

REACTION MECHANISMS FOR THE PREREDUCTION OF WINTERVELD CHROME SPINELS

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(presented by Dr. Finn)

SYNOPSIS

The reduction of Winterveld chrome spinel with carbon was studied under argon and hydrogen atmospheres, the effect of temperature, time, and particle size being investigated. A multistage reaction mechanism is proposed that is based on various techniques, including thermogravimetric analysis, X-ray diffraction, optical and scanning electron microscopy, energy-dispersive X-ray analysis, and analysis with the electron-microprobe.

Introduction

The deposits of chromite ore in South Africa occur in the Bushveld Complex (BC), and contain five major oxides (Cr_2O_3 , Fe_2O_3 , FeO , MgO , and Al_2O_3) and six minor oxides (V_2O_5 , TiO_2 , CaO , MnO , NiO , and ZnO)¹⁻³. The major oxides form chrome spinel, though some of the minor oxides are present in the lattice structure of the spinels. The rest of the oxides (mainly SiO_2) are regarded as being separate gangue materials.

The general chemical formula for chrome spinels is $\text{M}^{2+}\text{M}_2^{3+}\text{O}_4$, where M^{2+} represents the divalent metals, iron and magnesium, and M^{3+} represents the trivalent metals, iron, aluminium, and chromium⁴. In some cases, oxygen atoms may be replaced by sulphur atoms. The oxides of the abovementioned elements have different effects on the mechanism of reduction of chrome spinel. Generally, FeO and Cr_2O_3 are reducible, whereas MgO and Al_2O_3 are irreducible oxides. Reduction of the chromite ores in which Cr_2O_3 is

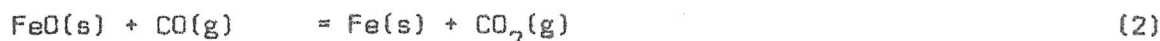
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combined mainly with FeO is therefore easy compared with that of ores containing Cr_2O_3 combined with MgO or Al_2O_3 ⁵.

Chrome spinel can be reduced with carbon according to the following reactions⁶.



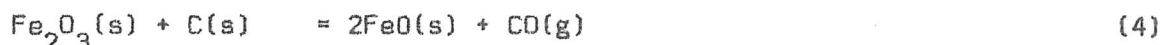
$$\Delta G^0, \text{ Joule} = 147\,900 - 150.2T \quad (298\text{K to } 1\,642\text{K})$$



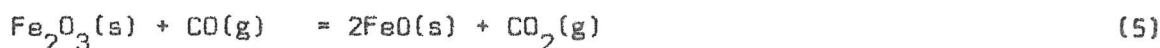
$$\Delta G^0, \text{ Joule} = -22\,802 + 24.27T \quad (298\text{K to } 1\,642\text{K})$$



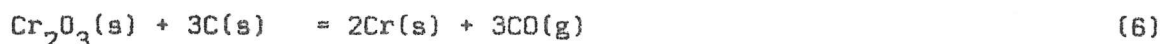
$$\Delta G^0, \text{ Joule} = 10\,355 - 10.17T \quad (1\,115\text{K to } 1\,808\text{K})$$



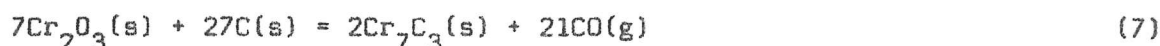
$$\Delta G^0, \text{ Joule} = 179\,578 - 217.94T \quad (298\text{K to } 1\,460\text{K})$$



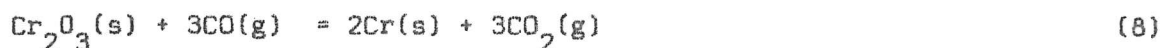
$$\Delta G^0, \text{ Joule} = 8\,870 - 43.47T \quad (298\text{K to } 1\,460\text{K})$$



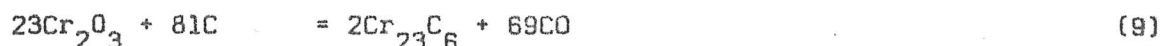
$$\Delta G^0, \text{ Joule} = 784\,081 - 522.79T \quad (298\text{K to } 2\,100\text{K})$$



$$\Delta G^0, \text{ Joule} = 5\,146\,870 - 3\,669T \quad (298\text{K to } 1\,673\text{K})$$



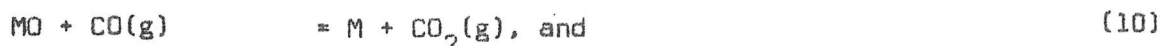
$$\Delta G^0, \text{ Joule} = 273\,010 + 0.63T \quad (298\text{K to } 2\,100\text{K})$$



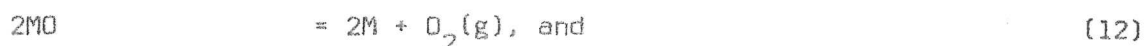
$$\Delta G^0, \text{ Joule} = 17\,235\,500 - 12\,101.4T \quad (298\text{K to } 1\,673\text{K})$$

Kolchin⁷ stated that metal oxides can be reduced by four different mechanisms, as follows :

1. indirect reduction of the metal oxides with carbon, i.e.,



2. dissociation of the oxides into their metals followed by oxidation of the carbon, i.e.,



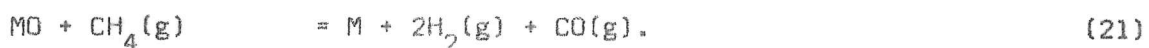
3. direct reduction of the metal oxides with carbon, i.e.,



4. evaporation of the metal oxides followed by reduction of the gaseous phase with carbon, i.e.,



Under a hydrogen atmosphere, reduction of the metal oxides may include the following reactions :



Experimental methods

In this study, use was made of chromite ore from the Winterveld Chromite Mine, which is located on the eastern edge of the Bushveld Complex (BC) and is the largest chromite mine in the world. This ore is used by Consolidated Metallurgical Industries (CMI) in a direct-reduction process prior to smelting in submerged-arc furnaces. In South Africa, therefore, interest in the mechanism of reduction of this ore with carbon is high.

