Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2037921 C 2006/11/21

(11)(21) 2 037 921

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 1990/08/03
(87) Date publication PCT/PCT Publication Date: 1991/02/21
(45) Date de délivrance/Issue Date: 2006/11/21
(85) Entrée phase nationale/National Entry: 1991/03/28
(86) N° demande PCT/PCT Application No.: AU 1990/000331
(87) N° publication PCT/PCT Publication No.: 1991/002101
(30) Priorité/Priority: 1989/08/04 (AUPJ 5628)

(51) Cl.Int./Int.Cl. *C22C 38/18* (2006.01),
C21D 6/00 (2006.01), *C22C 38/36* (2006.01),
C22C 38/56 (2006.01)

(72) Inventeur/Inventor:
DOLMAN, KEVIN FRANCIS, AU

(73) Propriétaire/Owner:
WEIR WARMAN LTD, AU

(74) Agent: OGILVY RENAULT LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : ALLIAGE DE FERROCHROME
(54) Title: FERROCHROMIUM ALLOY

(57) Abrégé/Abstract:

An erosion and corrosion resistant ferrochromium alloy comprising the following composition, in wt. %, 34 - 50 chromium, 1.5 - 2.5 carbon, up to 5 manganese, up to 5 silicon, up to 5 molybdenum, up to 10 nickel, up to 5 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. The alloy has a microstructure comprising eutectic chromium carbides in a matrix comprising one or more of ferrite, retained austenite and martensite, as herein defined. Optionally, the microstructure further comprises one of primary chromium carbides, primary ferrite or primary austenite in the matrix.

2037921

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{5} **:** C22C 37/06, 37/08	A1	**(11) International Publication Number:** **WO 91/02101** **(43) International Publication Date:** 21 February 1991 (21.02.91)

(21) International Application Number: PCT/AU90/00331

(22) International Filing Date: 3 August 1990 (03.08.90)

(30) Priority data:
PJ 5628 4 August 1989 (04.08.89) AU

(71) Applicant *(for all designated States except US):* WARMAN INTERNATIONAL LTD. [AU/AU]; 1 Marden Street, Artarmon, NSW 2064 (AU).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)* **:** DOLMAN, Kevin, Francis [AU/AU]; Lot 18, Katherine Street, Helena Valley, W.A. 6056 (AU).

(74) Agent: MUNT, Gregory, Richard; Griffith Hack & Co., 601 St. Kilda Road, Melbourne, VIC 3004 (AU).

(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US.

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: A FERROCHROMIUM ALLOY

(57) Abstract

An erosion and corrosion resistant ferrochromium alloy comprising the following composition, in wt. %, 34 - 50 chromium, 1.5 - 2.5 carbon, up to 5 manganese, up to 5 silicon, up to 5 molybdenum, up to 10 nickel, up to 5 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. The alloy has a microstructure comprising eutectic chromium carbides in a matrix comprising one or more of ferrite, retained austenite and martensite, as herein defined. Optionally, the microstructure further comprises one of primary chromium carbides, primary ferrite or primary austenite in the matrix.

* See back of page

A FERROCHROMIUM ALLOY

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.

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
up to 5	manganese
up to 5	silicon
up to 5	molybdenum
up to 10	nickel
up to 5	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, as herein defined.

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, carbon, manganese, silicon, molybdenum, nickel and copper is as follows:

36 - 40	chromium
1.9 - 2.1	carbon
1 - 2	manganese
0.5 - 1.5	silicon
1 - 2	molybdenum
1 - 5	nickel
1 - 2	copper

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

2037921

* 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_3 carbides 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.

Many modifications may be made to the alloy described above without departing from the spirit and scope of the invention.

CLAIMS

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

34 - 50	chromium
1.5 - 2.3	carbon
up to 5	manganese
up to 5	silicon
up to 5	molybdenum
up to 10	nickel
up to 5	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, said matrix also containing a 25-35 wt. % solid solution of chromium.

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

36 - 40	chromium
1.9 - 2.1	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.

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

36 - 40	chromium
1.9 - 2.1	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 one of eutectic chromium carbides, ferrite or austenite.

