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SURFACE IMPROVEMENT OF DUCTILE CAST-IRON

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ABSTRACT

Diffusion impregnation with chromium is widely used as a surface treatment for steel and gray cast-iron, but very limited in ductile cast-iron. Two types of ductile cast-iron, ferritic and 60% pearlitic, are surface chromised under different conditions using powder pack method.

The maximum attained chromised layer thickness of 22 μm with surface microhardness of 1950 HV is achieved after treatment at 1000°C for 30 hours. The rate controlling of the carbide layer growth process during chromising is being the diffusion of the chromium element and the direction of layer growth is determined to be inward chromium diffusion. The evaluation of the newly formed layers by corrosion, oxidation and wear resistance are carried out and discussed in the light of the obtained results.

KEY WORDS

Chromising; Ductile cast-iron; Surface treatment; Diffusion; Corrosion; Oxidation and Wear resistance.

INTRODUCTION

Ductile cast iron has been used in many industrial applications and provide excellent combination of low price, good castability, mechanical and physical properties. However, surface properties of ductile iron needs further improvement to meet the increasing demand of industrial applications.

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Chemical heat treatment are commonly applied to iron, steel and other materials and find a great attention specially when surface properties are important.

Diffusion impregnation with chromium is one of the important methods used for improving the surface properties of steel and gray iron [1-7]. However, little information are available concerning the chromisation of ductile cast iron in general.

The aim of the present work is to study the diffusion layer formation during chromising of ductile cast iron by using a ferro-chromium powder under different conditions and evaluate the performance of the chromised surface.

EXPERIMENTAL PROCEDURE

Two types of ductile cast iron are used. The chemical compositions of the 60% pearlitic type I and the ferrlitic type II ductile cast iron are in the following table :

% C	% Si	% Mn	% S	% P	% Mg	Remark
3.60	2.5	0.67	0.054	0.03	0.04	Type I
3.62	2.25	0.12	0.008	0.033	0.045	Type II

The surface of specimens with dimensions of 10x10x20 mm³ are highly polished before the chromising treatment.

A mixture of 50wt.% ferrochrome (64%Cr, 3.2%C, 0.28%Si, rest Fe), 45wt.% Al₂O₃ and 5% ammonium chloride. The mixture is packed in heat resistance steel box, the box then sealed, and dried at 800 + 10 °C for two hours. The prepared samples are packed in the dried mixture, each sample is minimum 30 mm-apart from each other and from the box walls. The chromising process is carried at 850, 900 and 1000 °C for various holding times, up to 30 hours for each temperature. Finally the treatment is followed by furnace cooling. The structural morphology of chromised specimens is investigated using both optical microscope and SEM fitted with X-ray scan spectral analyser. The microhardness values of the chromised layer and the layer thickness are measured using Schemadzu type microhardness tester. Corrosion resistance test is measured in saltwater (3.5 % NaCl) at room temperature using Wenking Potentiostatic type POS 73 . The scale resistance test is carried out at 700, 850 and 950 °C up to 50 hours in furnace atmosphere. The wear resistance test is performed using pin-on-bush machine under a load of 750 gms for various duration times up to 30 minutes at a sliding distance of 89176 cm .

RESULTS AND DISCUSSION

a) Microstructure analysis

The optical microscopy as well as the SEM examination for both cast iron types, after similar heat treatment fig (1 and 2) , reveals almost the same chromised layer

features. Moreover, an area of pearlitic structure is formed in the adjacent zone to the chromised layer of the ferritic cast iron and is formed at all different holding times and temperatures. The formation of such pearlitic structure could be attributed to the carbon diffusion from the specimen core towards the surface in order to form the expected carbide phases in the chromised layer. Therefore, a high carbon concentration gradient, more than 0.8 wt.% C, will be responsible for the observed pearlitic structure in the adjacent zone to the chromised layer.

The microstructure analysis of the chromised zone, also indicated the presence of two distinct layers as shown in fig. (3). The line-scan analysis for both elements, chromium and iron are plotted on the corresponding micrographs as shown in fig (2). The chromium distribution inside the diffusion zone shows a maximum concentration at the outer surface of the layer and gradually decreases to be zero at the boundary between the chromised layer and the matrix.

b) Diffusion layer formation

The thickness measurements of the chromised layers as shown in fig.(4) indicate that the thickness of the diffusion layer increases with temperatures and / or holding times. It is also to observe that, the rate of layer formation is higher the higher treatment temperatures.

The kinetic calculation for the layer growth of the phase formed by diffusion can be expressed by the following relation [8] :

$$W = k\sqrt{t} \quad (1)$$

Where (W) is the thickness of diffusion layer, (t) holding time and (k) is the proportionality constant. The constant (k) depends mainly on the diffusion coefficient of the phase and the concentration gradient. The constant (k) is usually expressed by Arrhenius type relation [34] :

$$k^2 = D_0 \exp - Q / RT \quad (2)$$

Where (D₀) the frequency term
 (Q) the activation energy
 (R) the gas constant and
 (T) the absolute temperature.

It would be expected from relation (1) that the thickness of the diffusion layer increases parabolically with holding time. A plot of layer thickness (W) against the square root of time at different chemical heat treatment temperature are shown in fig.(5) for both cast iron types. A linear relationship is generally observed for each treatment temperature during different holding times for both types of cast iron. It is also possible to indicate that (W) is greater, the higher the holding temperature.

