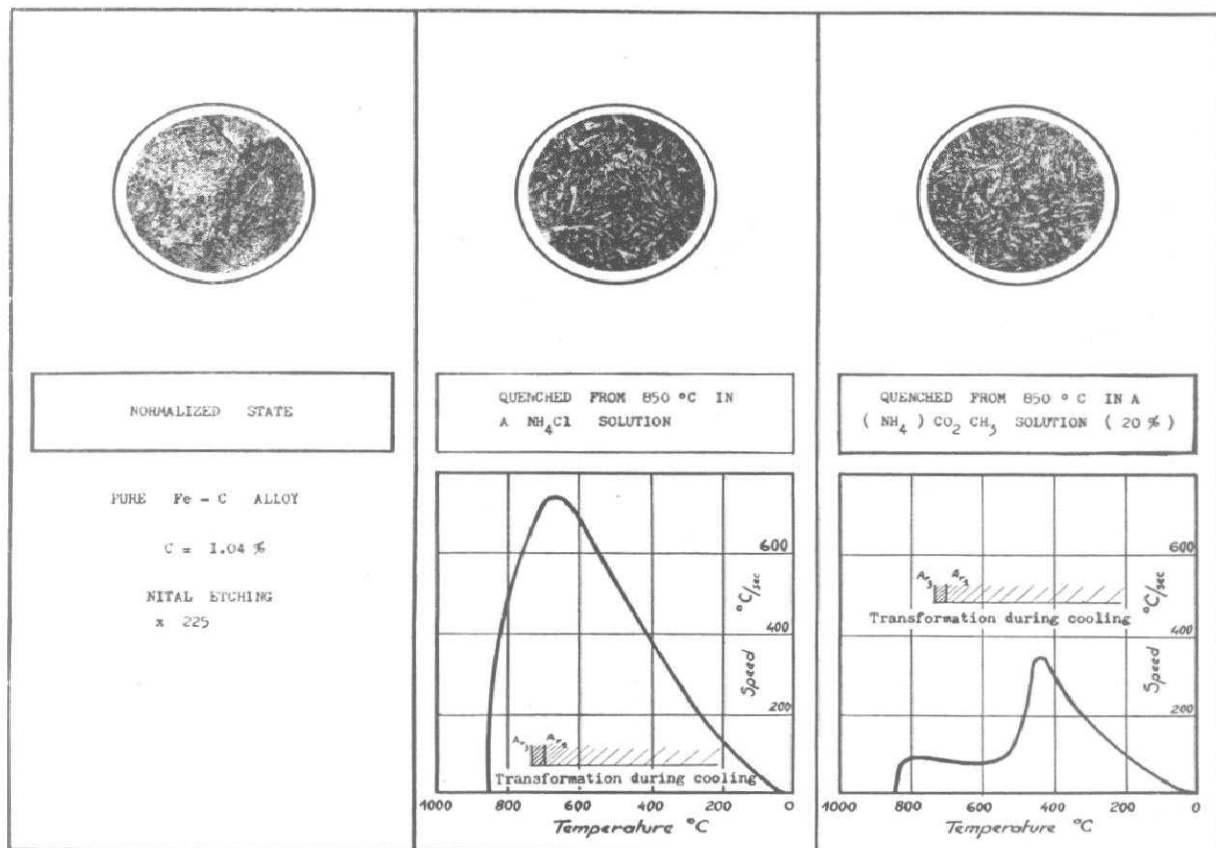
FIG. 7 — COOLING SPEED-TEMPERATURE CURVES

curve (FIG. 6). The three waves observed on the other side of this level exactly correspond to the three bubbles actually observed during cooling. The high slope of the curve between the level and the maximum corresponds to vaporization of water arising during the vanishing of the thick gaseous layer.

Application to Some Alloys of Iron, Nickel and Carbon

This part of our paper is less expanded than one, and chiefly the authors, could desire. Our studies on peculiar alloys are in their early stage. However, we are thinking that it would be interesting to illustrate this paper with some examples.

All our alloys were elaborated in our own laboratory in a vacuum and induction heating furnace from pure metals or elements.

Iron and nickel were very pure metals from iron-carbonyl and nickel-carbonyl respectively. Carbon was obtained by Glucose's pyrolysis.

Crucibles were built with pure alumina and a small amount of calcium aluminate as binding material.

Figs. 7, 8 and 9 show cooling speed-temperature curves and microphotographs of these alloys in their different quenched states.

