

CHAPTER 2

EXPERIMENTAL

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A) The materials

1-Nitric acid(HNO₃) from A.R. reagent.

2-Potassium hydrogen phthalate (KH-phthalate)
from Merck

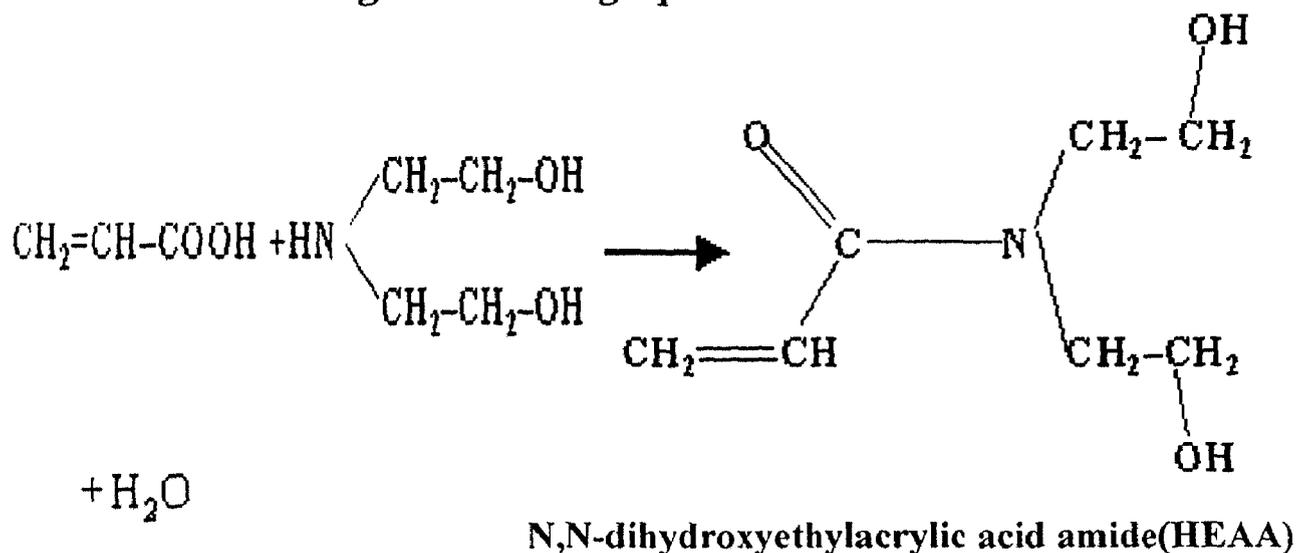
3-Sodium hydroxide(NaOH) from A.R. reagent.

4-N,N-dihydroxyethylacrylic acid amide(HEAA).

(i) Preparation of HEAA⁽¹¹⁷⁾.

N,N-dihydroxyethylacrylic acid amide(HEAA) was prepared in the following manner:

A mixture of freshly distilled diethanol amine (0.1mole; 10.5gm), acrylic acid (0.1mole; 7.2gm) and 10 ml xylene were refluxed using Dean and Stark apparatus until 0.1mole (1.8ml) of water was collected. The product was then cooled, filtered and dried by vacuum distillation of the solvent. A clear pale brown viscous material was obtained according to the following equation:



(ii) HEAA structure may provide better adsorption and coverage

The structure of HEAA was identified by:

- (a) UV spectra exhibited intense absorption band at $\lambda_{\max} = 222$ nm, attributed to the p-p* transition, and two shoulders at $\lambda_{\max} = 240$ nm and 330 nm which can be attributed to the n-p* transition.**
- (b) The IR spectrum exhibited the following bands: ν_{OH} at 3381 cm^{-1} , ν_{CH} (aliphatic) at 2934 cm^{-1} , ν_{CON} at 1732 cm^{-1} , $\nu_{\text{C=C}}$ at 1628 cm^{-1} .**
- (c) The $^1\text{H-NMR}$ spectrum (CDCl_3) showed the following signals: 3.71 (m, 8H, 4 CH_2), 4.18 (s, 2H, 2OH) and 4.70 (m, 3H, 4 $\text{CH}_2=\text{CH}$ -).**

B) Metal samples

Two types of carbon vanadium (C.V.) steel were used in this study. The first was low carbon vanadium (L.C.V.) and the second was medium carbon vanadium (M.C.V.) therefore, four specimens of every type have been used, one was kept without heat treatment, and the others were heat treated by using normalizing, spheroidizing, and quenching regimes.