The activation energy of the process can be calculated from equation (2) and using a plot of K^2 versus $1/T$. For the two types of cast iron, the pearlitic and ferritic type, the activation energy of chromising are 55.4 and 58.5 K cal / mol respectively while the activation energy of chromium diffusion in iron is about 51 K cal / mol [9]. In that respect it is possible to determine that, the controlling mechanism during layer formation is mainly the chromium diffusion in the iron matrix. Furthermore, it has been experimentally proved that the introduction of chromium into iron will retard the diffusion process of carbon in ferritic matrix [10]. This could explain the difference in activation energy calculated values which is slightly higher compared with the reported value for chromium diffusion in iron.

The depth of the diffusion layer may vary in different ways with temperatures, since it depends on the ratio of diffusion flows in the chromised layer and the adjacent layer, i.e., the substrate material. Moreover, the phase with higher temperature stability and whose diffusion coefficient increases more with temperature will be grow in thickness. Therefore, the observed growth of chromised layer could be an indication of the relatively higher stability of chromised layer with regard to the adjacent zone.

The rate determining of the carbide layer growth process during chromising is being the diffusion of the chromium element. Moreover, on the basis of line - scan analysis the direction of carbides layer growth is determined to be inward chromium diffusion. Since the chromised medium consisted of ferro - chrome powder mixture, where the iron represents, 32.5 % Fe by weight, there are two possible sources of iron for the layer formation. The obtained iron diffusion profiles in the chromised layers indicated that the iron concentration at the outer surface tends to be minimum. In that respect it would be possible to consider that the iron atoms flow is mainly coming from the specimen core. Moreover it has been pointed out that the direction of iron flow depends on the Fe:Cr ratio in the powder mixture [2]. In the present chromising condition and since iron is present in chromising mixture, the diffusion of iron from the mixture to the layer is difficult to be ignored during layer formation. Therefore, both the specimen core as well as the chromised medium are possible sources of iron.

c) Hardness measurement

For various chromising conditions, microhardness measurements are carried out at both surface and across the diffusion layers in order to evaluate the structure changes as well as the depth of the chromised zone.

The surface hardness value after chromising treatment, fig.(6), is clearly time dependent before saturation is reached, while it is time independent after saturation is achieved. Moreover, it is also possible to indicate that once saturation is reached, the maximum obtained hardness value is almost the same for both types of cast-iron, which means that the type of carbide responsible of such hardness is the same.

The maximum observed chromised layer depth is about 22 μm obtained after chromising at 1000 °C for 30 hours, fig.(4), while the maximum obtained surface hardness value is about 1960 HV. at the same treatment condition as shown in fig.(6). Such higher surface hardness value is comparable with the value obtained after chromising of high carbon steel [2], which has been attributed to the formation of $(\text{Fe,Cr})_7\text{C}_3$ carbide. The drop in hardness value along the cross section of chromised zone in fig. (7), could be due to the gradual decrease in chromium concentration in the carbide layer, as shown in the line-scan analysis, fig (2). This would also implies the formation of different types of carbide in accordance with the chromium concentration [12]. In the adjacent zone, next to chromised layer, a higher value of hardness has been obtained, compared with the original material value as a result of the formation of fine pearlite structure in the interface zone and / or the presence of iron-chromium carbide phase $(\text{Cr,Fe})_3\text{C}$.

d) Wear Resistance of the chromised surface

Wear tests are carried out at constant load for both chromised and non - chromised cast iron in order to evaluate the effect of the new chromised surface on wear resistance. The results of wear tests are presented in fig (8), it is clear that the weight losses increases in a linear pattern with sliding times for the non - chromised cast iron. On the other hand, the chromised surface shows a higher wear resistance compared with the original material. The figure shows a negligible weight loss up to 15 minutes sliding and about 60 % reduction in weight loss after 25 minutes sliding on the chromised surface compared with unchromised cast iron.

The chromised layer is known to have a low coefficient of friction [3], which consequently reduces the heat generated between the sliding pairs. Therefore, an increase of wear life for chromised layer can be expected. It would be then possible to indicate that increasing wear resistance of a material is not only due to higher hardness alone. Moreover, the diffusion of chromium element on cast iron surface is accompanied by the formation of carbide phase, the specific volume of which is considerably large compared with the original surface [13]. This could lead to an increase in residual compressive stress of the surface and consequently a possible increase in wear resistance of the chromised zone.

e) Corrosion resistance

The anodic polarization curve of chromised and non chromised ductile iron using a simulated sea water (3.5 % NaCl solution) is given in fig (9). The figure shows a typical behavior of non - chromised ductile iron, it can be divided into two distinct regions[14]. The first reactive part followed by polarized part at about 10 $\mu\text{A} / \text{cm}^2$ critical anodic current density. The anodic polarization curve of chromised ductile iron shows a completely different behavior, it is spontaneously passivated at 10 $\mu\text{A} / \text{cm}^2$ critical current density. The presence of such passive region, which is accomplished by strong anodic polarization, prevents the normal anodic reaction.