4. The alloy defined in claim 1 comprising in wt. %:

36 - 40	chromium
1.9- 2.1	carbon
1 - 2	manganese
0.5 - 1.5	silicon
1 - 2	molybdenum
1 - 5	nickel
1 - 2	copper.

5. A method of producing an erosion and corrosion resistant ferrochromium alloy comprising the following composition, in wt. %:

34 - 50	chromium
1.5 - 2.3	carbon
up to 5	manganese
up to 5	silicon
up to 5	molybdenum
up to 10	nickel
up to 5	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 method comprising heat treating the alloy at a temperature in the range of 600°-1000° C., and air cooling the alloy.

6. The method defined in claim 5, wherein the microstructure of the alloy further comprises one of primary chromium carbides, primary ferrite or primary astenite in the matrix.

7. The method defined in claim 5, wherein the alloy matrix contains a 25-35 wt. % solid solution of chromium.

8. The method defined in claim 5, wherein the alloy comprises in wt. %:

36 - 40	chromium

1.9 - 2.1	carbon
1 - 2	manganese
0.5 - 1.5	silicon
1 - 2	molybdenum
1 - 5	nickel
1 - 2	copper.

9. The method defined in claim 6, wherein the alloy comprises in wt. %:

36 - 40	chromium
1.9 - 2.1	carbon
1 - 2	manganese
0.5 - 1.5	silicon
1 - 2	molybdenum
1 - 5	nickel
1 - 2	copper.

10. The method defined in claim 7, wherein the alloy comprises in wt. %:

36 - 40	chromium
1.9 - 2.1	carbon
1 - 2	manganese
0.5 - 1.5	silicon
1 - 2	molybdenum
1 - 5	nickel
1 - 2	copper.

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

35.8 - 50	chromium
1.5 - 2.3	carbon
up to 5	manganese

up to 5	silicon
up to 5	molybdenum
up to 10	nickel
up to 5	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.

12. The alloy of claim 11, wherein the matrix comprises at least 25 wt. % solid solution of chromium.

13. The alloy of claim 11, further comprising 1-5 wt. nickel.

14. The alloy of claim 11, further having molybdenum present therein.

15. The alloy of claim 13, further having molybdenum present therein.

16. The alloy of claim 11, wherein carbon is present in the range of 1.5-2.1 wt. %.

17. The alloy of claim 11, wherein carbon is present in the range of 1.5-1.9 wt. %.

18. The alloy of claim 16, wherein nickel is present in the range of 1-5 wt. %.

19. The alloy of claim 17, wherein nickel is present in the range of 1-5 wt. %.

20. The alloy of claim 18, further having molybdenum present therein.

21. The alloy of claim 19, further having molybdenum present therein.

22. The alloy of claim 11, further comprising 40-50 wt. % chromium.

23. The alloy of claim 13, further comprising 40-50 wt. % chromium.

24. The alloy of claim 18, further comprising 40-50 wt. % chromium.

25. The alloy of claim 19, further comprising 40-50 wt. % chromium.

26. The alloy of claim 11, wherein at least one member selected from the group consisting of nickel, manganese, and copper is present in the alloy.

27 The alloy of claim 11, wherein at least two members selected from the group consisting of nickel, manganese, and copper are present in the alloy.

28. The alloy of claim 11, wherein nickel, manganese and copper are each present in the alloy.

29. A method of producing an erosion and corrosion resistant ferrochromium alloy comprising the following composition in wt. %:

34 - 50	chromium
1.5 - 2.3	carbon

the presence of at least one element selected from the group consisting of manganese, nickel and copper, wherein manganese, when present, will be in an amount up to 5%, wherein nickel, when present, will be in an amount up to 10%, and wherein copper, when present, will be in an amount up to 5%;

up to 5	silicon
up to 5	molybdenum

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, and

the method comprising heat treating the alloy at a temperature in the range of 600-1000°C, and air cooling the alloy.

30. The method of claim 29 comprising in wt. %:

36 - 40	chromium
1.9 - 2.1	carbon
1 - 2	manganese
0.5 - 1.5	silicon
1 - 2	molybdenum
1 - 5	nickel
1 - 2	copper.