Since the gangue constituents (mainly gabbro, norite, and pyroxenite) could mask the reduction mechanisms, it was decided that the spinel should be carefully separated from the gangue.

Winterveld chromite ore was obtained as run-of-mine ore and separated into its spinel and gangue materials. The chemical analysis of the spinel is given in Table I. The following separation techniques were used :

- (a) crushing and grinding,
- (b) screening (to particle sizes between 300 and 212 μm , 106 and 90 μm , and 45 and 38 μm respectively),
- (c) heavy-medium gravity separation (with diiodomethane),
- (d) magnetic separation (by use of the Frantz isodynamic separator), and
- (e) rescreening (for undersized particles).

Carbon in the form of spectroscopic graphite was used as the reducing agent. Fractions of chrome spinel and graphite of the same particle size were mixed homogeneously in a ratio of spinel to graphite of 4 by mass, each sample having a total mass of 5g. Experiments were first completed under an argon atmosphere and then under a hydrogen atmosphere. The samples were reduced for varied periods of time.

The experimental apparatus consisted of a Stanton-Redcroft thermobalance with a molybdenum-wound resistance furnace, gas connections, deoxidation furnace, temperature controller, Thyristorized PID temperature regulator and gas-cleaning agents, as shown in Figure 1.

The following techniques were applied for examination of the samples.

1. *Plotting of kinetic curves*

The kinetic curves were plotted as calculated percentage reduction *versus* time from the graphs of the Stanton thermobalance recorded for each sample during experiments.

2. *X-ray-diffraction analysis*

A Phillips X-ray diffractometer was used with Cu K α radiation. The phases formed at the end of each reduction stage were detected.

3. *Quantitative chemical analysis*

Conventional methods were applied for analysis.

4. *Techniques involving the use of the optical microscope and electron microprobe*

The phases formed during reduction were observed under the Leitz optical microscope, and photomicrographs were taken. Qualitative and quantitative analyses were carried out by use of a Cambridge scanning electron microscope with an attachment for energy-dispersive analysis with X-rays (EDAX). An electron microprobe was also used for analysis.

Experimental results

The rate of reduction is related to the rate of mass loss. Percentage reduction is defined as

$$\text{Reduction at time } t, \% = \frac{x}{y}$$

where x is the loss in mass of CO and y is the loss in mass of CO for total conversion of Fe₂O₃ to Fe, FeO to Fe, and Cr₂O₃ to Cr.

The rate of reduction is a function of temperature and particle size, increasing with temperature and decreasing with particle size (Figure 2), under an argon atmosphere.

The rate of reduction accelerated under a hydrogen atmosphere, the difference being higher at low temperatures, e.g., 1 000, 1 100, and 1 200° C (Figures 3 to 5), and lower at high temperatures, e.g., 1 300 and 1 400° C (Figures 6 and 7).

Argon Atmosphere

Samples of the chrome spinel at various stages of reduction (represented by triangles in Figures 3 to 7) under an argon atmosphere were mounted in epoxy resin, polished to 1 μ m on diamond wheels, and examined under a Leitz Panphot optical microscope. Photomicrographs taken at various stages of reduction between 7 and 95 per cent are shown in Plates I to VIII.

Reduction starts with the conversion of Fe_2O_3 to FeO . Up to 4 per cent reduction, no metallization is observed. FeO is then converted to metallic iron. At 7 per cent reduction (Plate I), nuclei of metal, which grow over the surface as reduction proceeds (Plates II and III), are uniformly distributed round the surfaces of the particles of chrome spinel. At the point when the nuclei have grown to the extent where they completely surround the particles (Plate IV), the metallic phase consists mainly of iron. However, some chromium is present, even in the early stages of reduction. The metallic rim thickens as reduction proceeds (Plates V and VI), but the particles retain their original size and shape. At advanced stages of reduction, the metallic material coalesces and gathers on one side of each of the particles (Plates VII and VIII). While retaining their original size and shape, the particles become porous in appearance (Plate VIII). This phenomenon is more obvious under the scanning electron microscope (SEM).

Samples taken at 5 and 65 per cent reduction of the chrome spinel were coated with carbon, and photographed with the Cambridge SEM, element maps being made by use of the EDAX attachment. Plates IX to XIV show a particle of chrome spinel at 5 per cent reduction and maps of the same particle for chromium, iron, aluminium, magnesium, and silicon. The uniform distribution of all these elements (except silicon) throughout the spinel and the absence of a metallic rim are indicative of low reduction. The small particle of unliberated siliceous gangue can be clearly discerned in the photomicrograph of the particle (Plate IX) and the silicon map (Plate XIV).

Plates XV to XIX show a particle of chrome spinel at 65 per cent reduction and maps of this particle for chromium, iron, aluminium, and magnesium. As can be seen from Plate XV, the chromium and iron are located predominantly in the metallic (light) phase, whereas the aluminium and magnesium are distributed throughout the spinel. No gangue is associated with this particle.

Point analysis of the metallic phase with EDAX for chromium and iron showed values of 60 and 40 per cent respectively. Analysis for carbon was not possible. Etching with picric acid X-ray-diffraction analysis indicated that the metallic phase was a carbide, probably $(\text{Fe,Cr})_7\text{C}_3$.

Point analysis with EDAX was done across a particle at 68 per cent reduction. The path of the trace is indicated on Plate XX, which clearly shows the porous structure of the highly reduced spinel referred to previously. The profiles across the particle for chromium, iron, magnesium and aluminium are shown in Figure 8. The metallic phase is rich in chromium, whereas the chromium and the iron in the spinel are depleted at the interface between the metal and the spinel but increase towards the centre of the particle. As mentioned earlier, the metallic phase is a chromium-iron carbide.

