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(54) A FERROCHROMIUM ALLOY

FERROCHROMLEGIERUNG

ALLIAGE DE FERRO-CHROME

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(73) Proprietor: **WARMAN INTERNATIONAL LIMITED**
Artarmon, NSW 2064 (AU)

(72) Inventor: **DOLMAN, Kevin, Francis**
Helena Valley, W.A. 6056 (AU)

(74) Representative: **Jennings, Nigel Robin et al**
KILBURN & STRODE
30 John Street
London WC1N 2DD (GB)

(56) References cited:

AU-A- 1 286 966
AU-B- 1 445 370
GB-A- 0 220 006
GB-A- 0 401 644
AU-A- 6 373 465
AU-B- 4 316 372
GB-A- 0 362 375
US-A- 3 086 858

- **DERWENT ABSTRACT, Week W1, Class M27, SU 414326 (DOLBENKO) 19 July 1974 (19.07. 74).**
- **DERWENT ABSTRACT Accession No. 61284X/32, Class M27, SU 489808 (AS URR CAST PROBLEM) 4 February 1976 (04.02.76).**
- **Handbuch der Fertigungstechnik, vol. 4/2, Carl Hanser Verlag München, (1987), pp. 954/955;**
- **Handbuch der Sonderstahlkunde, E. Houdremont, Springer Verlag (1956), pp 623-627**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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EP 0 438 560 B1

Description

The present invention relates to a ferrochromium alloy and more particularly to an erosion and corrosion resistant ferrochromium alloy.

The present invention is designed for use in the formation of parts for lining pumps, pipes, nozzles, mixers and similar devices which, in service, can be subjected to mixtures containing a corrosive fluid and abrasive particles.

Typical applications for such parts include flue gas desulphurization, in which the parts are exposed to sulphuric acid and limestone, and fertiliser production, in which the parts are exposed to phosphoric acid, nitric acid and gypsum.

U.S. patents, 4,536,232 and 4,080,198, assigned to Abex Corporation (the "Abex U.S. patents"), disclose ferrochromium alloys containing approximately 1.6 wt. % carbon and 28 wt. % chromium which are characterized by primary chromium carbide and ferrite islands in a martensite or austenite matrix containing a solid solution of chromium. The level of chromium in the alloys suggests that the alloys should exhibit good corrosion resistance characteristics. However, the performance of such alloys from the corrosion resistance viewpoint is not entirely satisfactory. Moreover, the Australian patent nos. AU-B-43163/72 and (2) AU-B-14453/70 as well as Britsh patent GB-A-401644 are concerned with erosion and corrosion resistant iron chromium alloys.

An object of the present invention is to provide a ferrochromium alloy which has improved erosion and corrosion resistance compared with the alloys disclosed in the Abex U.S. patents.

The mechanism for erosion and corrosion of alloys of the type disclosed in the Abex U.S. patents in acidic environments is by accelerated corrosion due to the continuous removal of the passive corrosion-resistant layer by erosive particles in the fluid stream.

In order to replenish the passive layer it is necessary to have the chromium concentration at as high a level as possible in the matrix.

However, simply increasing the chromium content to improve corrosion resistance tends to cause the formation of the sigma phase which is undesirable in view of the embrittlement problems associated with the sigma phase.

The present invention is based on the realization that by increasing both the chromium and carbon concentrations of alloys of the type disclosed in the Abex U.S. patents it is possible to increase the volume fraction of the chromium carbide phase, and thereby improve the wear resistance characteristics of the ferrochromium alloys, while maintaining the matrix at a chromium concentration which is at a level that will not lead to the formation of significant amounts of sigma phase. It can be appreciated that by improving the wear resistance of the ferrochromium alloys, in view of the mechanism by which erosion and corrosion occurs, as noted above, it is possible to realize an improvement in the erosion and corrosion resistance of the ferrochromium alloys.