Such behavior is due to the presence of protective surface layer. The fact that the protective layer can withstand the electrolyte oxidizing power indicates that the chromised layer is thermodynamically stable over a considerable range of oxidizing power and eventually destroyed under a relatively higher applied electrode potential.

f) Scale Resistance

The behavior of non-chromised ductile iron specimens are typically parabolic, such behavior is expected for ductile iron [15], while the chromised specimens show a completely different behavior under the same testing conditions as shown in fig (10). The chromised specimens have a slight gain in weight during heating up to 800 °C for 50 hours. A little gain in weight recorded at 950 °C after 12 hours heating time, it was 2.5 mg / cm² and 3.7 mg / cm² for the chromised ductile iron type I type II respectively.

The chromised layer is thermodynamically stable and can withstand oxidation up to 800 °C for 50 hours without any loss in weight, the rate of oxidation at 950 °C is equal to 0.3 and 0.2 mg / cm² / h for both tested chromised iron type I and type II respectively. The decrease in oxidation resistance at 950 °C could be due to resorption of diffusion coat [16].

CONCLUSION

Chromising chemical heat treatment have been carried out using two types of ductile cast iron with different structures, 60 % pearlitic and full ferritic structure. Different temperatures and holding times are used for the chromising process. The following conclusions can be drawn out of the present work.

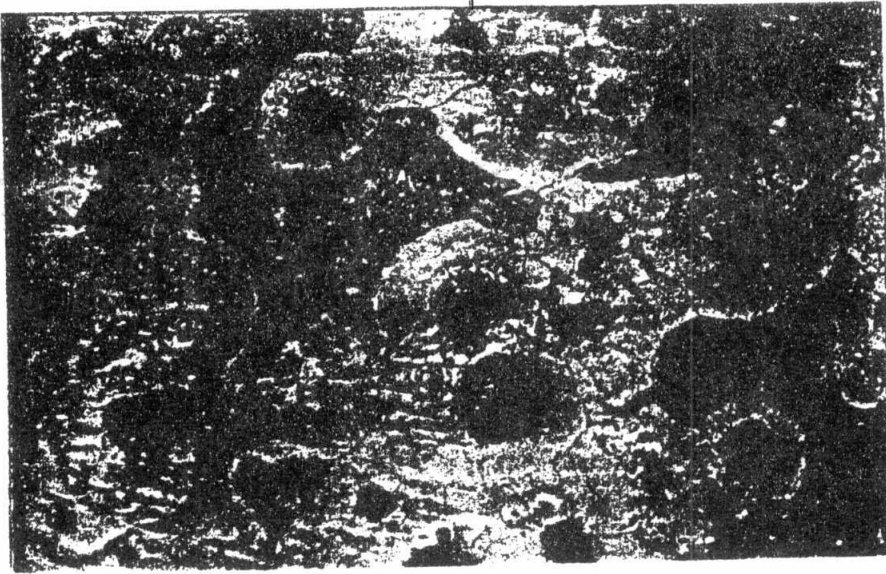
- 1-The structure differences of the ductile cast iron have a very little effect on the chromised layer formation, performed using a ferro chromium powder mixture.
- 2-The maximum attained chromised layer thickness is equal to 22 µm after 30 hours holding time at 1000 °C with a maximum hardness of 1950 HV.
- 3-The obtained carbide layer grows inward and the growth process is controlled by the chromium diffusion. The layer thickness is found to be time and temperature dependant.
- 4-The wear resistance of the chromised surface was improved to large extent compared with non chromised surface.
- 5-Chromising diffusion coating of ductile cast iron causes passivation in simulated sea water. The passivation critical anodic current density is equal to or less than 10 µA / cm².

6-The chromised layer prevent the formation of any oxide layer up to 50 hour heating at 800°C .

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(A)



(B)

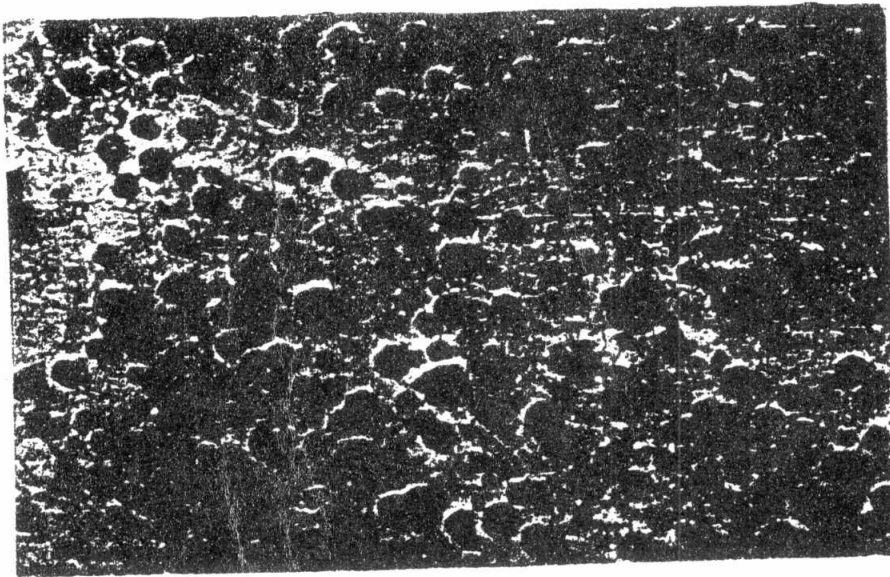


Fig (1) The microstructure of as-received ductile cast iron
(a) Type I (b) Type II (X = 100)