Because results obtained with EDAX are less precise than those obtained with the electron microprobe, samples were submitted to the Mineralogy Division of the National Institute for Metallurgy for electron-microprobe analysis (EMA). Figure 9 shows a trace from the edge of a particle at 7 per cent

reduction. As a carefully analysed, unreduced particle of chromite was used as a standard, the analyses for chromium and iron in the metallic phase are too low. At a distance of 12 μm from the surface of the particle that is 100 μm in size, the spinel is unaltered, but as the surface is approached, there is depletion of the iron in the spinel with concurrent enrichment of chromium, magnesium, and aluminium.

Figure 10 shows an EMA trace across a particle at 41 per cent reduction. The metallic phase is richer in chromium, whereas the spinel is nearly free of iron. The gradient for chromium in the spinel is from 30 per cent chromium at the metal-spinel interface to 40 per cent chromium at a distance of 10 μm from the interface. The magnesium and aluminium contents are essentially constant throughout the spinel.

Hydrogen Atmosphere

Samples from various stages of reduction (represented by circles in Figures 3 to 7) under a hydrogen atmosphere were mounted in epoxy resin, polished to 1 μm on diamond wheels, and examined under a Leitz Panphot optical microscope. Photomicrographs showing various stages of reduction of between 5 and 65 per cent can be seen in Plates XXI to XXVI.

At a reduction of 8 per cent (Plate XXI), nuclei of metal can be observed on the surface of the particle and on cracks in the interior. These nuclei grow as reduction proceeds, forming a rim round the particle and bands along cracks in the particle (Plates XXII to XXIV). At high degrees of reduction (Plates XXV and XXVI), a network of metal forms throughout the interior of the particle, virtually filling it at 65 per cent reduction.

A sample at 80 per cent reduction was submitted to the Mineralogy Division of the National Institute for Metallurgy for EMA. Figure 11 shows a trace across a particle of 43 μm width. Although the average particle size was 100 μm , some particles appear to be smaller in section as a result of the variable depth of polishing. This trace, therefore, does not represent the true centre of this particle.

This trace is much more complex than the EMA traces for particles reduced under an argon atmosphere. Due to the numerous bands of metal throughout the particle and the effective beam width of 1.6 μm , the analysis often reflects a composite of the alloy and the spinel. The interior is depleted in iron, though not to the same degree as in the previous instance (Figure 10), and there is a gradient of chromium toward the large metallic rim on the edge of the particle.

X-ray-diffraction Analysis

X-ray-diffraction (XRD) patterns were obtained for finely ground samples (with a particle size smaller than 38 μm) from various stages of reduction under hydrogen and argon atmospheres. The results are shown in Table II.

In the early stages of reduction, i.e., up to 25 per cent, the dominant phases under argon and hydrogen atmospheres are iron and Fe_3C in the metallic phase and chrome spinel in the non-metallic region, whereas, at 40 to 45 per cent reduction, $(\text{Fe}, \text{Cr})_7\text{C}_3$ and chrome spinel are found. At very high degrees of reduction, i.e., at 80 per cent, the phases are $(\text{Fe}, \text{Cr})_7\text{C}_3$ and MgAl_2O_4 spinel.

Carbon Monoxide Atmosphere

A test was done for investigation of the possibility that chromite can be reduced with carbon monoxide. This possibility was discounted by Barcza *et al.*⁸ but demonstrated by Rankin⁹.

Particles of chrome spinel were placed in a recrystallized Al_2O_3 crucible that, in turn, was placed in a graphite crucible. This dual crucible arrangement was placed in a furnace at $1450^\circ C$ for 16 hours in a stream of carbon monoxide. After reduction, the particles were mounted on double-sided tape and coated with carbon for observation under the SEM. Plate XXVII shows a typical particle with extensive metallic nuclei. EDAX analysis indicates that the metallic phase is 96 per cent iron, and 4 per cent chromium. X-ray-diffraction analysis indicates that the metallic phase was a mixed carbide, viz. Fe_3C and $(Cr, Fe)_7C_3$.

DISCUSSION

Argon Atmosphere

Examination of the curves for reduction *versus* time (Figures 3 to 7) show that there are three distinct periods :

- (a) that during which the rate of reduction is slow, i.e., at reductions of between 0 and 10 per cent,
- (b) that during which the rate of reduction increases, i.e., at reductions between 15 per cent and 50 per cent, and
- (c) that during which the rate of reduction is decreasing, i.e., at reductions higher than 50 per cent.

Between these areas a transition period occurs. Previous efforts by Barcza *et al.*⁸ using a single-reaction equation were partially successful, but the "goodness of fit" was low.

In the modelling of a reaction, the first requirement is a knowledge of the mechanisms of the reactions involved. It is proposed that, in the reduction of Winterveld chrome spinel, at least three stages occur as reaction proceeds.

Stage I. The Reduction of Fe_2O_3 to FeO

This is probably a gas-solid reaction involving mechanisms proposed by numerous authors for the reduction of iron ore. This is a short stage in the reduction of chromite, and will not be discussed further here.

Stage II. The Nucleation of Metallic Iron

Nucleation was discussed in detail in a recent publication by Rao¹⁰ who states : "the formation of nuclei is greatly favoured at sites where the lattice structure has been distorted ...".

The reduction of ferric iron to ferrous iron in the spinel structure distorts the spinel lattice, since the divalent iron tries to occupy trivalent sites.

Once nuclei have formed, further growth of these nuclei occurs in preference to the formation of additional nuclei due to considerations in regard to surface free energy. During the growth stage, the rate of reaction accelerates.

Stage III. Rim Formation

The completion of rim formation signals the onset of the period during which the rate of reduction decreases. The rim continues to grow as iron and chromium diffuse from the interior of the spinel to the metal-spinel interface where they are reduced into the metal.

Mechanisms of Reduction

The overall reduction of chrome spinel in the presence of solid carbon is given by



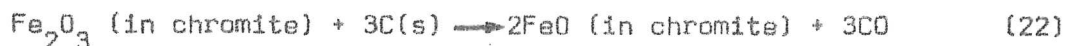
followed by



However, the direct reaction between solid chromite and solid carbon can occur only at points of contact. If it is assumed that the particles are spherical and of equal size in a volume ratio of 1, i.e., a mass ratio of 3.5, and that they are as closely packed as possible, six contact points per chromite particle will occur between the chromite and the carbon. Metal can form only at these points of contact, and then at a slow rate.

