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Partial Report
on
Chromizing of Steels

NAVAL RESEARCH LABORATORY
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ABSTRACT

The time penetration relationship at various temperatures and other factors that affect the chromizing process were studied. Low carbon iron alloys and steels containing alloying elements that form stable carbides can be chromized successfully. However, plain carbon steels cannot be chromized. The chromized layers can be hardened by carburizing to 730 Brinell.

INTRODUCTION

(a) Authorization

1. The investigation of chromizing of steels was authorized verbally by the Director of the Naval Research Laboratory 1 July 1941.

(b) Statement of Problem

2. Steels which contain over 13% chromium are resistant to corrosion under a great variety of severe conditions and are especially resistant to salt water corrosion.

3. In recent years, methods of putting a high chromium alloy case on steels (chromizing) by means of a volatile chromium chloride have appeared in the literature, which appear to have commercial possibilities. The chromized case differs from an electroplated coat in that it is integral with the base metal, has all the properties of a high chromium steel, and should respond to treatments such as carburizing and nitriding for the improvement of hardness.

4. Since chromized steels have high corrosion-resistant properties and may be used as a substitute for high chromium steels, and since the chromized case can be hardened to give a good tough wear-resisting surface, it was decided to investigate the time-temperature relationship and study other factors that affect the chromizing process.

(c) Known Facts Bearing on the Problem, and Theoretical Considerations

5. The method first used(1)(2) to put a high chromium case on steel consisted of heating a low carbon steel in intimate contact with chromium at temperatures of 1200 - 1400°C (2200 - 2550°F) which would allow the chromium to diffuse into the steel. The usefulness of this process was limited because the extremely high temperatures introduced excessive grain growth in the steel and increased the cost of the operation.

6. Later, a method(3)(4)(5)(6)(7)(8) was developed in which volatile chromium chloride was passed over the steel. A reaction took place in which chromium atoms replaced iron atoms in the metal, and the iron formed a volatile iron chloride. This mechanism operated according to the following equation:

$$CrCl_2 + Fe = Cr + FeCl_2$$

Chromium atoms diffuse inwardly and iron atoms outwardly, forming a layer high in chromium content and integral with the base metal.

7. Of the two mechanisms, chemical reaction and diffusion, that which operates at the slower rate determines the rate of formation of the layer. Diffusion being the slower, any factors that influence it affect the process.

8. The rate of diffusion is greatly influenced by temperature and crystal structure of the parent metal. That the diffusion of chromium is much greater in ferrite than in austenite has been shown by various investigators(9)(10). Thus a depth concentration curve for the diffusion of chromium(9) at 1200°C shows that the concentration falls off gradually for a considerable distance and then drops sharply at 13% chromium, the point coincident with the end of the gamma loop. The percentage of chromium at the surface will vary from 35 to 70% depending upon the temperature and time of treatment.

9. Three methods have been used for the production of a high chromium layer:

(a) Dry hydrogen is passed through fuming hydrochloric acid, then over the chromium source, and finally over the pieces to be chromized.

(b) A powdered chromium source(12) is mixed with barium chloride and packed around the steel. Hydrogen is passed through the system to prevent oxidation.

(c) The object to be treated is placed in a bath of molten chromium chloride, care being taken to prevent the presence of moisture and oxygen.

(d) Narrative of Original Work

10. Apparatus was constructed to chromize steels on a laboratory scale by using volatile chromium chloride. Test runs were made mainly by passing hydrogen chloride over ferro-chromium at 760°C, producing chromium chloride which then passed over the specimen at various temperatures. In addition, one run was made by the packing method.

11. For the purpose of this study a plain carbon, a chromium-molybdenum steel, and an iron alloy containing practically no carbon with one-half per cent molybdenum were selected (Table 1).

12. Since it is known that high chromium steels may be nitrided(13) to a depth of 0.01 inch with a hardness of 1150 Vickers, or carburized(14) to a hardness of 700 Brinell, it was thought worth while to try one of these methods to increase the hardness of the chromized layer. In this case the carburizing method was used.