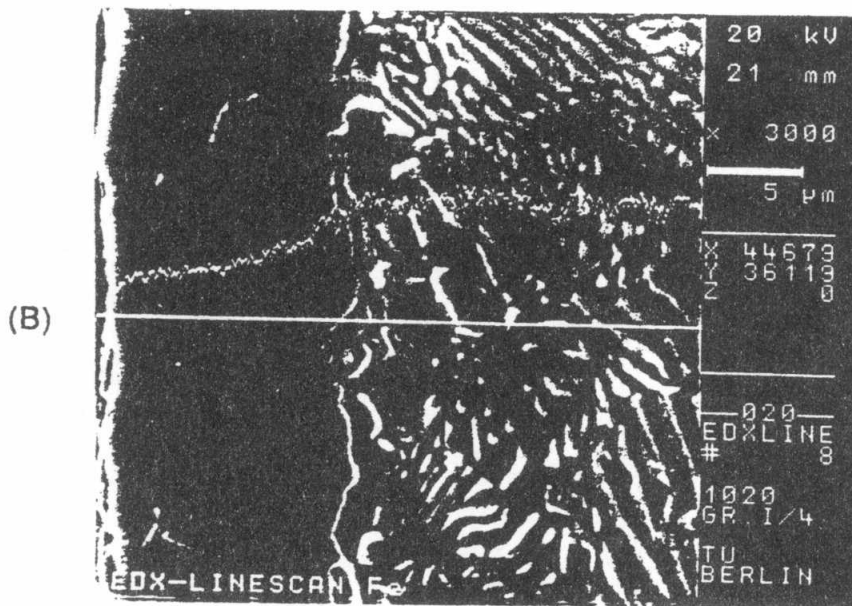
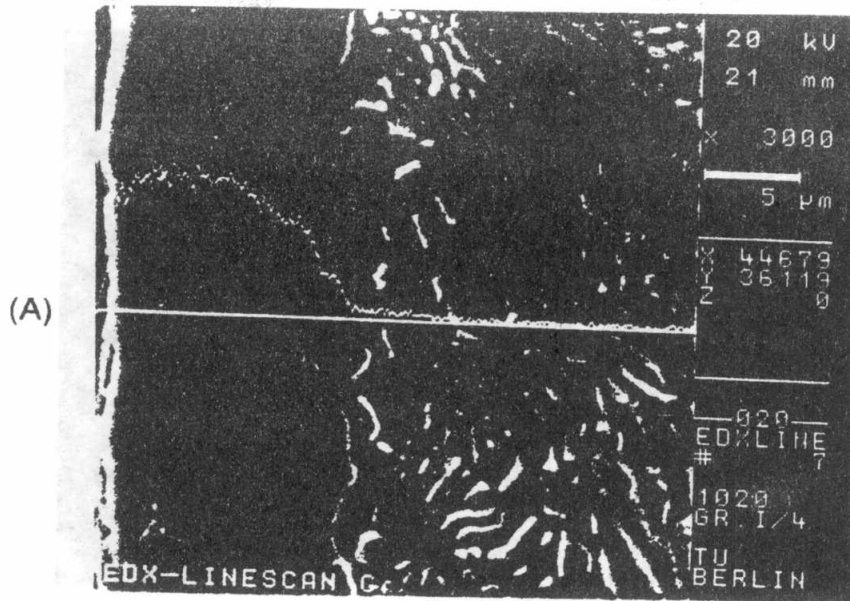


Fig (2) Line scan analysis after chromising of D.C.I.
Type II at 950 C for 16 hrs (X = 3000).
(A) Linescan Cr (B) Linescan of Fe

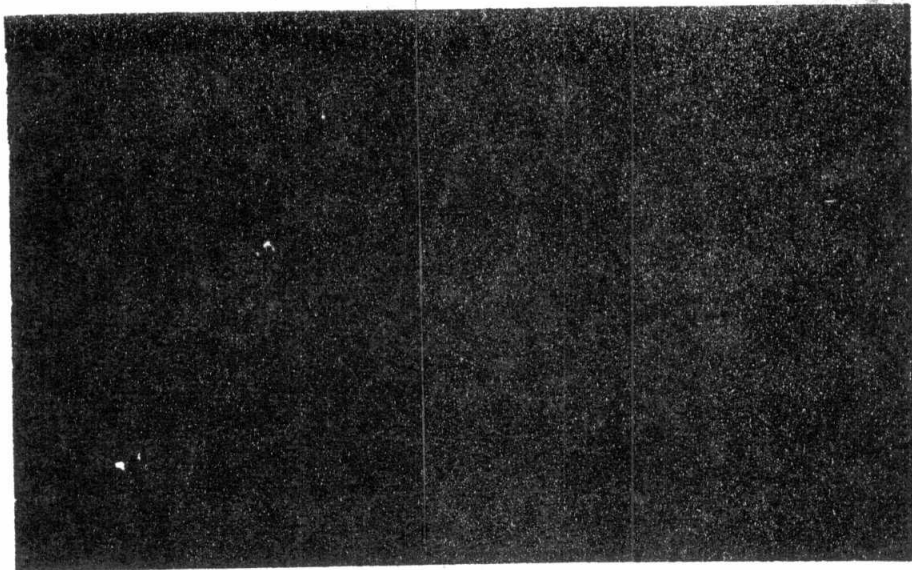


Fig (3) The two different carbide zones ,
chromised at 950 C for 24 hrs [X = 650] .