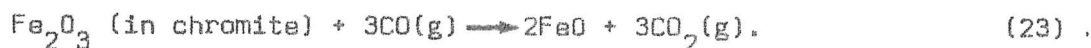
Rankin⁹ has shown that, in the presence of carbon (without physical contact with the chrome spinel), carbon monoxide will reduce the iron and some of the chromium in the spinel. As shown in Plate XXVII, this reduction occurs at the surface of the particle, with the resulting metallic phase forming nuclei up to 100 μm in length.

Although it has been established that carbon monoxide will reduce the spinel, identification of the mechanisms responsible for the accelerating rate of reduction is still necessary. Firstly, in a system of chrome spinel and carbon in an inert gas (argon) no carbon monoxide is present initially. However, at chromite-carbon contact points, the reaction



can occur.

This reaction is very favoured thermodynamically, as is the subsequent reaction



However, the building up of carbon dioxide in the system would eventually stop reaction (23).

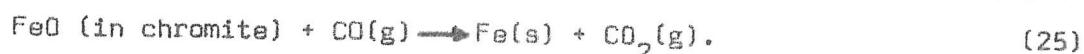
In the presence of carbon at elevated temperatures, the reaction



is highly favoured. Rankin⁹ calculated the ratios of carbon monoxide to carbon dioxide for reactions (23) and (24) and found that they favour the reduction of iron oxides (and of chromium oxides) at between 1 100 and 1 600° C.

Note the relative stoichiometry of reactions (23) and (24). Every molecule of Fe_2O_3 reduced requires three molecules of carbon monoxide and generates three molecules of carbon dioxide (reaction (23)). These three molecules of carbon dioxide will react with three molecules of carbon to generate six molecules of carbon monoxide, thus doubling the amount of carbon monoxide available for reaction (23). This mechanism could account for the acceleration in Stage I of the reduction.

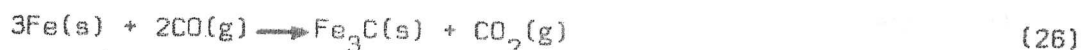
Rankin⁹ has also shown that the ratio of carbon monoxide to carbon dioxide, which is generated by reaction (24), exceeds that required for



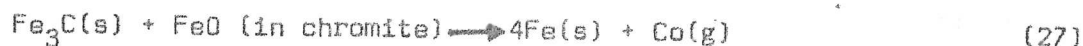
Nuclei of iron can therefore form as a result of reaction (25), probably at surface defects in the particles of chrome spinel.

Once formed, the nuclei grow. Unlike the reaction during the reduction of other oxides such as iron oxide, nickel oxide, and lead oxide, these nuclei grow by spreading over the surface of the particle and by growing outwards rather than by spreading into the particle and consuming it.

The growth of nuclei is mainly according to reaction (25) but, at the same time, the iron is being carburized as follows :



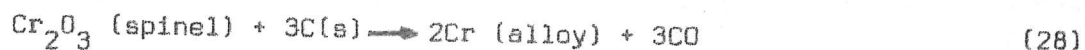
The formation of iron carbide (cementite) is clearly indicated by etching and XRD. Thermodynamically, iron carbide (and chromium carbide) will reduce chrome spinel according to the reaction



This iron carbide, which is formed in metal nuclei, is in intimate contact with the chrome spinel and is probably a secondary reaction during the growth stage of the nuclei.

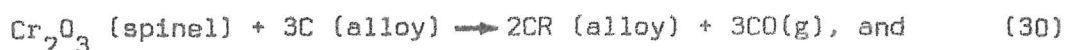
Once the metallic rim has completely covered the particle of chrome spinel, gas-phase reaction (25) is no longer possible, and reaction with carbon in the rim (27) becomes dominant. At this stage in reduction, most of the iron has been removed from the spinel structure as shown by the EDAX and EMA results.

The metallic rim becomes progressively enriched with chromium as the net reaction



occurs. This reaction probably occurs in the following steps :





As carbon is consumed at the alloy-spinel interface, the carbon concentration decreases, thus setting up a gradient of carbon in the alloy rim. The diffusion coefficient for carbon in iron¹¹ is about $10^{-6} \text{ cm}^2/\text{s}$ at 1100°C and $10^{-5} \text{ cm}^2/\text{s}$ at 1400°C . The alloy rim is about 5 to 20 μm in thickness, so the diffusion of carbon will be fast.

Chromium oxide is also consumed at the alloy-spinel interface during reaction (30). Although no data are available for the diffusion coefficients of iron and chromium in chrome spinel, data are available for several divalent and trivalent metals in similar structures¹¹. These vary between 10^{-9} and $10^{-7} \text{ cm}^2/\text{s}$.

If one considers spherical particles with an initially uniform composition, the solution¹² to the diffusion equation is as follows.

$$M = \frac{C_s - C_o}{3} \cdot r_o \left\{ 1 - \frac{6}{\pi^2} \left[\sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(- \frac{Dn^2 \pi^2 t}{r_o^2} \right) \right] \right\},$$

where

M is the amount of material that has left the particle at time, t , per unit area (g/cm^2),

C_s is the surface concentration (g/cm^3),

C_o is the initial concentration (g/cm^3),

r_o is the radius of the particle (cm),

D is the diffusion coefficient (cm^2/s), and

t is time (s).

This equation was solved on the following assumptions :

- (1) the particle size is 100 μm , i.e., the radius is 0.005 cm,
- (2) the diffusion coefficients are between 10^{-7} and $10^{-9} \text{ cm}^2/\text{s}$,
- (3) $C_2 = 0$, i.e., when a Fe^{2+} or Cr^{3+} arrives at the surface it is immediately reduced to metal, and
- (4) the diffusion of iron and chromium occurs at the same rate.

These results are shown in Figure 12, and represent an upper limit for the diffusion rate, as the alteration of 3 or 4 would lower the rate of diffusion.