31. The method defined in claim 5, wherein the alloy comprises 1-5 wt. % nickel.

32. The method defined in claim 5, wherein the alloy has molybdenum present therein.

33. The method as defined in claim 31, wherein the alloy has molybdenum present therein.

34. The method as defined in claim 5, wherein the alloy comprises 35.8-50 wt. % chromium.

35. The method as defined in claim 5, wherein the alloy comprises 40-50 wt. % chromium.

36. The alloy of claim 1, wherein chromium is present in a range of 40-50 wt. %.

2037921

FIGURE 1

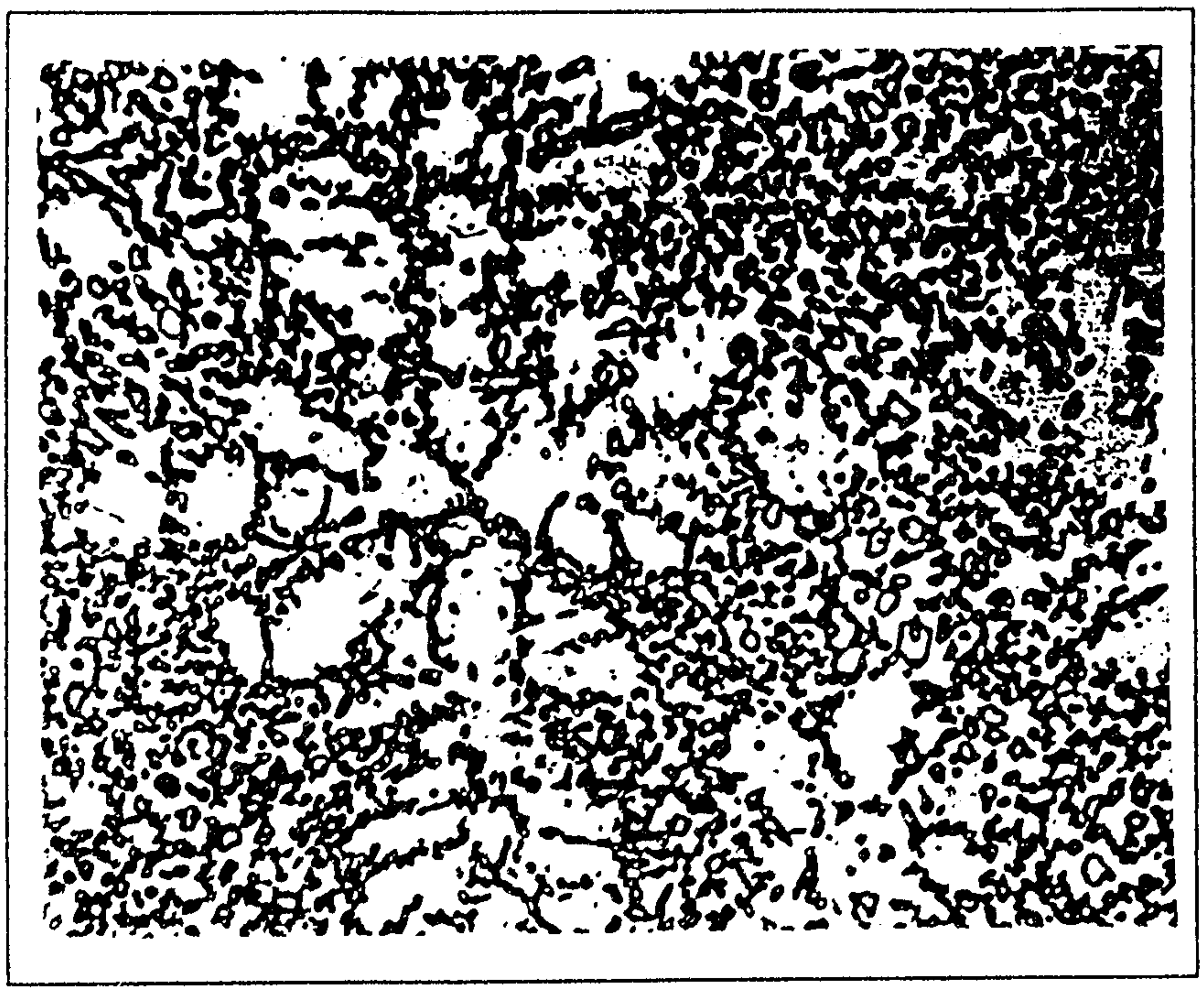
OPTICAL MICROGRAPH MAG. X 300

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

2037921

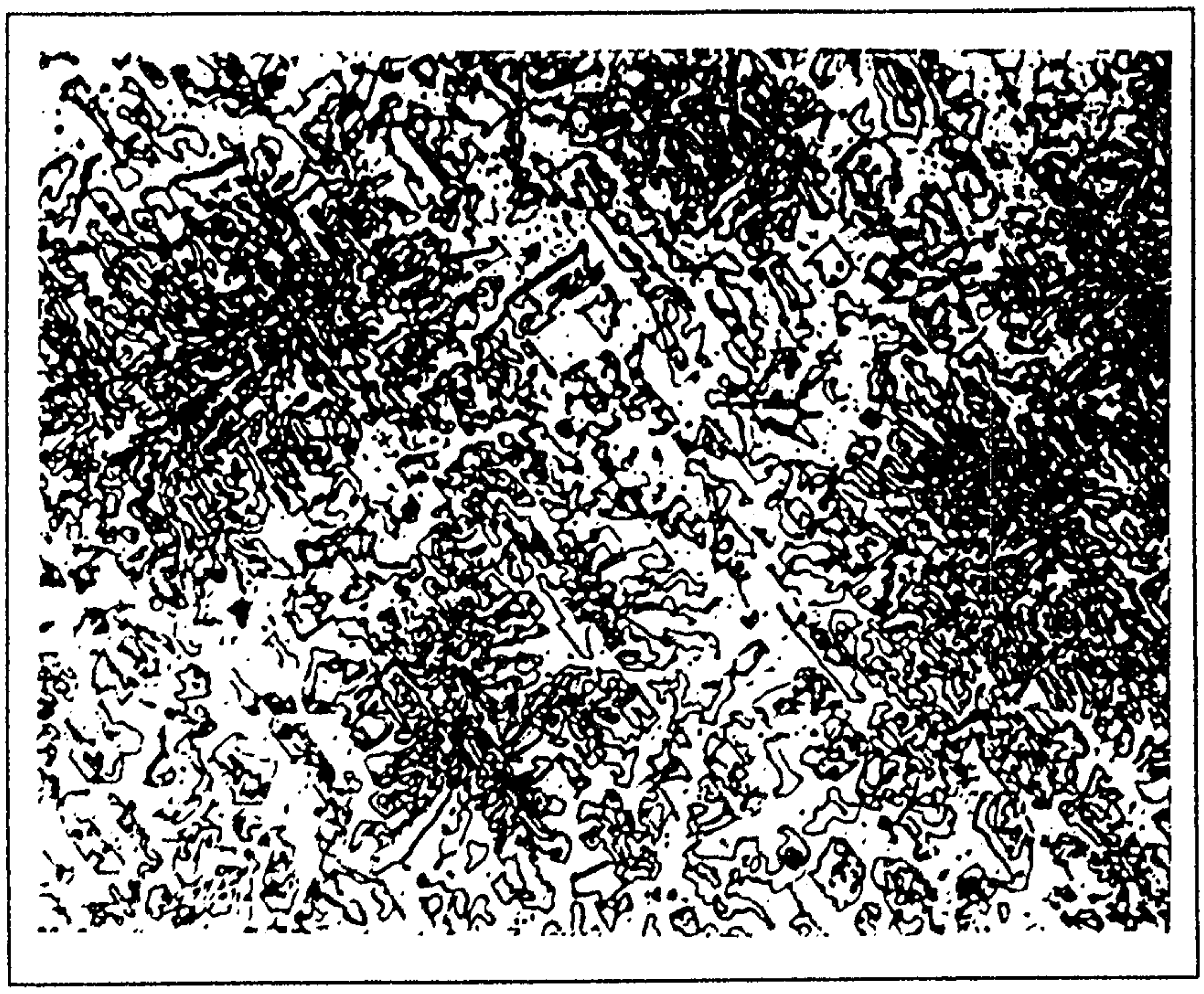


OPTICAL MICROGRAPH MAG. X 300

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