METHODS

(a) Preparation of the Alloys.

13. The low carbon molybdenum alloy was prepared by melting ingot iron and scrap molybdenum wire in a 17-pound high frequency induction furnace and deoxidizing with 95% ferro-silicon before pouring. The resulting ingot was forged into 3/8" rods. The other steels were commercial.

(b) Description of Experiments

14. The chromizing apparatus is shown in Plate 2 and a diagrammatic sketch in Plate 3. Tank hydrogen was passed over copper gauze at 700°C to remove oxygen and then through two sulphuric acid bubbling towers to remove water vapor. A mercury pressure regulator and a flow gage were placed in the line to control and measure the flow. The purified dry hydrogen was then passed into a chamber filled with glass beads where it mixed with hydrogen chloride. Anhydrous hydrogen chloride was introduced directly into the system since further purification was not necessary. The mixture of the two gases passed through a quartz tube first entered a furnace containing ferro-chromium in porcelain boats at a temperature of 760°C, then into the furnace containing the specimen to be chromizid. At the exit end of the apparatus, a sulphuric acid bottle was placed to prevent the back diffusion of water vapor.

15. The temperature of the chromizing furnace was automatically controlled and any fluctuation in temperature held to a minimum by inserting a thermocouple in the furnace windings. As it was impossible to measure the temperature of the specimen during a run because of the contamination of the thermocouple by chromium, the temperature was determined by inserting a thermocouple into the specimen before the run and adjusting the temperature in the furnace windings.

16. After preliminary trials, it was found that 2.5 and 12 cc per minute of hydrogen chloride and hydrogen respectively gave good results.

17. The depth of the chromized layer was determined by polishing a cross-section of the specimen and etching in a 2% Nital solution which attacked the regions with less than 13% chromium and sharply delineated the higher chromium regions. The layers were measured at 400 magnification.

18. In the packing method an equimolar mixture of ferro-chromium and barium chloride ($BaCl_2 \cdot 2H_2O$) was put inside a tubular sample of alloy A and placed in the furnace. Hydrogen was passed through the furnace to prevent oxidation.

DATA OBTAINED

19. The chemical composition of the steels is given in Table 1, the chromizing results in Table 2, and the time-penetration relationship at 1000°C in Plate 4.

20. Figures 1 to 5, Plate 5, show the cross-section of the chromized layer. When 2% Nital is used, the specimen is etched up to the 13% chromium boundary (Fig. 1); however, when a ferric chloride-hydrochloric acid solution is used, the columnar structure of the chromized layer is revealed (Fig. 2).

21. The presence of carbon greatly influences the chromizing process. Fig. 3 shows the structure of alloy B when subjected to chromizing treatment

for 8 hours at 1000°C. Instead of obtaining a clearly defined chromized layer, a carbide layer was formed which inhibited diffusion of chromium into the metal. In comparison, the chromium-molybdenum steel C chromized without difficulty. It appears that in order to chromize successfully the carbon must be combined with elements such as chromium or molybdenum so that the diffusion of the carbon is decreased. If this is not done, the carbon will diffuse from the interior of the steel faster than chromium can diffuse inwardly and form a carbide ring. That this is true is shown by Fig. 4, in which the specimen was exposed to the hydrogen for a time sufficient to remove the carbon from the grain boundaries; upon subsequent chromizing, the chromium penetrated into the grain boundaries only and did not enter into the grains.

22. Since the corrosion resistance of the chromized layers was expected to be the same as that of the high chromium alloys, no detailed study was made except to subject the specimens to a drastic acid treatment. Fig. 5 shows specimens of alloys A and C after holding in a boiling 25% nitric acid solution until the original base metal was completely dissolved. The chromized layer was not affected by this treatment.

23. The result of carburizing the chromized layer was an increase in hardness from 267 to 811 Knoop hardness (240 to 730 Brinell).