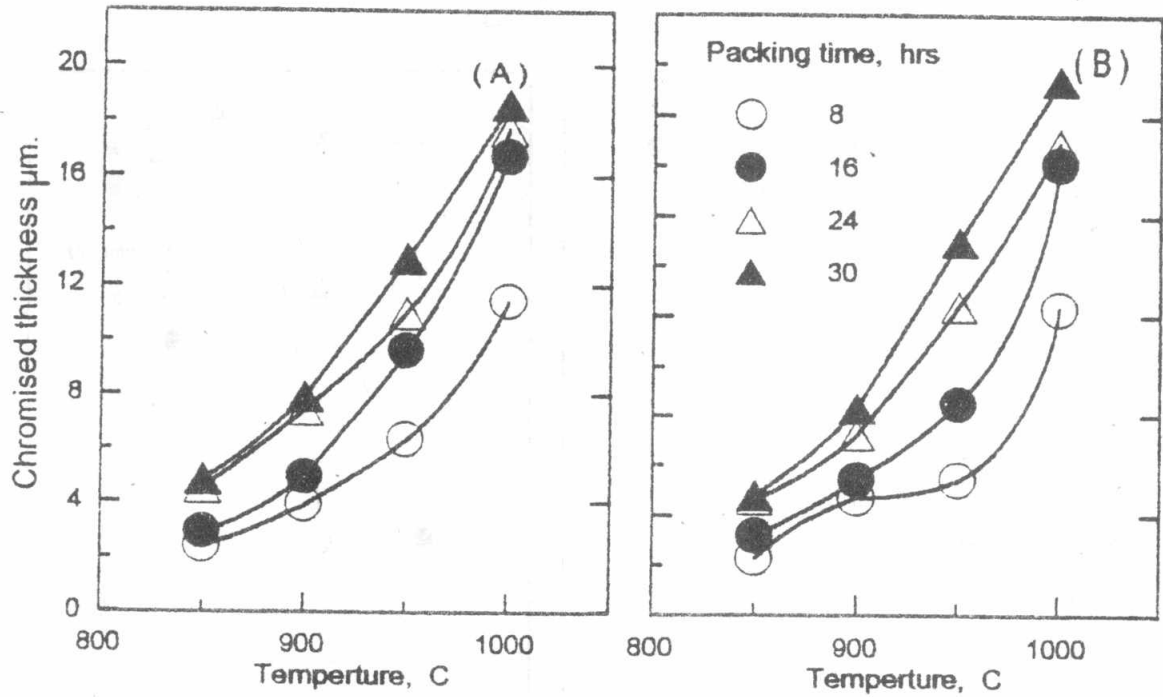


Fig.(4) Chromized layer thickness against packing temperature for D.C.I. after different packing times. (A) Type I and (B) Type II

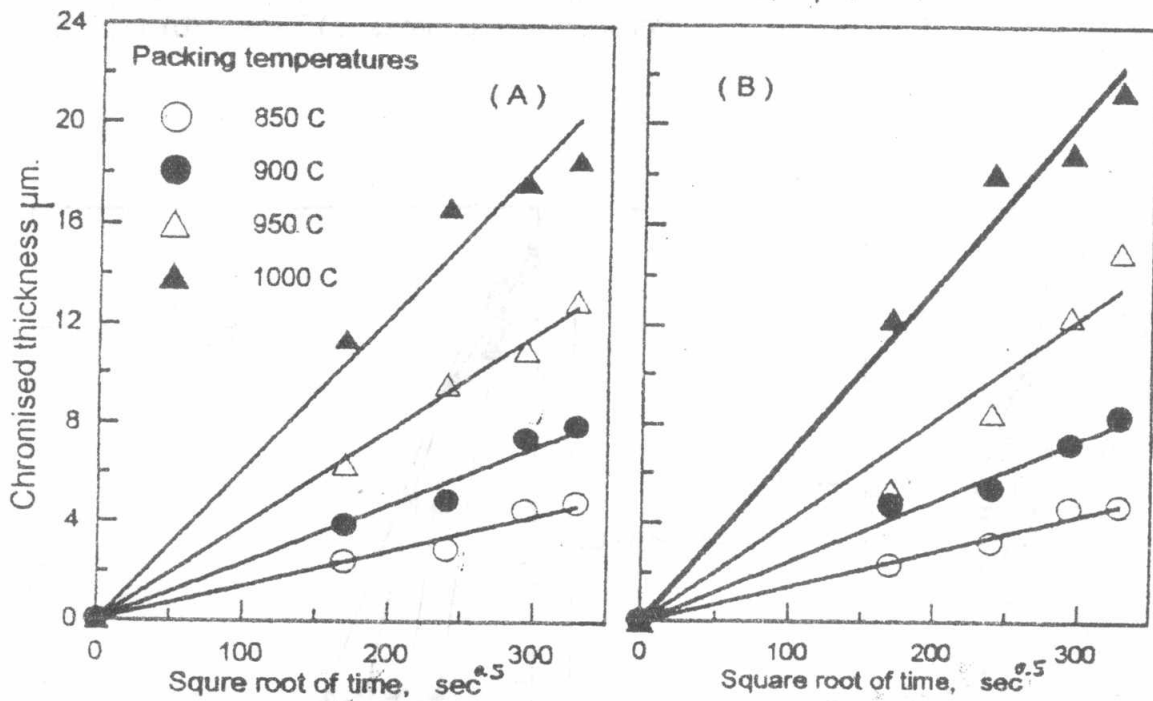


Fig.(5) Chromized layer thickness against square root of packing time of D.C.I. at different temperatures. (A) Type I and (B) Type II.