1-Chemical composition of the metal samples

The chemical composition of the metal samples was determined using emission spectrometer, with the aid of ARL quantimeter (model 3100-292 IC). The chemical composition of both types of vanadium carbon steel samples are given in Table(1):

Table (1): Chemical composition of metal used

Sample	C% W/w	Mn % W/w	S % W/w	P % W/w	Si % W/w	Cu % W/w	V % W/w
Low carbon	0.15	0.90	0.065	0.045	0.23	0.15	0.09
Medium carbon	0.29	0.98	0.070	0.045	0.33	0.19	0.09

2- Heat treatment

Heat treatment of two types of C.V.steel was carried out in an electric muffle furnace. Charcoal was placed around the samples to avoid oxidation. Heat treatment regimes, which used are: Normalizing, Spheroidizing and Quenching.

i- Normalizing regime

As-received sample was putting in an electric muffle furnace where the temperature raising in to 920 °C (Austentizing temperature), through five hours. Then, sample remains in furnace for one hour at 920 °C (Holding time), followed by gradually cooling of sample in air. The phase, which formed due to this heat treatment, is fine pearlite. The steps of this regime are shown diagrammatically in Fig (9).

ii-Quenching regime

As-received sample was putting in an electric muffle furnace where the temperature raising in to 920 °C (Austentizing temperature) through five hours. Then, sample remains in furnace for one hour at 920 °C (Holding time), followed quenching of sample in oil (light mineral oil).

The phase, which formed due to this heat treatment, is martensite. The steps of this regime are shown diagrammatically in Fig (10).

iii-Spheroidizing regime

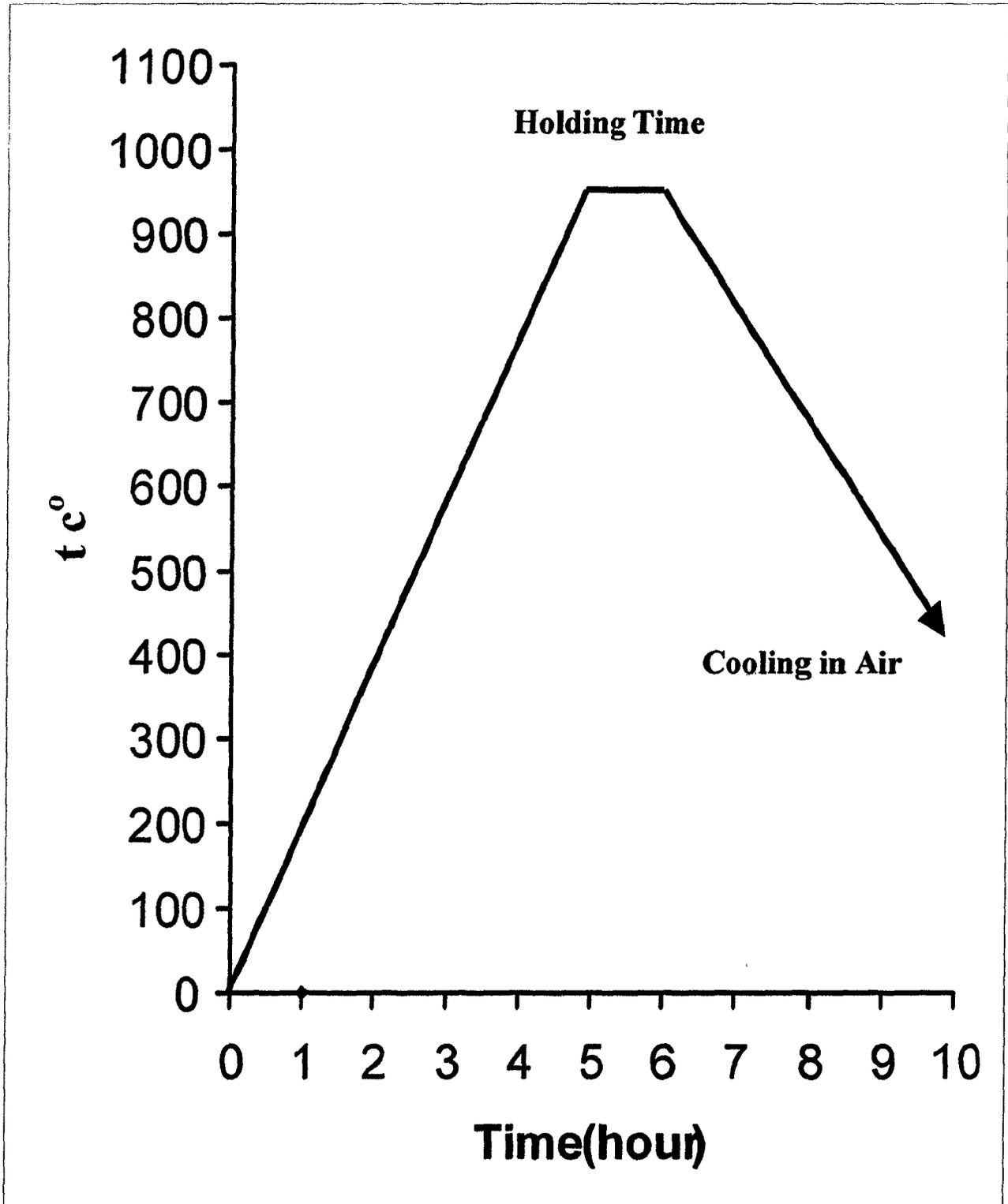
As-received sample was putting in an electric muffle furnace where the temperature raising in to 800 °C through four hours. Then, sample remained in furnace for one hour at 800 °C (Holding time),Then, decreasing temperature from 800 °C to 700 °C trough one hour. Then, sample remains in furnace for six hour at 700 °C, followed by gradually cooling in furnace.