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

24. Low carbon iron alloys may be chromized readily, but plain carbon steels cannot because the chromium carbide layer that is formed prevents further diffusion of chromium.

25. Steels can be chromized successfully if they contain alloying elements such as chromium or molybdenum which form stable carbides and prevent the outward diffusion of carbon.

26. The packing method (barium chloride and chromium) gave the same results as the hydrogen chloride method. This method should be more economical and give more uniform coatings than other methods.

27. Chromized layers may be hardened by carburizing to 730 Brinell.

(b) Opinions

28. Chromized steels should have definite applications in corrosion problems, as they are practically unaffected by sea water and can withstand boiling 25% nitric acid successfully.

29. Carburized-chromized layers should be useful in applications where both corrosion and erosion are encountered. In addition, since high-carbon high-chromium steels are known for their resistance to wear and ability to withstand oxidation at high temperatures, the carburized chromized steels may be applicable where surface wear is important.

30. The chromizing process has certain limitations because the fairly high temperature involved may cause large structures to become distorted unless proper support is used.

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(11) Adcock - Journal, Iron and Steel Institute, Vol. 124, 99, 1931.

(12) - Fr. Patent 844,283.

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(14) E. Wedawski - Arch. F. D. Eisenhuttenwesen, Vol. 11, 195, 1937-1938.