From a comparison between Figure 12 and Figures 3 to 7, it can be seen that the diffusion calculation predicts a rate that is far too rapid during the

early stages of reduction. Diffusion cannot therefore be rate limiting. However, in the later stages of reduction after the period of decreasing rate, the diffusion rates approach those of the reduction rates and it is therefore possible that diffusion limits the rate of reduction during the period of decreasing.

It is beyond doubt that the iron and the chromium diffuse to the surface of the spinel and react there to form a metallic rim. Further investigation is in progress for verification of the reaction mechanisms proposed and the development of a mathematical model to fit these mechanisms.

Hydrogen Atmosphere

The stages noted under an inert atmosphere also occur under a hydrogen atmosphere but at a much faster rate (see Figures 3 to 7).

Thermodynamically, hydrogen is capable of reducing the iron and chromium oxides in chromite provided that the water generated can be removed. Carbon is an excellent "sink" for water at elevated temperatures via reaction (18). In addition, the diffusivity of hydrogen in oxides is very high. The photomicrographs (Plates XXIII to XXVII) clearly show the penetration of gas into the spinel along microcracks and line defects. Once this reaction band of metal forms, continuing reaction can occur due to the diffusion of carbon through the metal, since these bands all appear to be connected with the surface.

This network of metal throughout the particle greatly reduces the diffusion path for the iron and the chromium within the spinel, as shown in Figure 11. It is possible that the diffusion of carbon through the metal becomes rate limiting in the advanced stages of reduction under hydrogen atmospheres.

Conclusions

1. The reduction rate of Winterville chrome spinel in the presence of carbon increases with
 - (a) increasing temperature and
 - (b) decreasing particle size.
2. There are three stages in the rates of reduction :
 - (a) a slow stage, as the nuclei form
 - (b) an accelerating rate as the nuclei grow, and
 - (c) a decreasing rate after a complete rim has formed.
3. The reduced metal converts to carbide as reduction progresses.
4. Carbon monoxide will reduce Winterville chrome spinel in the presence of carbon.
5. Hydrogen accelerates the rate of reduction of Winterville chrome spinel, its effect being higher at low temperatures.

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12. BARRER, R.M. Diffusion in and through solids.
Cambridge, Cambridge University Press,
1951. pp. 28-29.

Analysis, mass %												
Size fraction μm	Cr ₂ O ₃	FeO	Total Fe	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	V ₂ O ₅	MnO	Zn	Co	Ni
Between 300 and 212	47.3	18.3 17.8	20.3 20.2	11.1	15.3	0.10	0.55	0.35	0.25	0.60	0.05	0.89
Between 106 and 90	47.0 47.2	18.6 18.2	20.1	11.0 11.0	15.2 15.2	0.12 0.11	0.55 0.55	0.36 0.36	0.25 0.25	0.63 0.63	0.05	0.90 0.89
Between 45 and 38	47.3	17.3	19.6 19.8	11.1	15.3	0.20	0.56	0.36	0.21	0.60	0.05	0.90

TABLE I. Chemical analysis of the Winterveld chrome spinels.

Sample no.	Reduction %	Atm	Temp. °C	Time min	Theoretically possible phases	Phases present
Sp 87	11	H ₂	1 000	85	Fe, Fe ₃ C (residue Cr-Sp)	Fe, trace Fe ₃ C, (Mg,Fe)(Fe,Al,Cr) ₂ O ₄
Sp 102	24	H ₂	1 200	26	Fe, Fe ₃ C (residue Cr-Sp)	Fe, Fe ₃ C (residue Cr-Sp)
Sp 111	40	H ₂	1 400	10	Fe, (Fe,Cr) ₇ C ₃ (residue Cr-Sp)	Fe, (Fe,Cr) ₇ C ₃ (residue Cr-Sp)
Sp 110	82	H ₂	1 400	60	Fe-Cr-carbide, MgAl ₂ O ₄	Fe-Cr-carbide, MgAl ₂ O ₄
Sp 109	26	Ar	1 400	10	Fe, Fe ₃ C ₇ (residue Cr-Sp)	Fe, Fe ₃ C (residue Cr-Sp)
Sp 83	45	Ar	1 300	50	Fe, Fe ₃ C, Cr-Fe-carbide (residue Cr-Sp)	Fe, trace Fe ₃ C, Cr-Fe-carbide (residue Cr-Sp)
Sp 108	81	Ar	1 400	50	Fe-Cr-carbide, MgAl ₂ O ₄	Fe-Cr-carbide, MgAl ₂ O ₄

TABLE II. The results of X-ray-diffraction analysis.