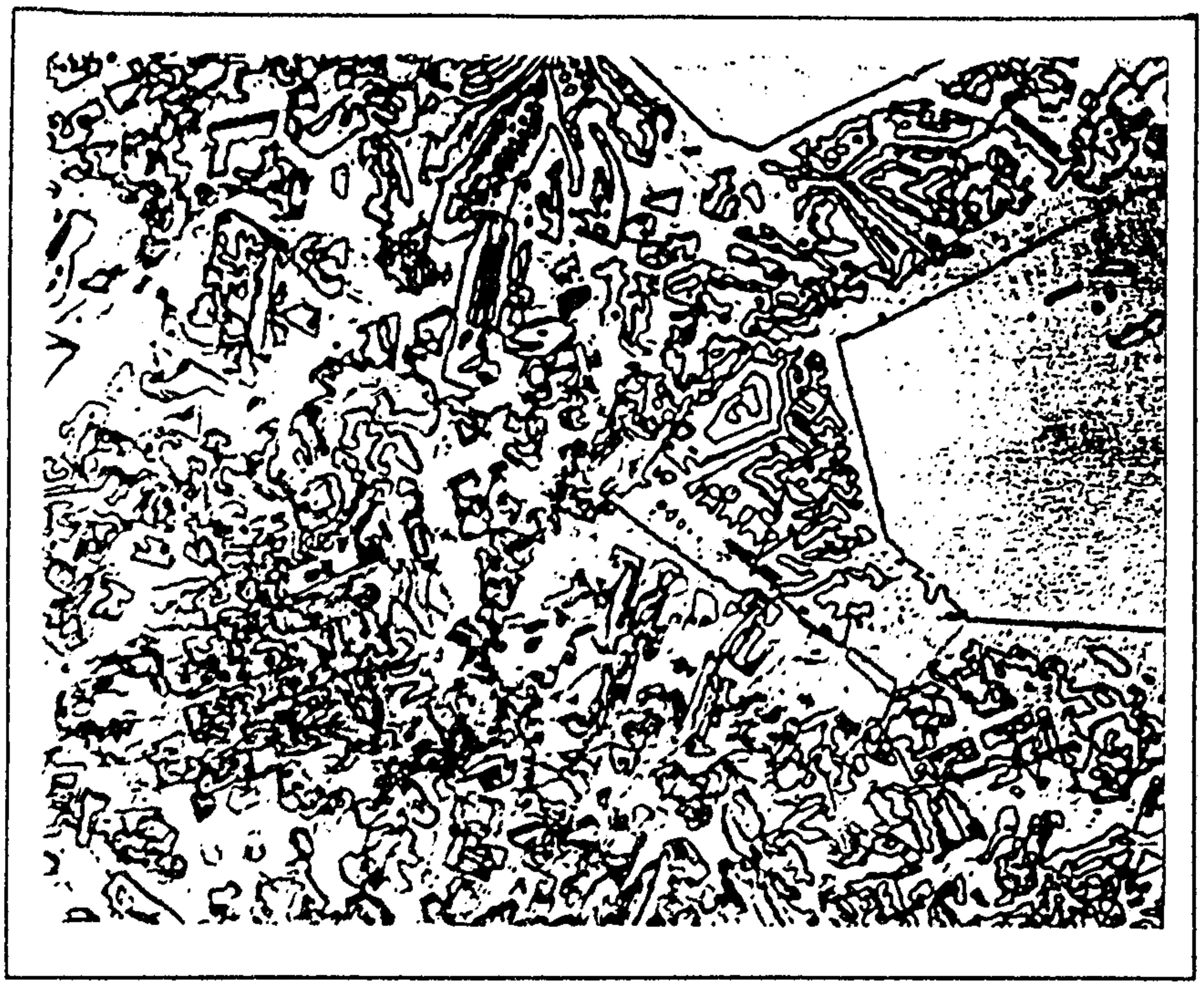


OPTICAL MICROGRAPH MAG. X 300

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

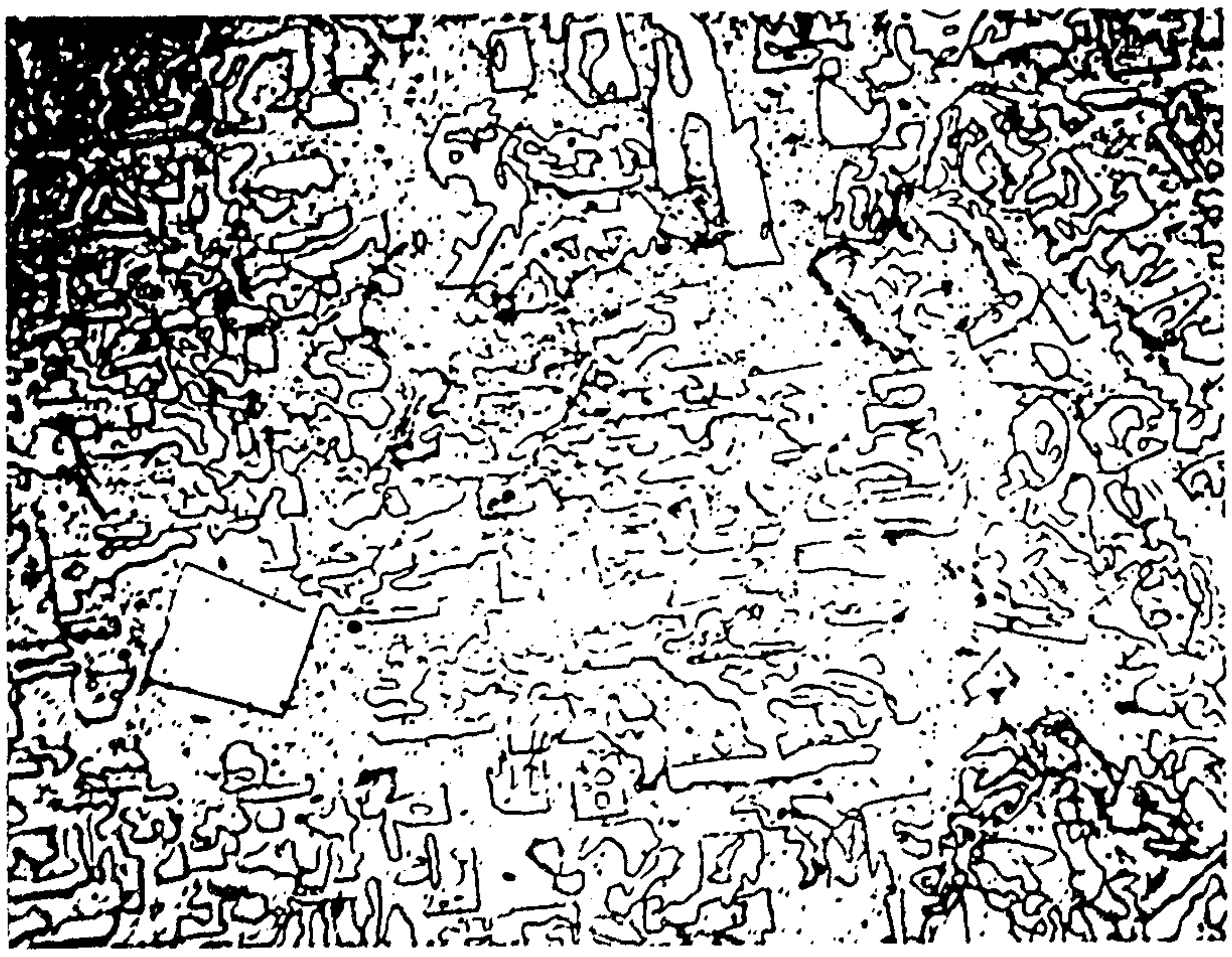


OPTICAL MICROGRAPH MAG. X 300

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