The phase, which formed in this case is spheres of cementite particles (spheroidized particles) in completely ferritic matrix. The steps of this regime are shown diagrammatically in Fig.(11)

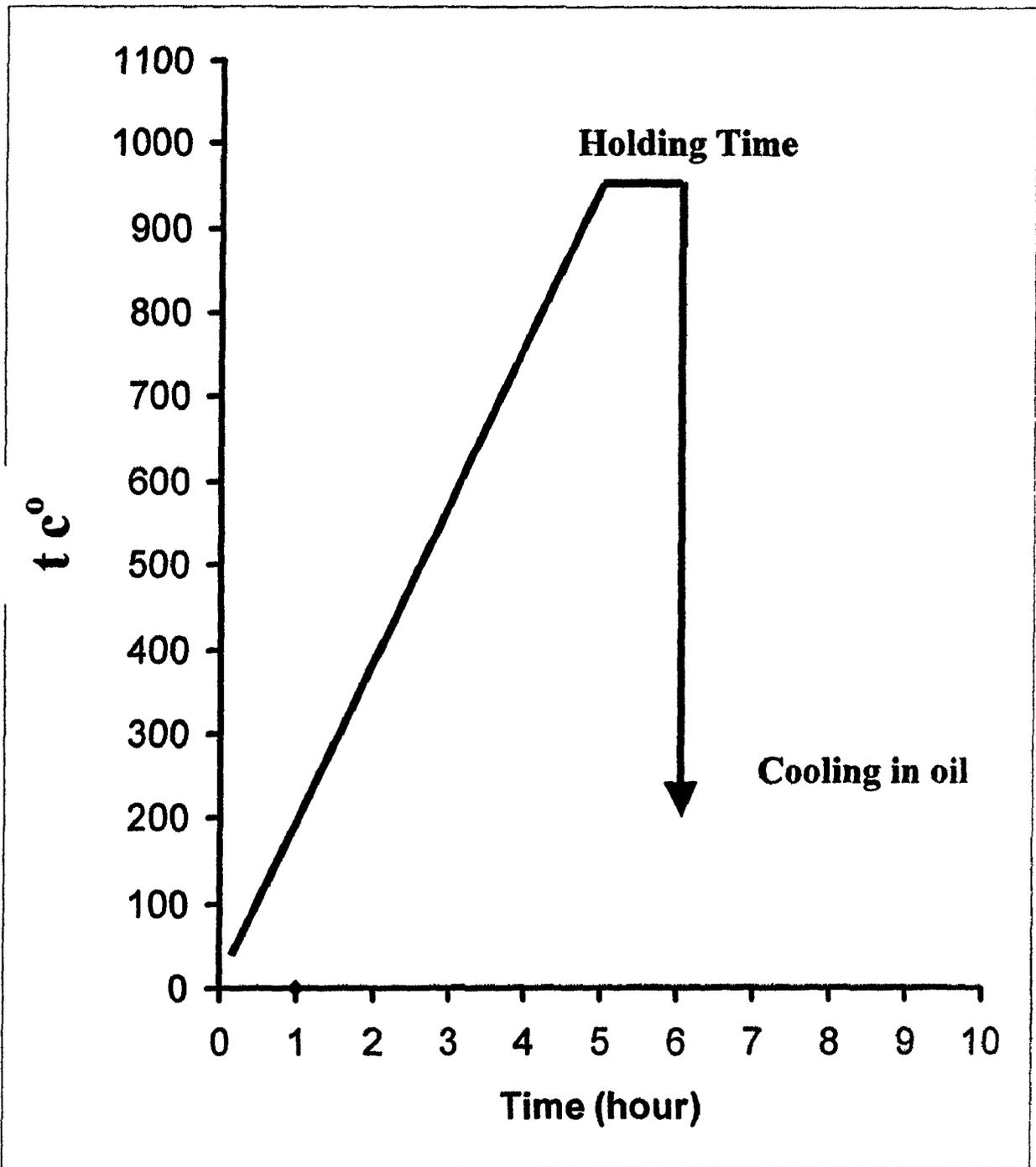
3-Microscopic inspection

Microscopic inspection was made for metal samples before and after heat treatment, they characterized by using optical microscope technique (Nikon, made in Japan).which has shown in Fig (12). The samples would be prepared with grinding, polishing and etching according to standard method for microscopic inspection as the following:

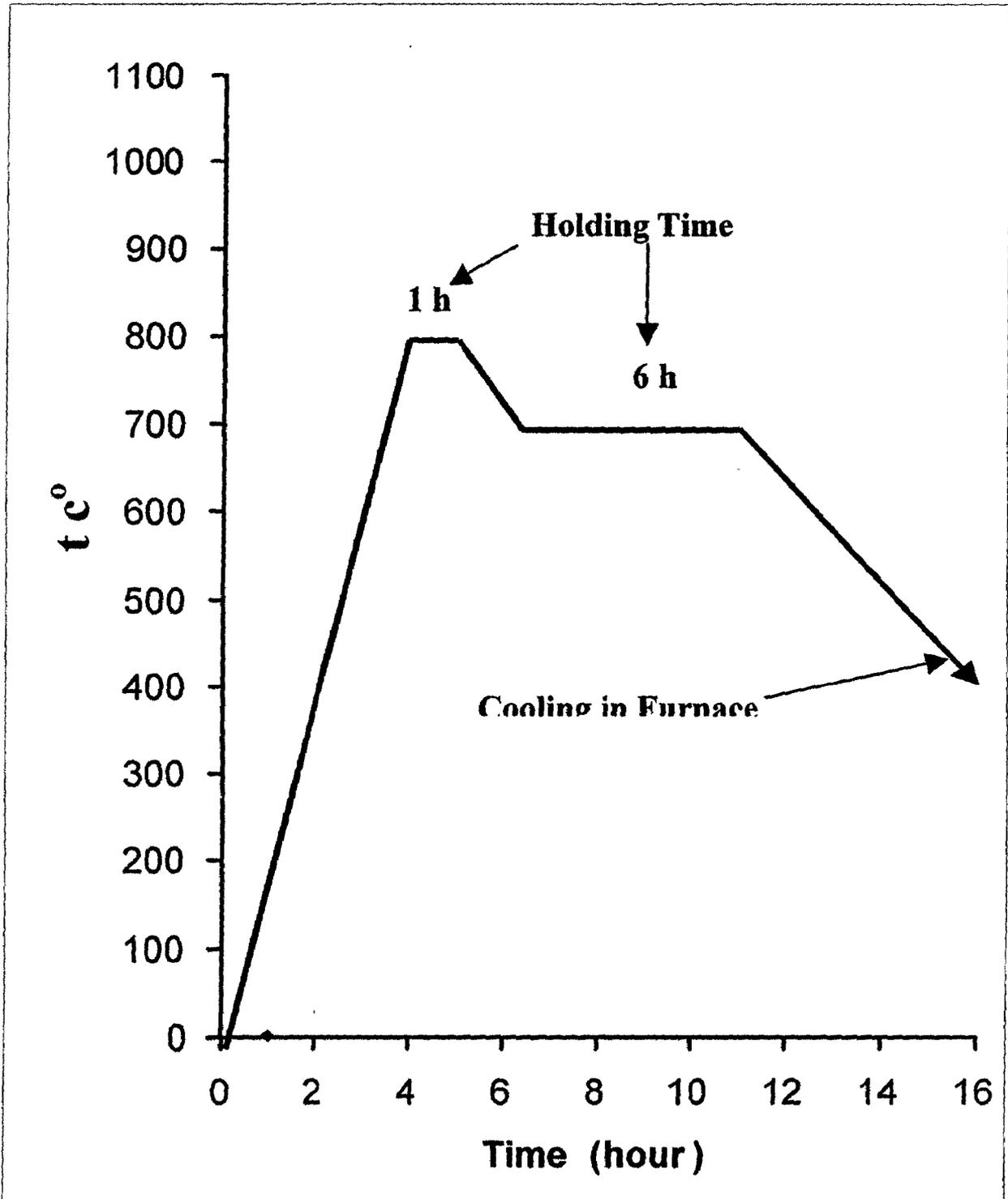
- 1)Grinding: using mechanical grinder In Fig (13).for grinding metal sample with different grades of apperceive papers, initially with course grade and gradually to binder ones, then finally with the finest grade.**
- 2)Polishing: using alumina past in mechanical polisher in Fig (13) for finally polishing of sample surface be mirror bright.**
- 3)Etching: etchant of 2% nital (2 ml of conc. HNO₃ in 98 ml of C₂H₅OH) for etching metal sample, to show the different phases under microscope.**