According to the present invention there is provided an erosion and corrosion resistant ferrochromium alloy comprising the following composition, in wt. %.

34 - 50	chromium
1.5 - 2.5	carbon
1 to 2	manganese
0.5 to 1.5	silicon
1 to 2	molybdenum
1 to 5	nickel
1 to 2	copper

up to 1% of each of one or more micro-alloying elements selected from the group consisting of titanium, zirconium, niobium, boron, vanadium and tungsten, and

balance, iron and incidental impurities, with a microstructure comprising eutectic chromium carbides in a matrix comprising one or more of ferrite, retained austenite and martensite.

The term "ferrite" is herein understood to mean body-centred cubic iron (in the alpha and/or delta forms) containing a solid solution of chromium.

The term "austenite" is herein understood to mean face-centred cubic iron containing solid solutions of carbon and chromium.

The term "martensite" is herein understood to mean a transformation product of austenite.

It is preferred that the matrix contains a 25-35 wt. % solid solution of chromium.

It is preferred that the microstructure further comprises one of primary chromium carbides, primary ferrite or primary austenite in the matrix.

The preferred amount in wt % of the elements chromium is 36 to 40 and % carbon is 1.9 to 2.1

With the foregoing preferred composition it is preferred that the matrix contains a 29-32 wt. % solid solution of chromium.

In accordance with the invention, increasing both the chromium and carbon contents of the ferrochromium alloy

above the levels disclosed in the Abex U.S. patents permits the formation of a greater volume fraction of hard carbides to enhance wear resistance. More specifically, and preferably, a stoichiometric balance in the increase in chromium and carbon contents permits the formation of a greater volume fraction of chromium carbides without increasing the chromium content of the matrix to a critical level above which sigma phase embrittlement occurs.

It has been found that preferred alloys of the present invention exhibit superior corrosion and erosion resistance to the alloys disclosed in the Abex U.S. patents. This is illustrated in Table 1 below which lists the results of laboratory scale potentiodynamic corrosion and disc wear tests on alloys disclosed in the Abex U.S. patents and preferred alloys of the present invention. The compositions of the alloys are listed in Table 2 below.

Table 1: Corrosion and Erosion Test Results

	Corrosion * (mm/yr)	Erosion ** (mm^3/hr)
ABEX Alloy #1	5.60	488
ABEX Alloy #2	2.50	614
Casting # 1	0.07	370
Casting # 2	0.43	444

* 10% Sulphuric Acid, 25°C to ASTM G61

** 40 weight % Silica Sand Slurry @ 18 m/s

Table 2: Composition of Alloys of Table 1

	Cr	C	Mn	Si	Mo	Ni	Cu	Fe
ABEX Alloy #1*	28.4	1.94	0.97	1.48	2.10	2.01	1.49	Bal
ABEX Alloy #2**	27.5	1.65	1.21	1.47	2.00	2.00	1.39	Bal
Casting # 1	35.8	1.95	0.96	1.48	2.10	2.04	1.48	Bal
Casting # 2	40.0	1.92	0.96	1.59	1.95	1.95	1.48	Bal

* As-cast alloy with composition within range of U.S. Patent 4,536,232

** Heat treated alloy with composition within range of U.S. Patent 4,536,232

It will be noted from Table 1 that the corrosion and erosion resistance of the preferred alloys of the present invention is significantly better than that of the Abex alloys.

The alloy of the present invention has a different microstructure to that of the alloys disclosed in the Abex U.S. patents. The difference is illustrated in the accompanying figures which comprise photocopies of photomicrographs of an alloy disclosed in the Abex U.S. patents and preferred alloys of the present invention.

Figure 1 shows the microstructure of an Abex alloy which comprises 28.4% chromium, 1.94% carbon, 0.97% manganese, 1.48% silicon, 2.10% molybdenum, 2.01% nickel and 1.49% copper, the balance substantially iron. The microstructure consists of primary austenite dendrites (50% volume) and a eutectic structure comprising eutectic carbides in a matrix of eutectic ferrite, retained austenite and martensite.