In every case, Ar_3 and Ar_1 points are given for comparison with remarkable points of the speed-temperature curves. M_S and M_F have not been determined.
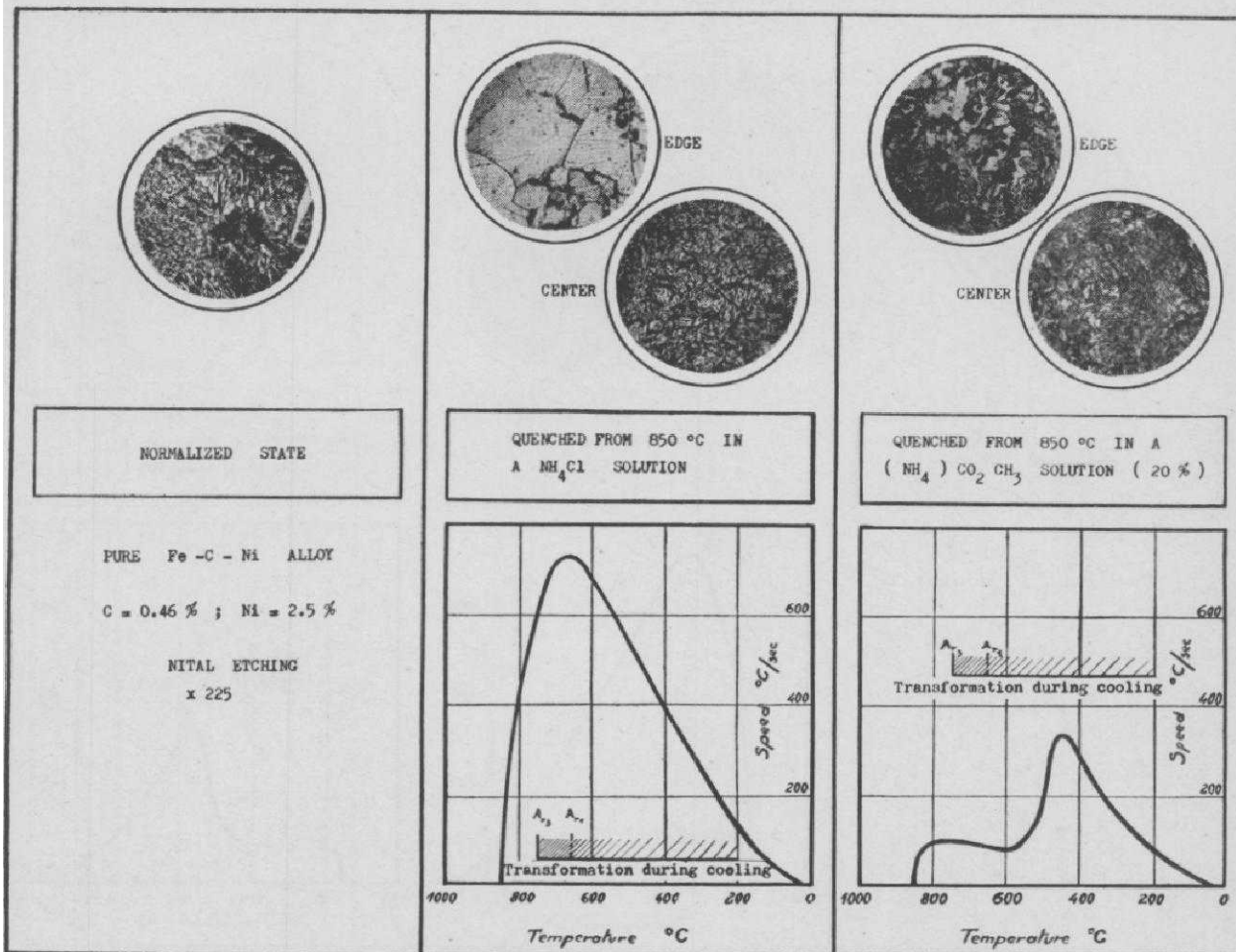
FIG. 8 — COOLING SPEED-TEMPERATURE CURVES

Our identifications are summarized in Table 1.

The most surprising result is the keeping up of austenite in the very rapid quenching observed in the edge of the sample. We do not know the actual value of the cooling speed in this outer part, but only a lower limit, 680°C. per second, near the Ar_3 point, measured at the centre of the specimen.

This fact seems surprising when one considers the relatively small nickel percentage, 2·5 per cent.

Our arguments for identification of this austenitic phase are the following:

(1) The presence of this phase in a part of the sample where the cooling effect is surely higher than in the centre where the identification of the martensitic phase cannot suffer discussion.

(2) By softening at 400°C. during 2½ hr. we observed carbide precipitation in the austenitic grain.

Perhaps more direct, magnetic proofs were not yet tried.