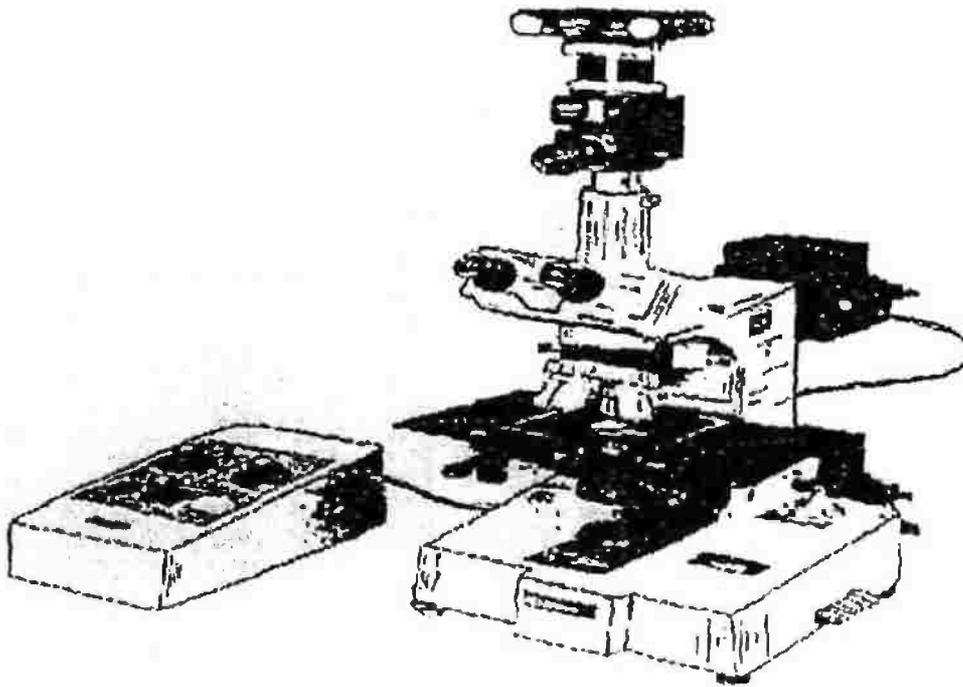
Fig(9): Heat treatment regime(Normalizing) for L and M.C.V. steel samples.