Table 1

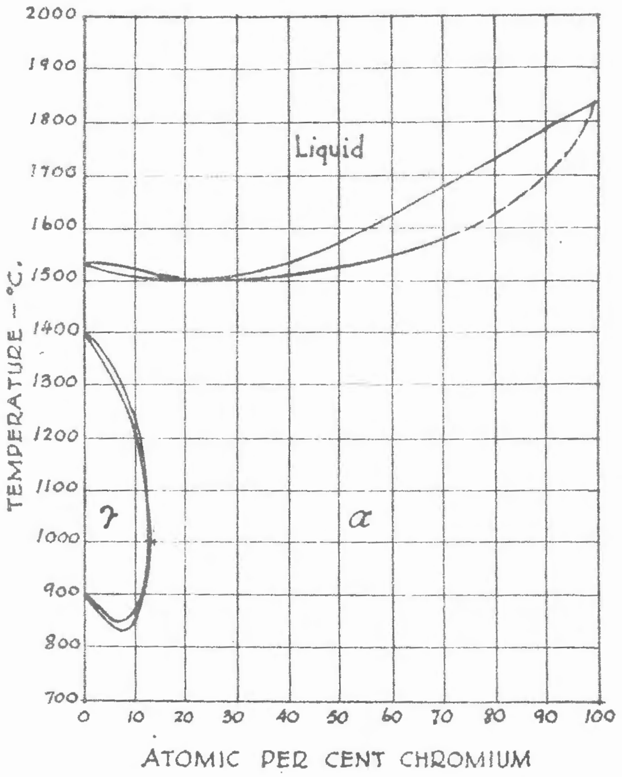
Chemical Analysis

Alloy	C	Si	Mn	Cr	Mo
A	0.06				0.50
B	.18	.43	.20		
C	.14	.49	.49	1.81	0.70

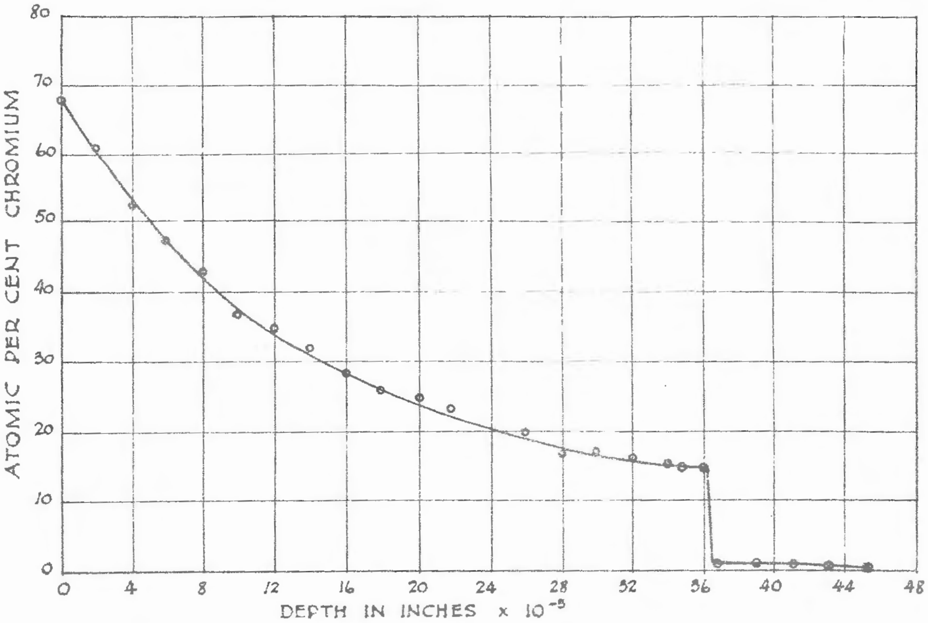
Table 2

Chromizing Results

Alloy	Temp. °C	Time Hrs.	Depth of Layer mm	Comments
C	813	16	nil	
C	813	24	nil	
C	909	4	nil	
C	909	6	.008	
A	1000	4	.030	
A	1000	6	.035	
A	1000	8	.040	
A	1000	16	.068	
A	1000	24	.090	
C	1000	5	.025	
C	1000	16	.048	
C	1000	24	.062	
B	1000	4	nil	
B	1000	8	nil	Formed carbide layer
A	1000	16	.068	Packing method



Iron-chromium constitutional diagram according to Adcock.



Depth-concentration curve.