Figure 2 shows the microstructure of one preferred alloy of the present invention which comprises 35.8% chromium, 1.94% carbon, 0.96% manganese, 1.48% silicon, 1.94% carbon, 0.96% manganese, 1.48% silicon, 2.06% molybdenum, 2.04% nickel, 1.48% copper, the balance substantially iron. The microstructure is hypereutectic with primary ferrite dendrites (20% volume) and a eutectic structure comprising finely dispersed eutectic carbides in a matrix of eutectic ferrite. It is noted that when compared with the microstructure of the Abex U.S. patent shown in Figure 1 the microstructure of Figure 2 reflects that there is a reduced volume of primary dendrites and an increased volume of the eutectic matrix and since the eutectic matrix has a relatively high proportion of carbides there is an overall increase in the volume fraction of hard carbides in the alloy when compared with the Abex alloy. It is noted that the foregoing phenomenon is also apparent to a greater extent from a comparison of the microstructures shown in Figs. 3 to 5 and Fig. 1.

Figure 3 shows the microstructure of another preferred alloy of the present invention which comprises 40.0% chromium, 1.92% carbon, 0.96% manganese, 1.59% silicon, 1.95% molybdenum, 1.95% nickel, 1.48% copper, the balance substantially iron. The microstructure consists of eutectic carbides in a matrix of eutectic ferrite.

Figure 4 shows the microstructure of another preferred alloy of the present invention which comprises 40.0% chromium, 2.30% carbon, 2.77% manganese, 1.51% silicon, 2.04% molybdenum, 1.88% nickel, 1.43% copper, the balance substantially iron. The microstructure is hypereutectic with primary M_7C_3 carbides and a eutectic structure comprising eutectic carbides in a matrix of eutectic ferrite.

Figure 5 shows the microstructure of another preferred alloy of the present invention which comprises 43% chromium, 2.02% carbon, 0.92 manganese, 1.44% silicon, 1.88% molybdenum, 1.92% nickel, 1.2% copper, the balance substantially iron. The microstructure in this case is hypereutectic with trace amounts of primary M_7C_3carbides and a eutectic structure comprising eutectic carbides in a matrix of eutectic ferrite.

Any suitable conventional casting and heat treatment technology may be used to produce the alloys of the present invention. However, it is preferred that the alloys are formed by casting and then heat treating at a temperature in the range of 600 to 1000°C followed by air cooling.

Claims

1. An erosion and corrosion resistant ferrochromium alloy comprising the following composition, in wt. %.

34 - 50	chromium
1.5 - 2.5	carbon
1 - 2	manganese
0.5 - 1.5	silicon
1 - 2	molybdenum
1 - 5	nickel
1 - 2	copper

up to 1% of each of one or more micro-alloying elements selected from the group consisting of titanium, zirconium, niobium, boron, vanadium and tungsten, and balance, iron and incidental impurities, with a microstructure comprising eutectic chromium carbides in a matrix comprising one or more of ferrite, retained austenite and martensite.

2. An alloy as claimed in Claim 1, characterised in that the microstructure further comprises one of primary chromium carbides, primary ferrite or primary austenite in the matrix.

3. An alloy as claimed in Claim 1 or Claim 2, characterised in that the matrix contains a 25-35 wt. % solid solution of chromium.

4. An alloy as claimed in any preceding Claim, characterised by an chromium content of 36 - 40 wt % and a carbon content of 1.9 - 2.1 wt %.

5. A method of producing an alloy as claimed in any preceding Claim, characterised by heat treating the alloy at a temperature in the range of 600 - 1000°C and air cooling the alloy.