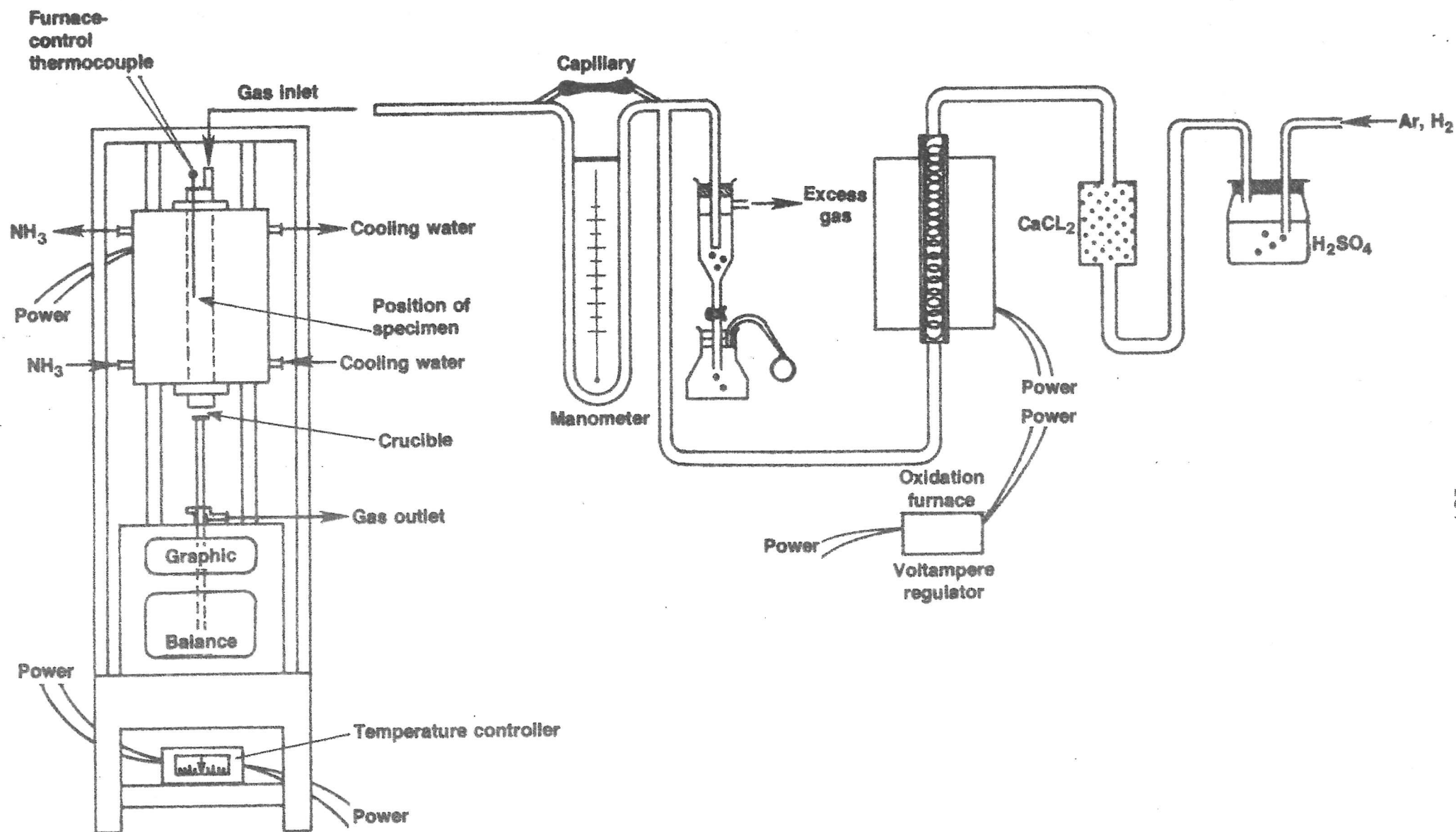


FIGURE 1. Experimental apparatus