PLATE I

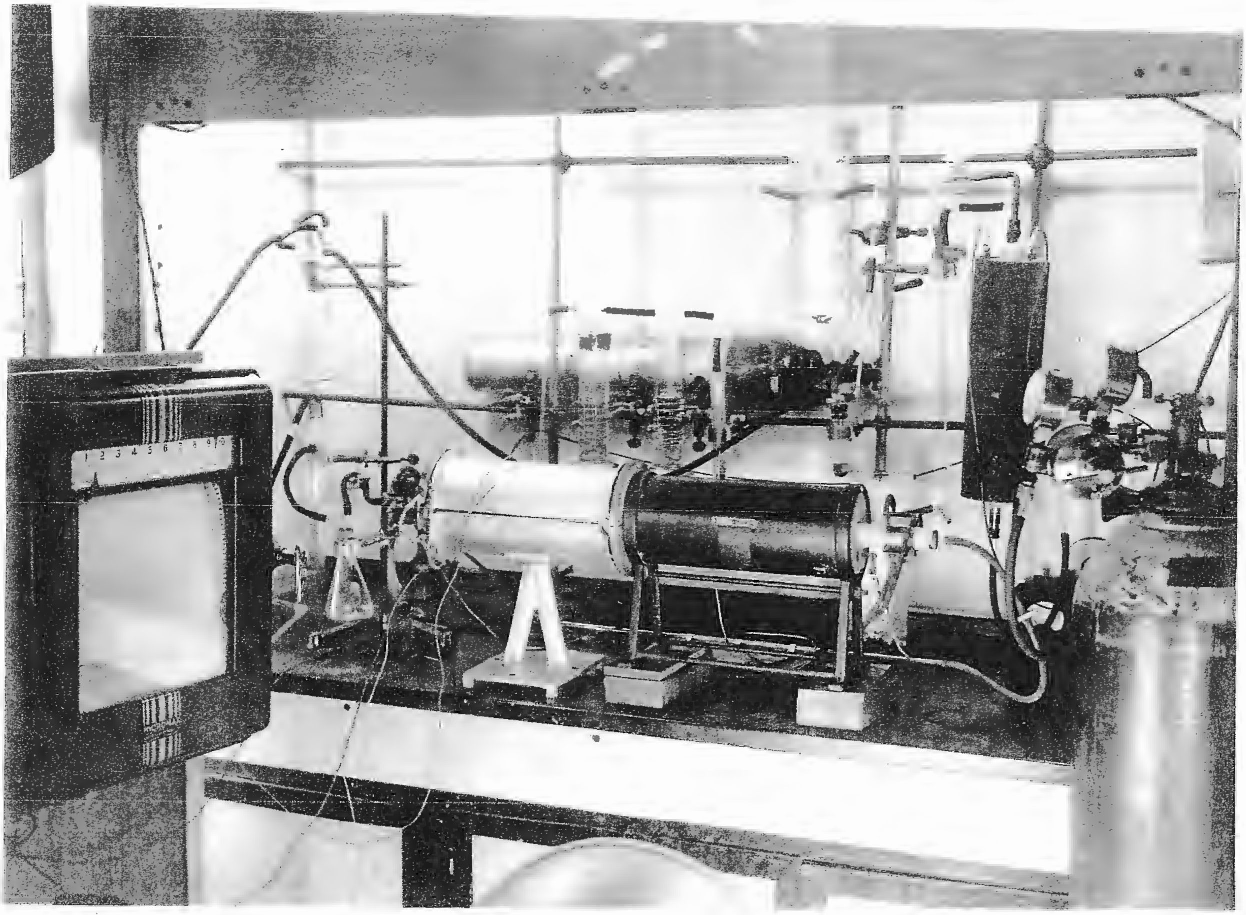