Patentansprüche

1. Erosions- und korrosionsbeständige Ferrochromlegierung, umfassend die folgende Zusammensetzung in Gew. %:

34-50	Chrom
1,5-2,5	Kohlenstoff
1-2	Mangan
0,5-1,5	Silizium
1-2	Molybdän
1-5	Nickel
1-2	Kupfer

und bis zu jeweils 1 % von einem oder mehreren der mikrolegierenden Elemente, ausgewählt aus der aus Titan , Zirkon, Niob, Bor, Vanadin und Wolfram bestehenden Gruppe, Rest Eisen und beiläufige Verunreinigungen, mit einer Mikrostruktur, welche eutektische Chromcarbide in einer Matrix aus einem oder mehreren Bestandteilen aus der Reihe Ferrite, verbliebenem Austenit und Martensit enthält.

2. Legierung gemäß Anspruch 1, dadurch gekennzeichnet, daß die Mikrostruktur ferner einen Bestandteil aus der Reihe primärer Chromcarbide, primärer Ferrit oder primärer Austenit in der Matrix enthält.

3. Legierung gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Matrix eine 25-35 gew.%ige feste Lösung von Chrom enthält.

4. Legierung nach einem der voranstehenden Ansprüche, gekennzeichnet durch einen Chromgehalt von 36-40 Gew. % und einen Kohlenstoffgehalt von 1,9-2,1 Gew. %.

5. Verfahren zur Herstellung einer Legierung gemäß einem der voranstehenden Ansprüche, gekennzeichnet durch eine Wärmebehandlung der Legierung bei einer Temperatur im Bereich von 600-1000° C und die Luftkühlung der Legierung.

Revendications

1. Alliage de ferro-chrome résistant à l'érosion et à la corrosion, comprenant la composition suivante :

34 à 50% en poids	de chrome
1,5 à 2,5% en poids	de carbone
1 à 2% en poids	de manganèse
0,5 à 1,5% en poids	de silicium
1 à 2% en poids	de molybdène
1 à 5% en poids	de nickel
1 à 2% en poids	de cuivre

jusqu'à 1% en poids de chacun de l'un ou de plusieurs des éléments pour microalliage choisis dans le groupe consistant en titane, zirconium, niobium, bore, vanadium et tungstène, et
le restant étant constitué par du fer et des impuretés accidentelles, avec une microstructure comprenant des carbures de chrome eutectiques dans une matrice comprenant un ou plusieurs constituants parmi une ferrite, une austénite conservée et une martensite.

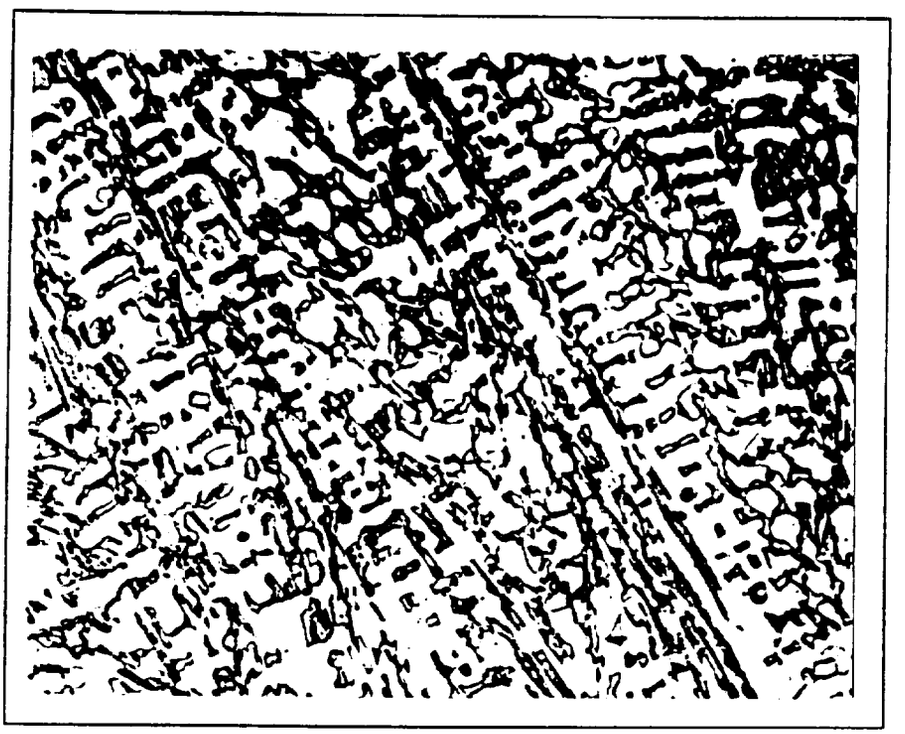
2. Alliage suivant la revendication 1, caractérisé en ce que la microstructure comprend de plus l'un parmi des carbures de chrome primaires, une ferrite primaire ou une austénite primaire dans la matrice.