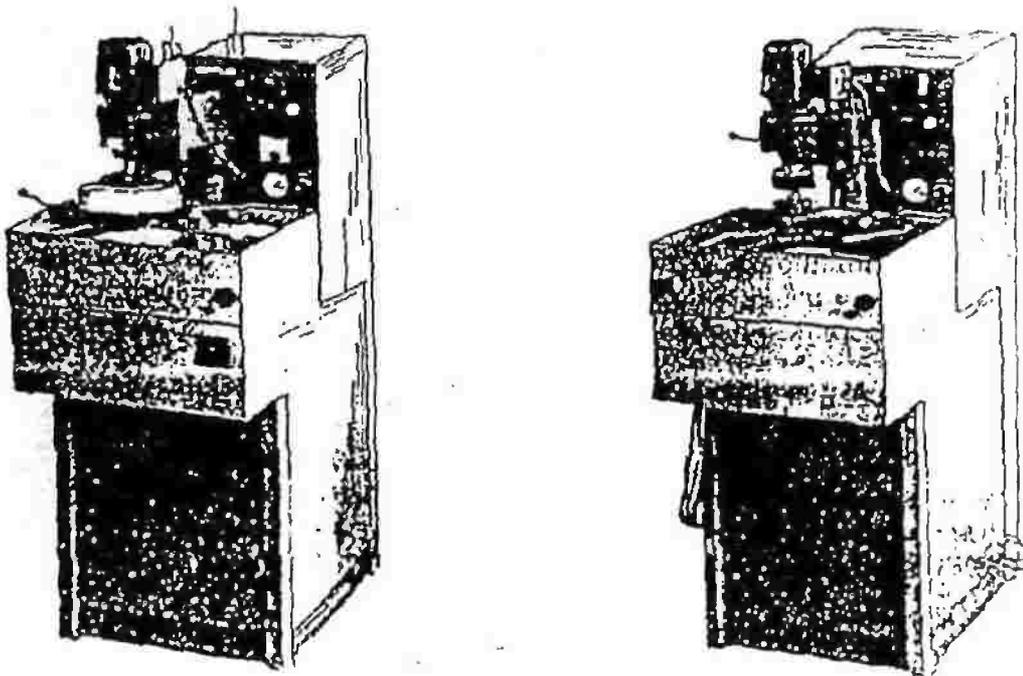
Fig(10): Heat treatment regime for (Quenching) L and M.C.V steel samples.



Fig(11): Heat treatment regime for (Spheroidizing) L and M.C.V steel samples.



Fig(12):Nikon Metaphor metallurgical microscope with large stage and 35-mm camera with automatic exposure control. (Courtesy of Nikon. Inc., Instrument division)



Fig(13): The Struers Abraplan automatic grinder(left) and Abraplan automatic polisher (right). (Courtesy of Struers. Inc.).

C) preparation of solutions

All solutions were prepared from analytical grade chemical reagents and used without further purification. Different concentration of HNO_3 (0.1, 0.3, and 0.5 M) were prepared and standardized by NaOH (where NaOH standardized against KH-phthalate), while 10^{-4} M HEAA in 0.1 M HNO_3 solution was prepared by dissolved 0.016 gm from HEAA in 1 liter of 0.1 M HNO_3 solution and dilute these solution by 0.1 M HNO_3 solution to prepared others inhibition solutions. These solutions were used as corrosion media. Stock solutions were prepared using distilled water.

D) preparation of metal samples

The working electrode having the chemical composition given in Table (1). Vanadium steel in the form of rods. The surface areas which exposed to corrosion for was casting, normalizing, quenching, and spheroidizing L.C.V.steel are 0.5595, 0.5385, 0.5242 and 0.5463 cm^2 , respectively, but the surface areas exposed to corrosion are 0.5476, 0.5115, 0.5541 and 0.5608 cm^2 for as cast, normalizing, quenching, and spheroidizing M.C.V.steel respectively. Every rod was weld from one side to a copper wire used for electric connection. The samples were embedded in glass of just larger diameter than the samples. Epoxy resin was used to stick the sample to glass tube as shown in Fig. (14). These also insured that constant cross-sectional area would be exposed to solution through the experiments. The exposed area was grinded with different apperceive papers in the normal way, initially with course grade and gradually to finer grade, then finally with the finest grade. Then, polishing using alumina paste on mechanical polisher in Fig.(13) for finally polishing of sample surface to be mirror bright, followed by washing with distilled water then with acetone and finally with doubly distilled water, just before immersion in the electrolyte cell

F)The procedure of measurement

Cathodic and anodic polarization technique was used for determination of corrosion rate. The electric set up used for polarization measurements is shown diagrammatically in Fig(15),

where the circuit consists of the electrolytic cell (A), the reference electrode (B) the working electrode (F), and auxiliary electrode (D).