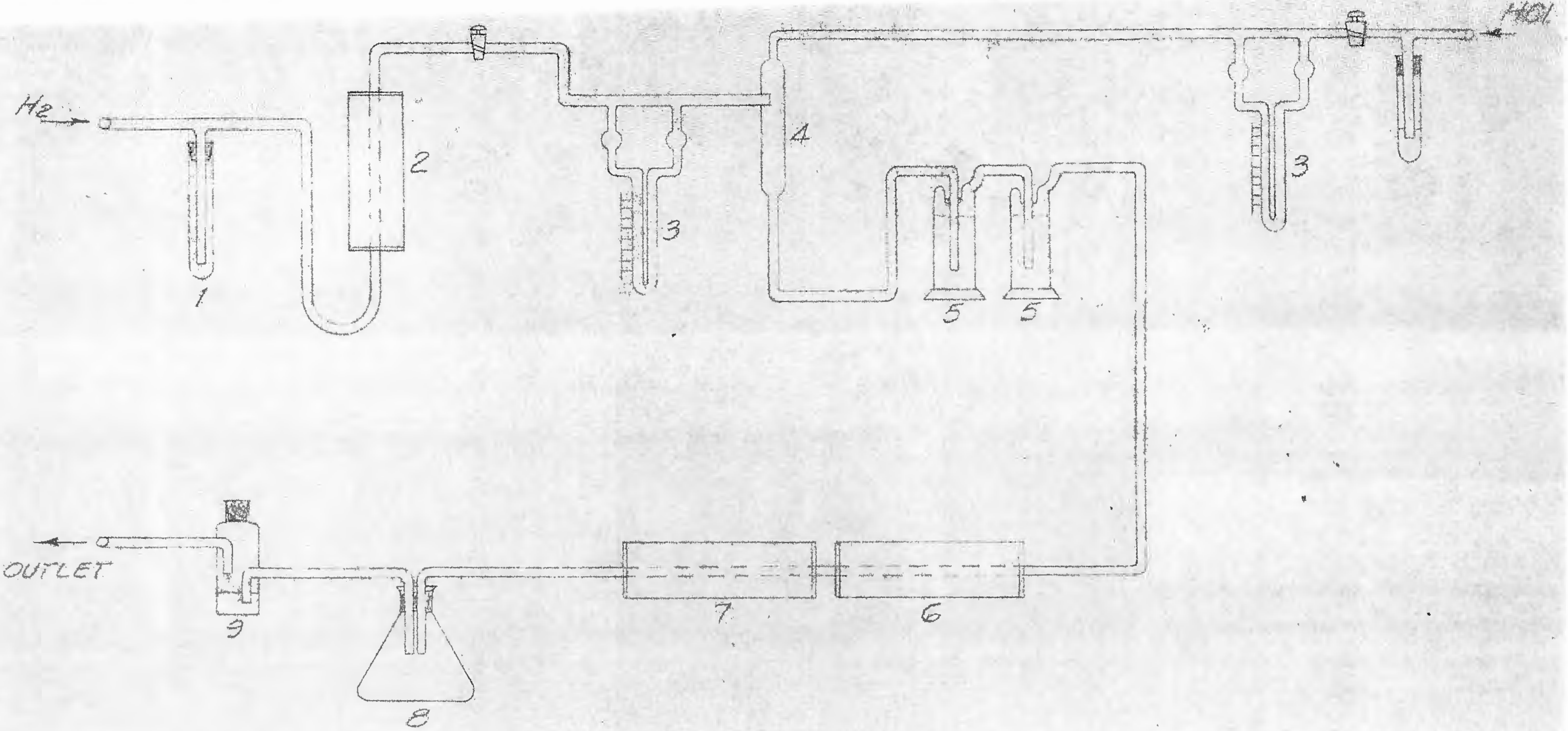