3. Alliage suivant les revendications 1 ou 2, caractérisé en ce que la matrice contient une solution solide de 25 à 35% en poids de chrome.

4. Alliage suivant l'une quelconque des revendications précédentes, caractérisé par une teneur en chrome de 36 à 40% en poids et une teneur en carbone de 1,9 à 2,1% en poids.

5. Procédé pour la production suivant l'une quelconque des revendications précédentes, caractérisé par un traitement à chaud de l'alliage à une température comprise dans une gamme de 600°C à 1000°C et un refroidissement à l'air de l'alliage.

FIGURE 1

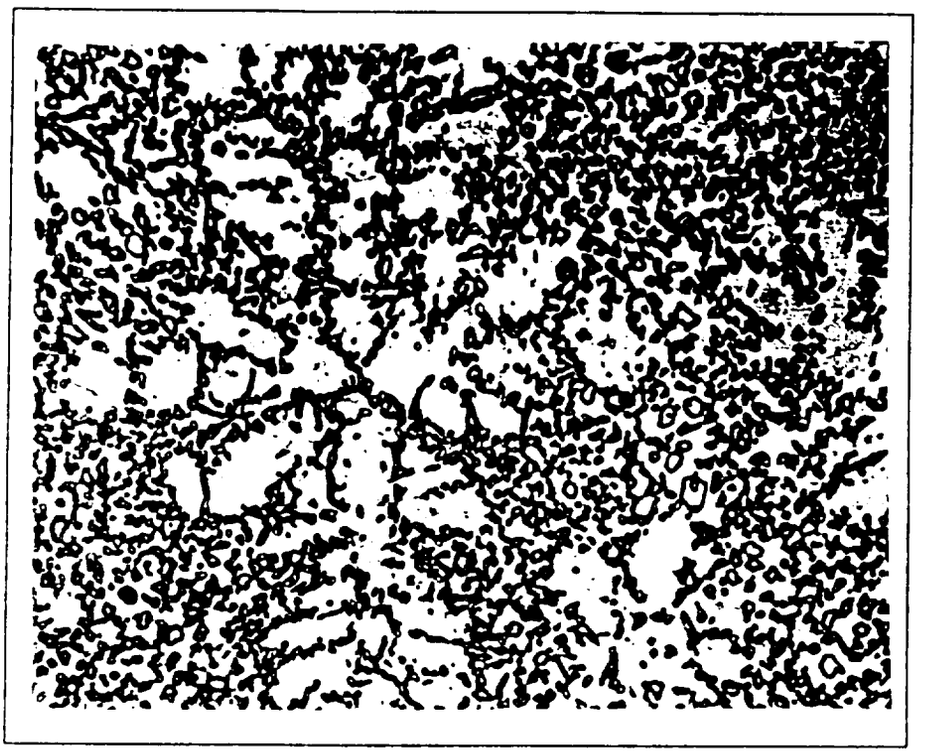


OPTICAL MICROGRAPH MAG. X 300

CHEMICAL ANALYSIS:

Cr	C	Mn	Si	Mo	Ni	Cu	Fe
28.4	1.94	0.97	1.48	2.10	2.01	1.49	bal

FIGURE 2

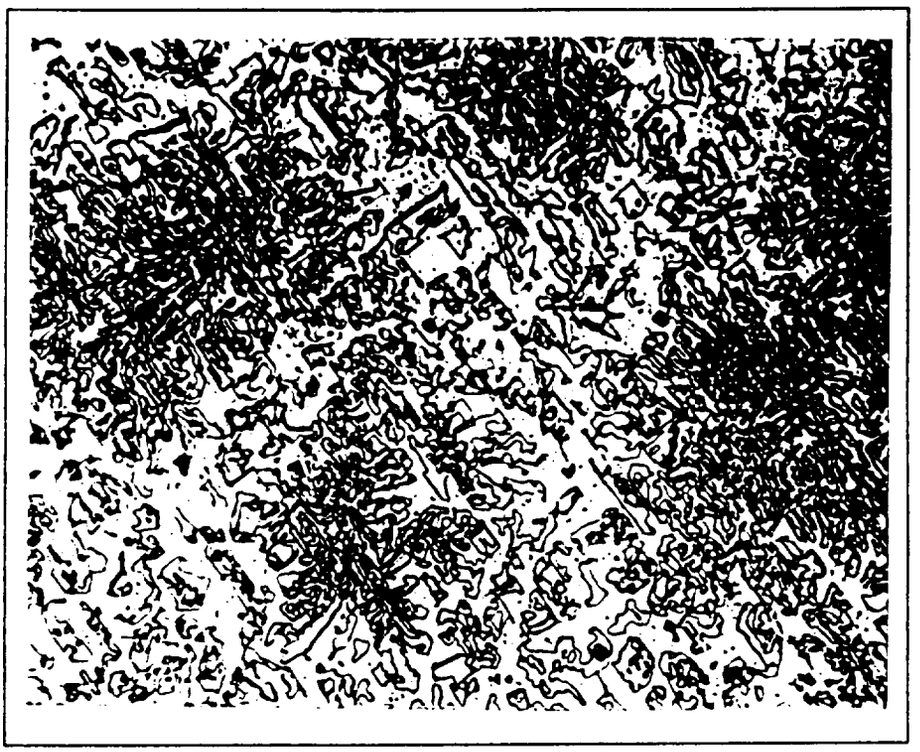


OPTICAL MICROGRAPH MAG. X 300

CHEMICAL ANALYSIS:

Cr	C	Mn	Si	Mo	Ni	Cu	Fe
35.8	1.95	0.96	1.48	2.00	2.04	1.48	bal

FIGURE 3

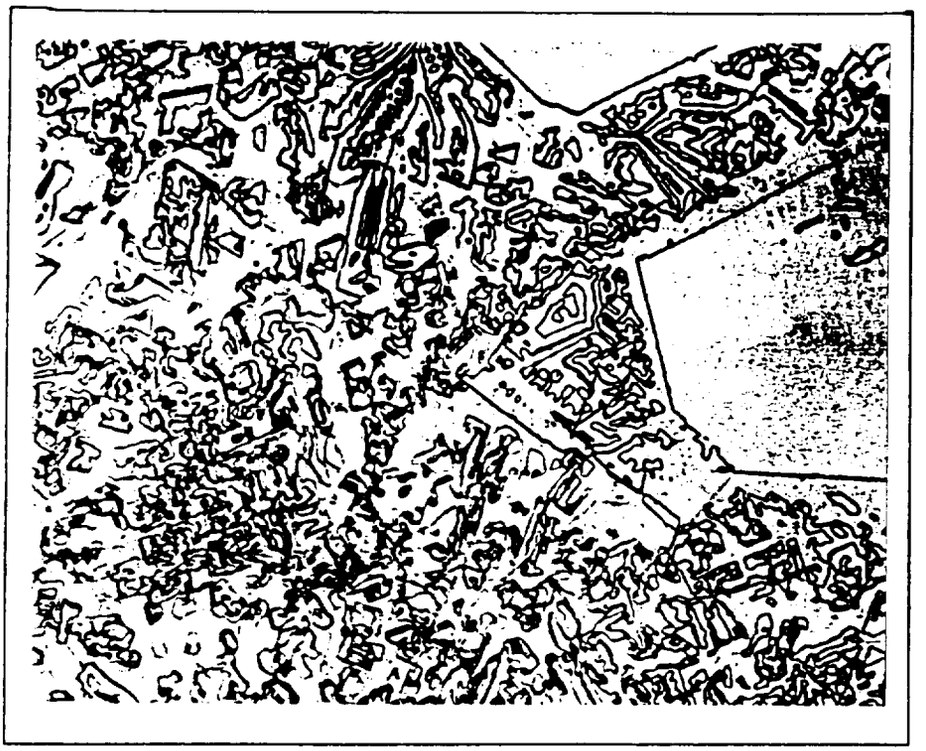


OPTICAL MICROGRAPH MAG. X 300

CHEMICAL ANALYSIS:

Cr	C	Mn	Si	Mo	Ni	Cu	Fe
40.0	1.92	0.96	1.59	1.95	1.95	1.48	bal

FIGURE 4

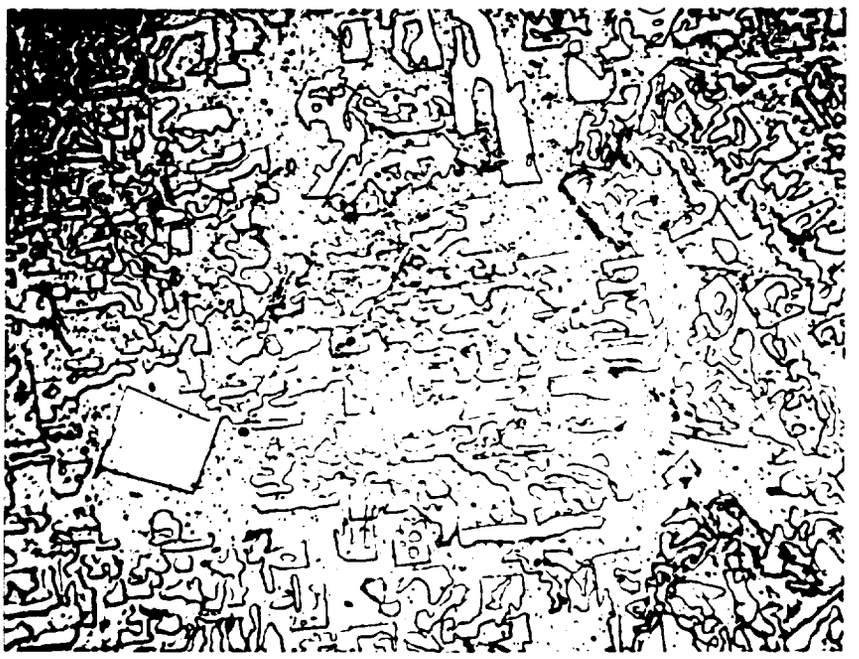


OPTICAL MICROGRAPH MAG. X 300

CHEMICAL ANALYSIS:

Cr	C	Mn	Si	Mo	Ni	Cu	Fe
40.0	2.30	2.77	1.51	2.04	1.88	1.43	bal

FIGURE 5



OPTICAL MICROGRAPH MAG. X 420

CHEMICAL ANALYSIS:

Cr	C	Mn	Si	Mo	Ni	Cu	Fe
43.0	2.02	0.92	1.44	1.88	1.92	1.20	bal