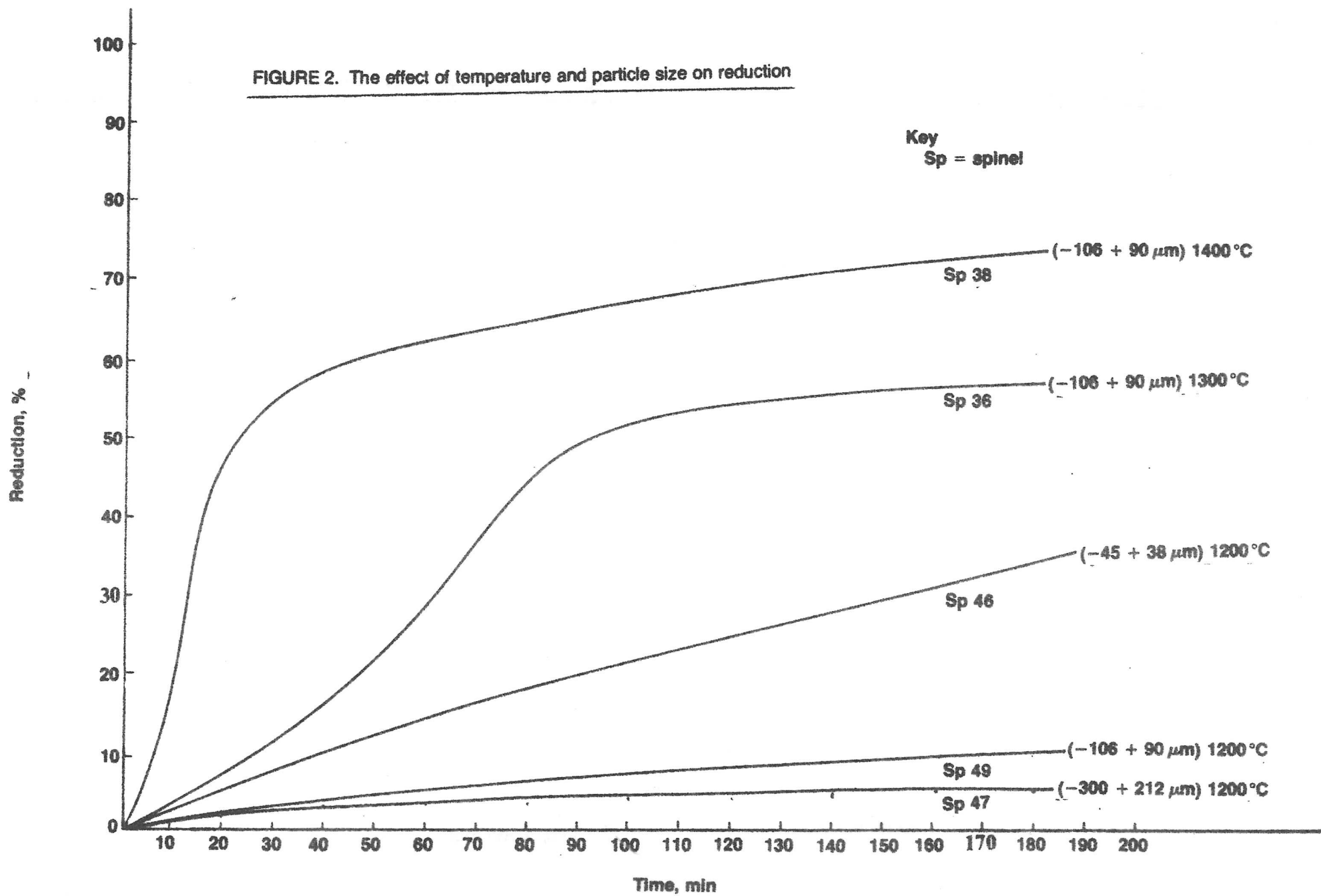
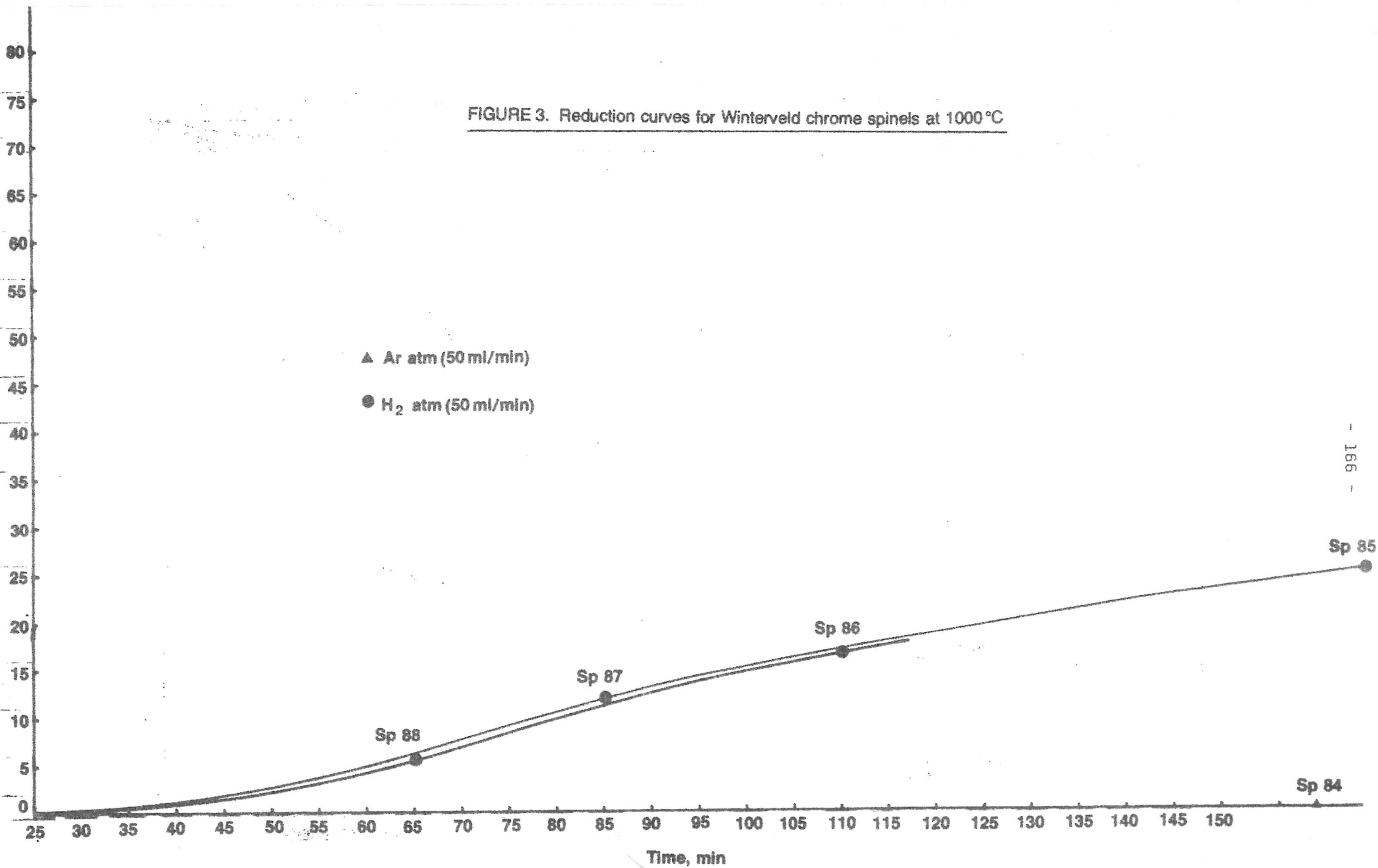