The polarization current was draw from the constant current unite (C) having the range from 100μ A to 20 mA. the potential of the working electrode was measured using the potentiometer (EXTECH Model-3000 KARL FISCHER Digital pH-mV meter). Before each run, the cell was first washed with doubly distilled water and then with portion from the used HNO_3 . Firstly the open circuit potential of the working electrode was measured relative to the reference electrode until an equilibrium constant potential is reached, then the working electrode was polarized by cathodic current density which was increased step-wise and the corresponding cathodic potential was recorded after mixed intervals of time for each step. These steps were repeated for anodic polarization to record anodic potential.

1- Auxiliary electrode:

A graphite rod was used as auxiliary electrode.

2-Reference electrode:

It was a saturated calomel electrode (SCE) prepared from very pure chemicals. The calomel past was shaken with repeated changes of saturated KCl before it was introduce in the container over the pure mercury. Over the surface of the calomel past, there were always present crystals of KCl in order to ensure saturation with that compound. This electrode was written as follow:

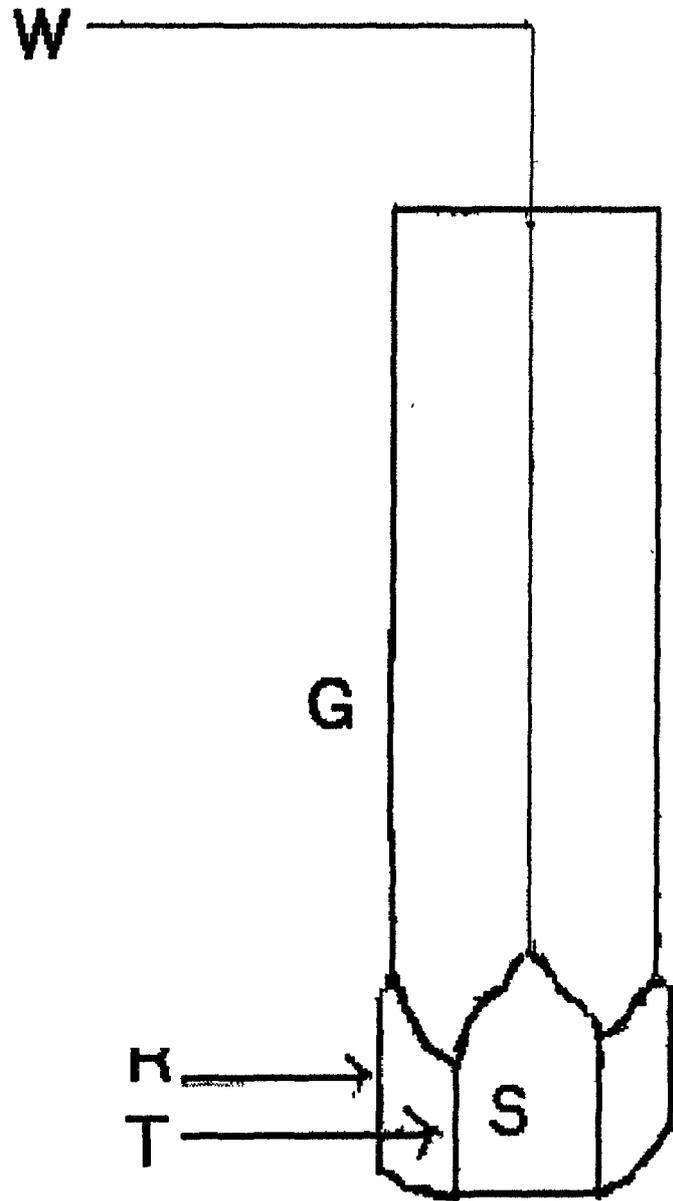
$(\text{Hg} \mid \text{Hg}_2\text{Cl}_{2(s)}, \text{KCl}_{(aq)} \text{ sat.}) E=-241 \text{ mV at } 25^\circ\text{C}.$

F) Solution of measurement.