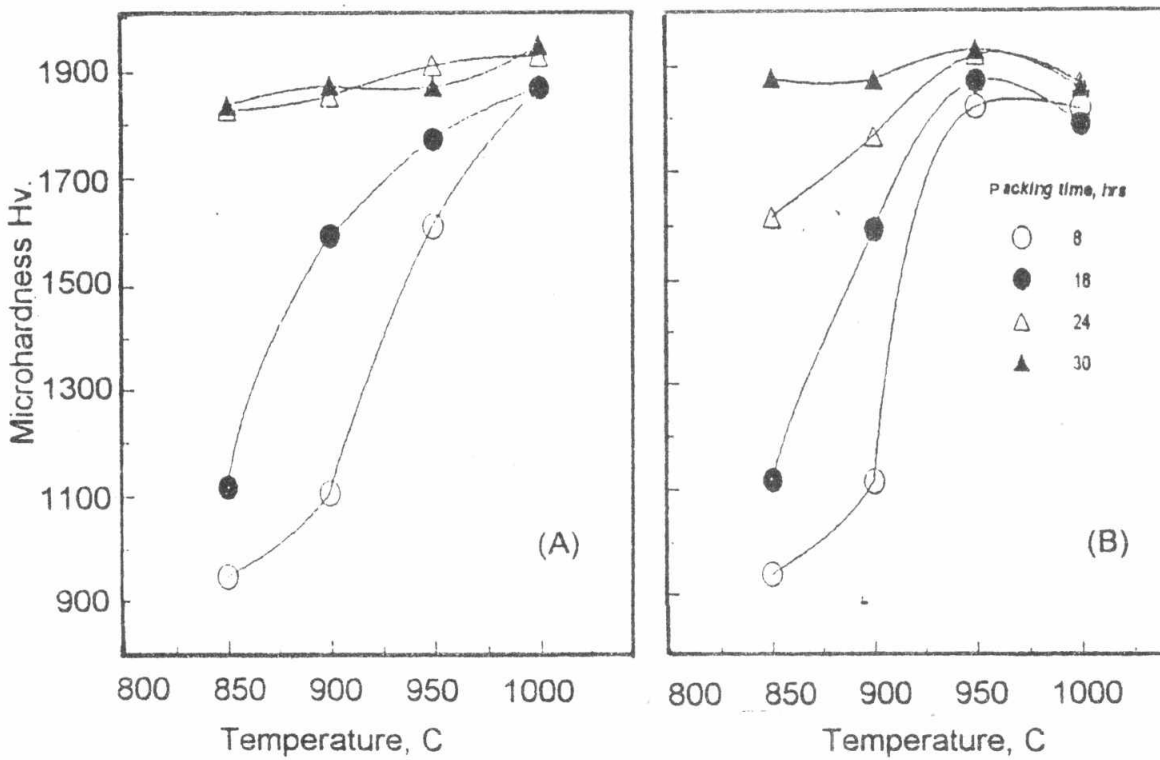


Fig (6) Surface microhardness number Hv. against the chromising temperature for different packing times (a) Type I (b) Type II