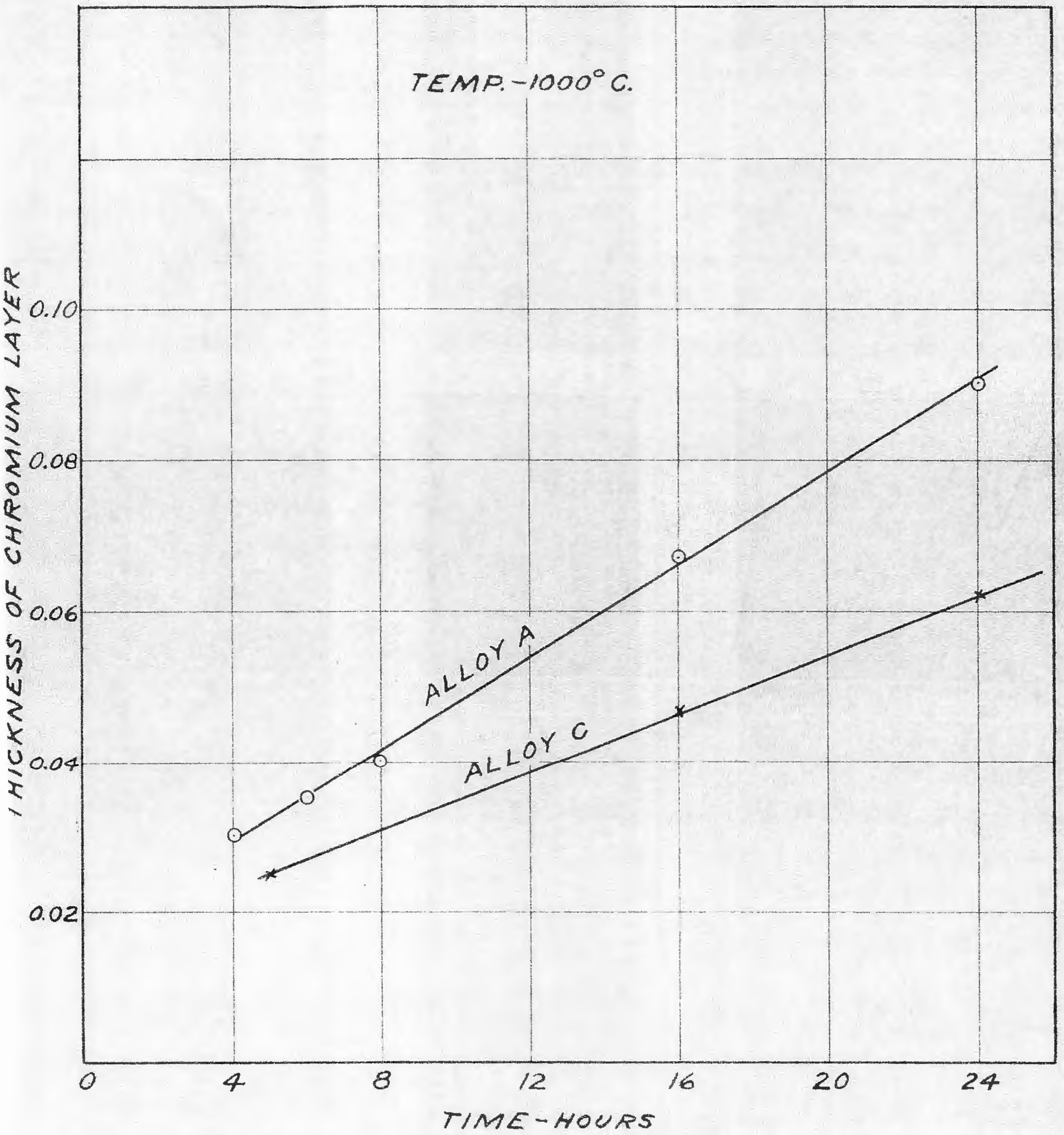
PLATE 2



SCHEMATIC DIAGRAM OF CHROMIZING ASSEMBLY

1. Mercury constant pressure regulators
2. Copper gauze deoxidizing furnace
3. Flowmeter
4. Mixing tube
5. Milligan Bubbling Towers
6. Furnace for production of $C_r\ Cl_2$
7. Chromizing furnace
8. Erlenmyer flask
9. Sulphuric acid valve

PLATE XI



TEMP. -1000° C.
THICKNESS OF CHROMIUM LAYER
0.10
0.08
0.06
0.04
0.02
ALLOY A
ALLOY C
0
4
8
12
16
20
24
TIME - HOURS

PLATE 4

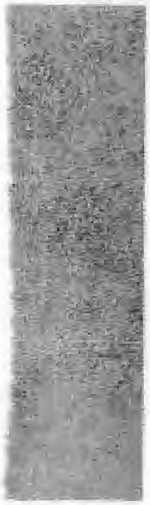


FIG. 1

CHROMIZED ZONE
NITAL ETCH 250X

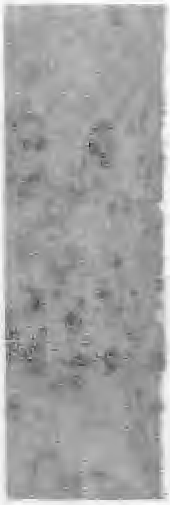


FIG. 2

CHROMIZED ZONE
FE CL_3 + HCL ETCH 250X

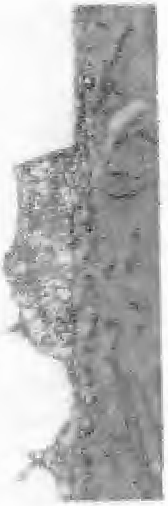


FIG. 3

CARBIDE FORMATION
AT SURFACE 500X

FIG. 4

DIFFUSION OF CHROMIUM
ALONG GRAIN BOUNDRIES 250X

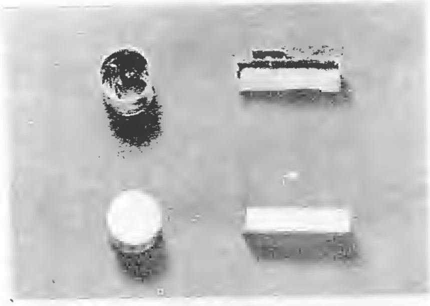


FIG. 5

CHROMIZED SPECIMENS
BEFORE AND AFTER TREATMENT
WITH BOILING HNO_3

PLATE 5