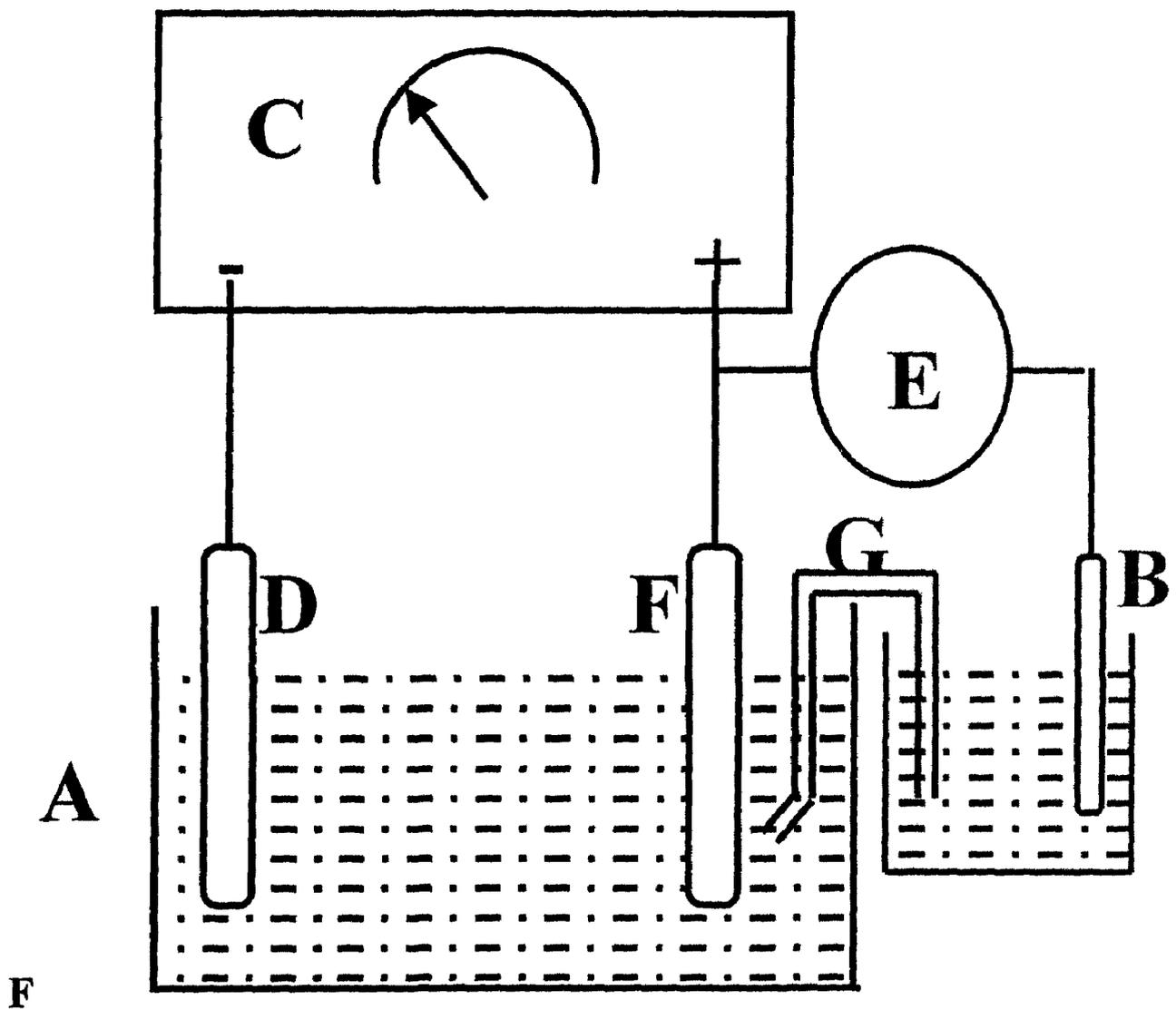
The electrolytic cell was filled with 200 ml of the solution. The electrodes were introduced through the multinecks of the cell. All electrode potentials were measured with respect to the saturated calomel electrode (SCE). The cathodic and anodic polarization processes of the L. and M. C.V. steel samples before and after heat treatment were studied in the following corrosion media:

- 1) **HNO₃ solution of different concentrations: 0.1, 0.3 and 0.5M at 25, 35, 45 and 55 °C.**
- 2) **0.1M of HNO₃ in presence of five concentration HEAA (2x10⁻⁵, 4x10⁻⁵, 6 x10⁻⁵, 8 x10⁻⁵ and 10⁻⁴M) at 25,35, 45 and 55 °C.**

W: Connecting wire.
G: Glass tube.
R: Silicon rubber.
S: Metal sample.
T: Teflon tape.



Fig(14): Sample electrode specimen for polarization.



Fig(15): The Electrical Circuit for Cathodic Polarization Measurements.

- A : Polarization cell**
- B : Reference Electrode**
- C : Constant Current Unit**
- D : Auxiliary Electrode**
- E : Potentiometer**
- F : Sample Electrode**
- G : Salt Bridge**