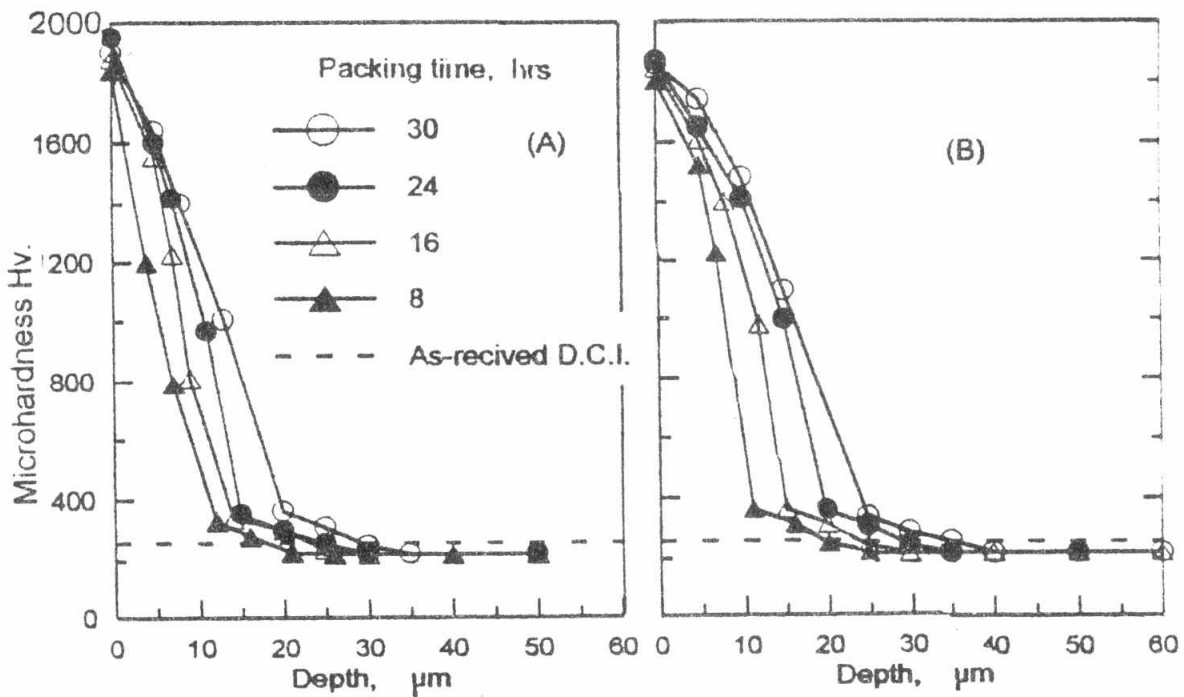


Fig.(7) Microhardness number against the depth for chromized D.C.I. Type-I. for different backing times. (a) At 1000 C and (b) At 950 C.

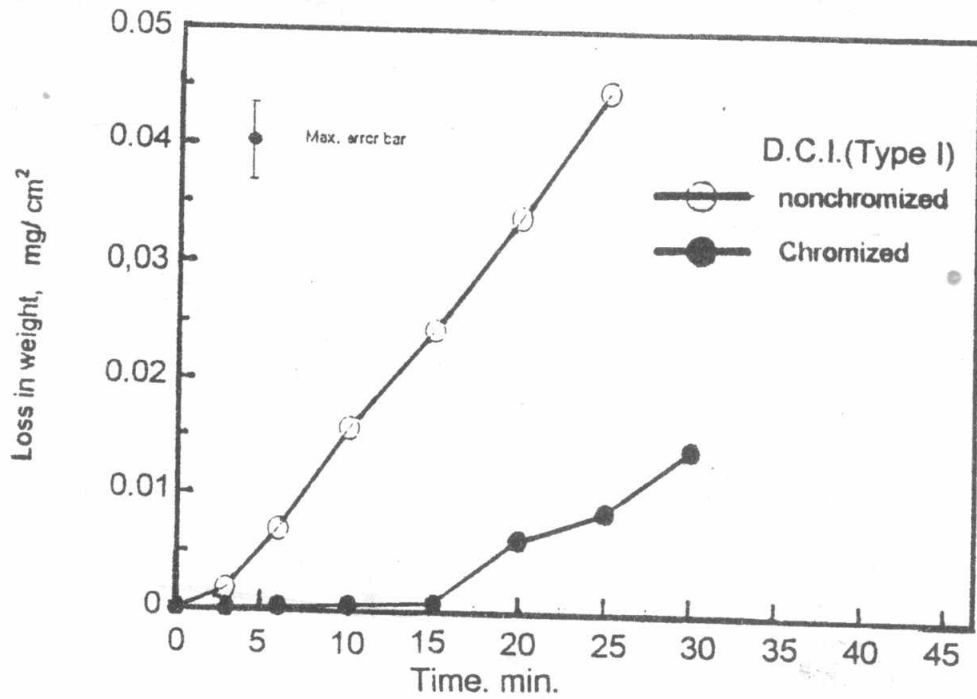


Fig (8) Loss in weight against running time for chromised and nonchromised D.C.I.

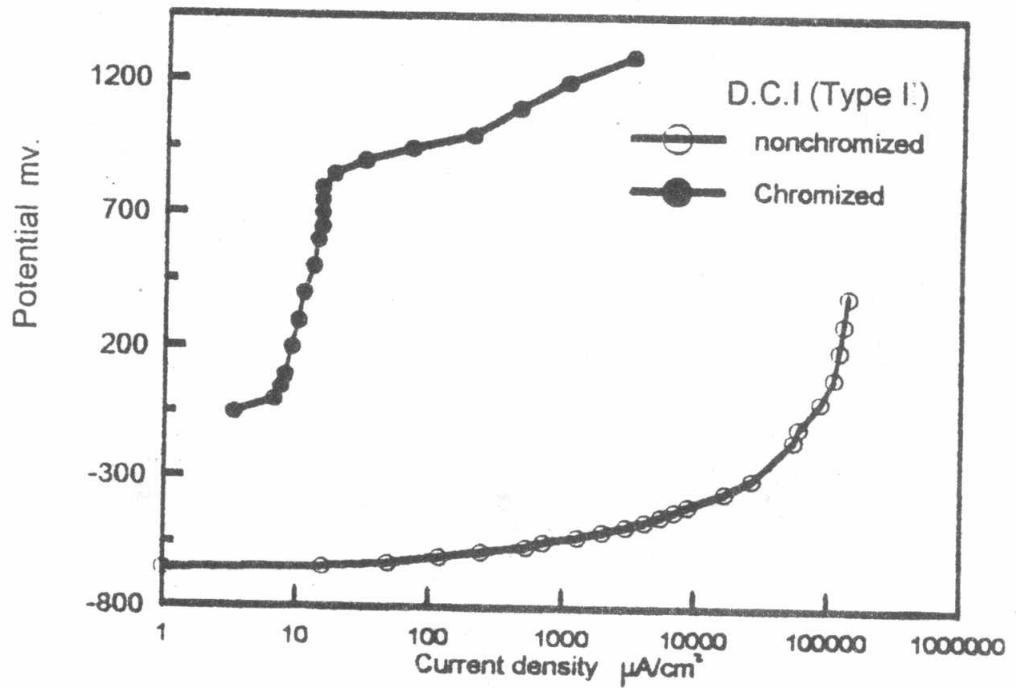


Fig (9) Anodic polarization curves of chromised and nonchromised D.C.I. in a solution of 3.5 wt. pct. NaCl