The difference between hard quenching in NH_4Cl solution and soft quenching in $(NH_4)CO_2CH_3$ solution was strongly marked at high temperature, that is to say, at Ar_3 point, but showed weakly at low temperature, that is to say, in the M_S-M_F interval. The following numeral values illustrate, in a quantitative manner, this assertion: cooling speed near Ar_3 point by quenching in NH_4Cl solution is 650°C. per second in the case of our Fe-C-Ni, C: 0·46, Ni: 2·5 alloy,
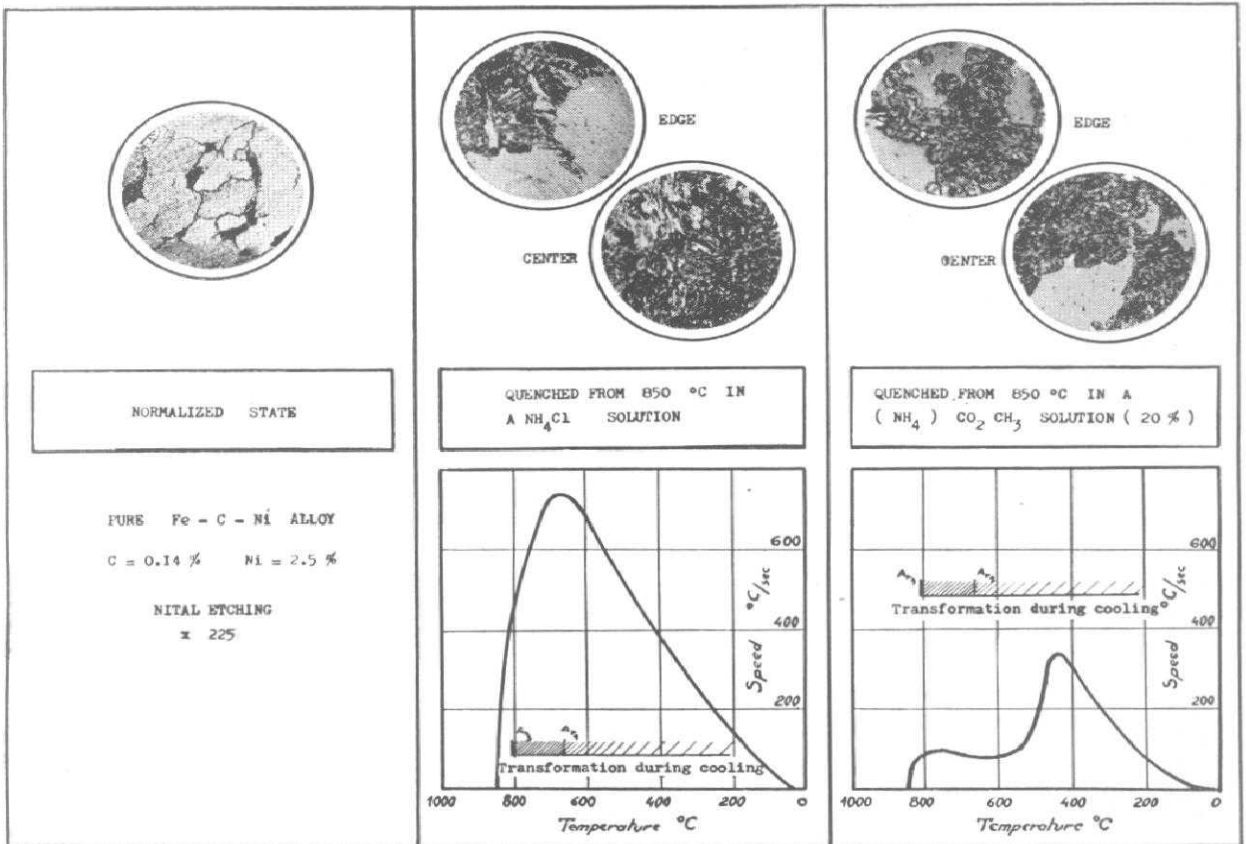
FIG. 9 — COOLING SPEED-TEMPERATURE CURVES

TABLE 1

ALLOYS	NORMALIZED	QUENCHED FROM 850°C.	
		in NH₄Cl Sol.	in (NH₄)CO₂CH₃ Sol.

Fe-C   C: 1·04
  Fig. 7
	Pearlite + Fe₃C
	Apparent austenitic
	  grain boundaries
		Martensite	Martensite

Fe-C-Ni
 	
C: 0·46 Ni: 2·5
 	
Fig. 8
	Pearlite + ferrite	Edge: Austenite
		
		Centre: Coarse
		  martensite
			Edge: Bainite + retained
			  austenite
			Centre : Bainite + fine
			  martensite + few re-
			  tained austenite

Fe-C-Ni
 	
C: 0·14 Ni: 2·5
 	
Fig. 9
	Ferrite + few pearlite	Edge: Coarse auste-
		  nite ? + fine marten-
		  site + retained auste-
		  nite
		Centre: Fine marten-
		  site + few retained
		  austenite
			Edge: Ferrite + lamellar
			  bainite
			
			Centre: Ferrite + fine
			  bainite

and only 100°C. per second when quenching in a $(NH_4)CO_2CH_3$ solution.

Conversely, in the M_S-M_F assumed but not determined interval, this cooling speed attains 240°C. per second by quenching in a NH_4Cl solution and 150°C. per second in a $(NH_4)CO_2CH_3$ solution.

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