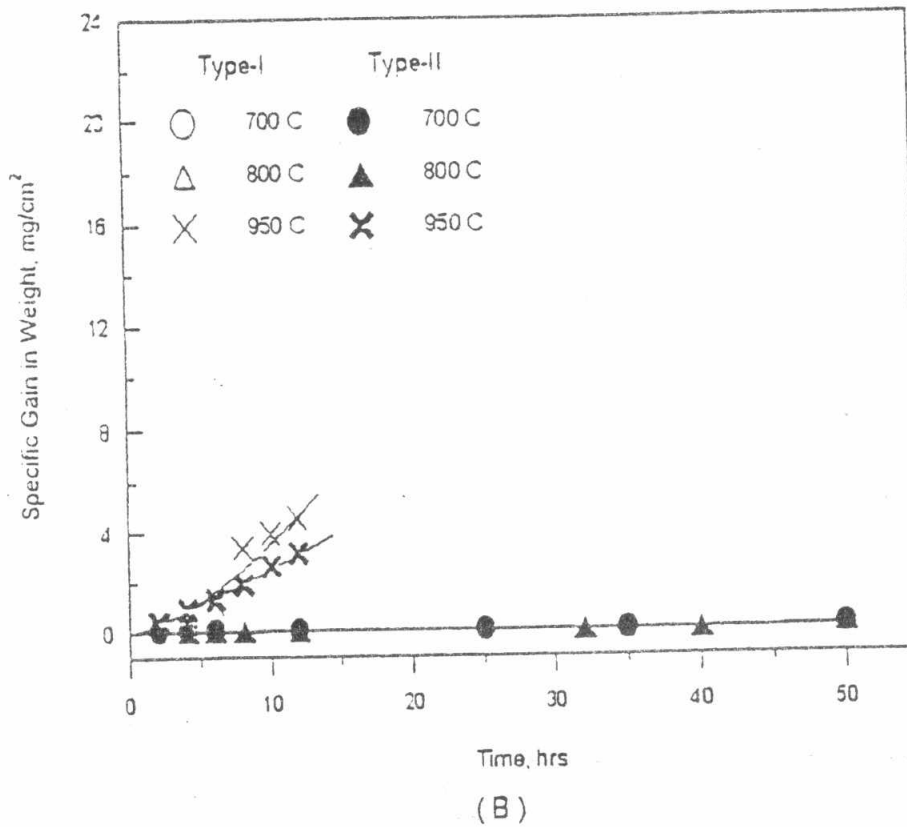
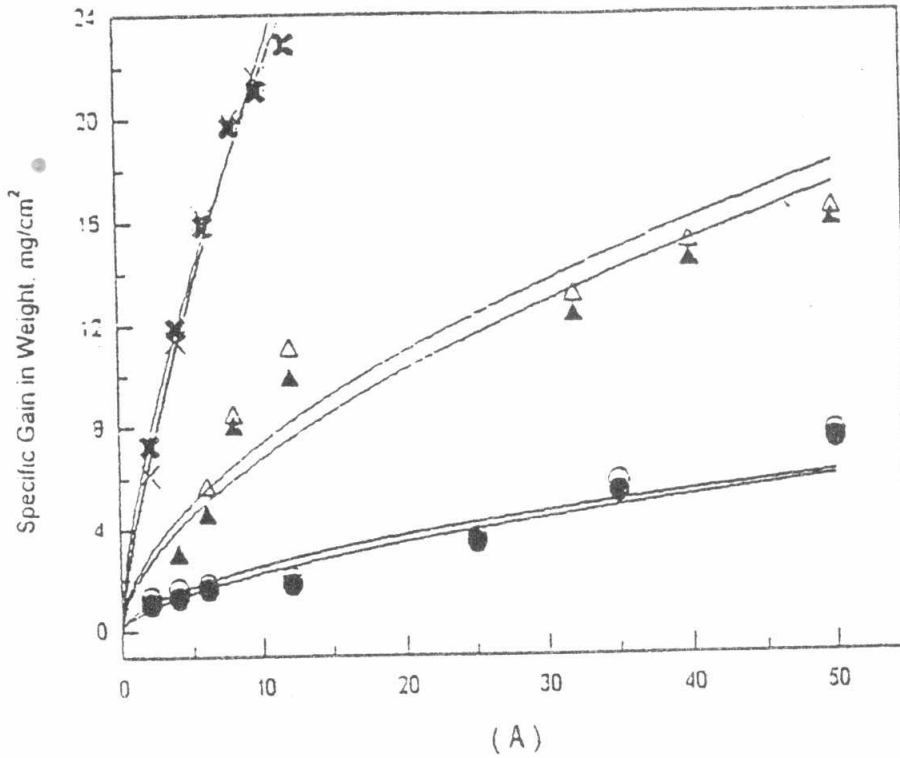


Fig. (10) Scale resistance of chromised and nonchromised D.C.I. at different temperatures.
 (A) Nonchromised; (B) Chromised.