FIGURE 3. Reduction curves for Winterveld chrome spinels at 1000°C



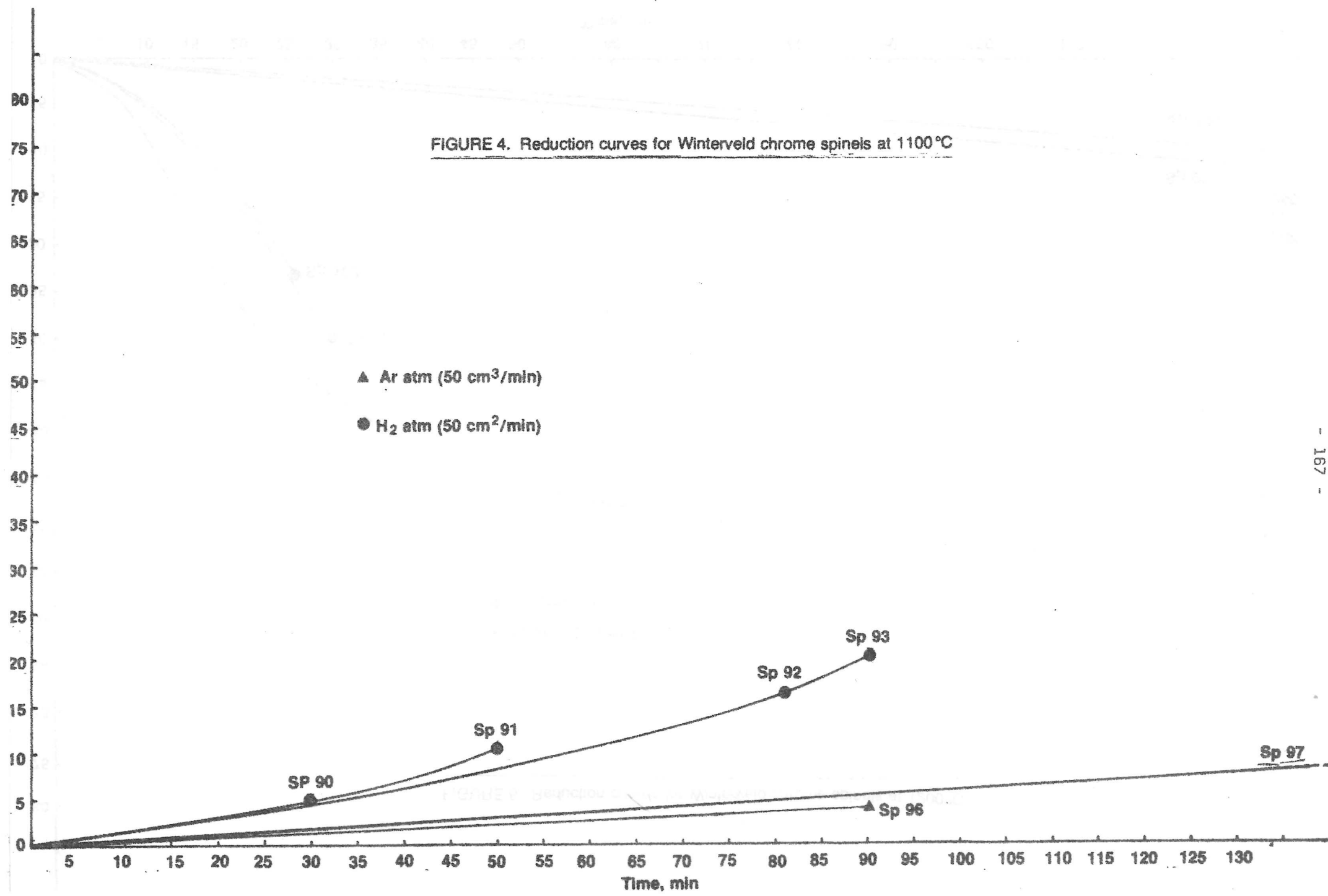
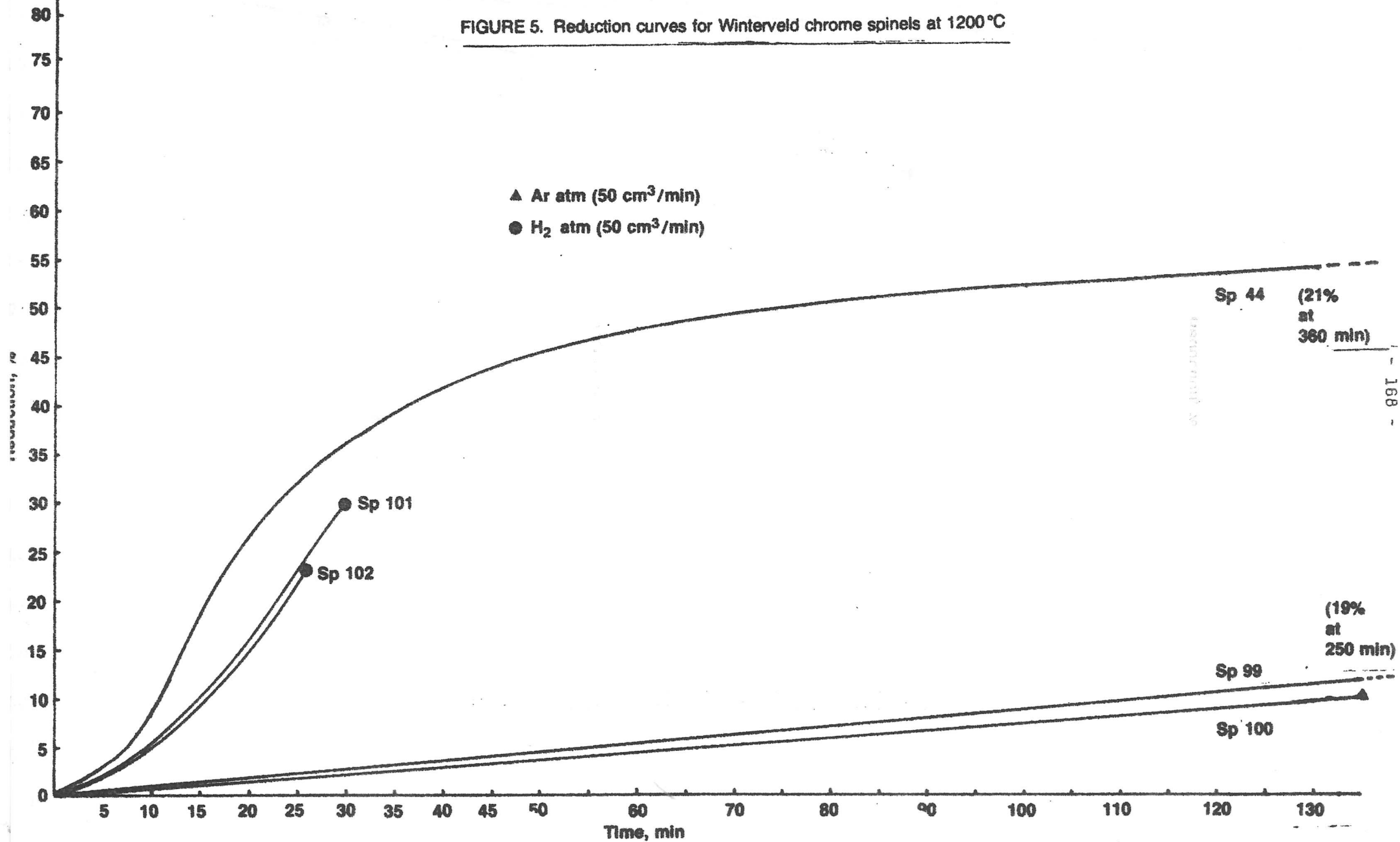


FIGURE 5. Reduction curves for Winterveld chrome spinels at 1200°C



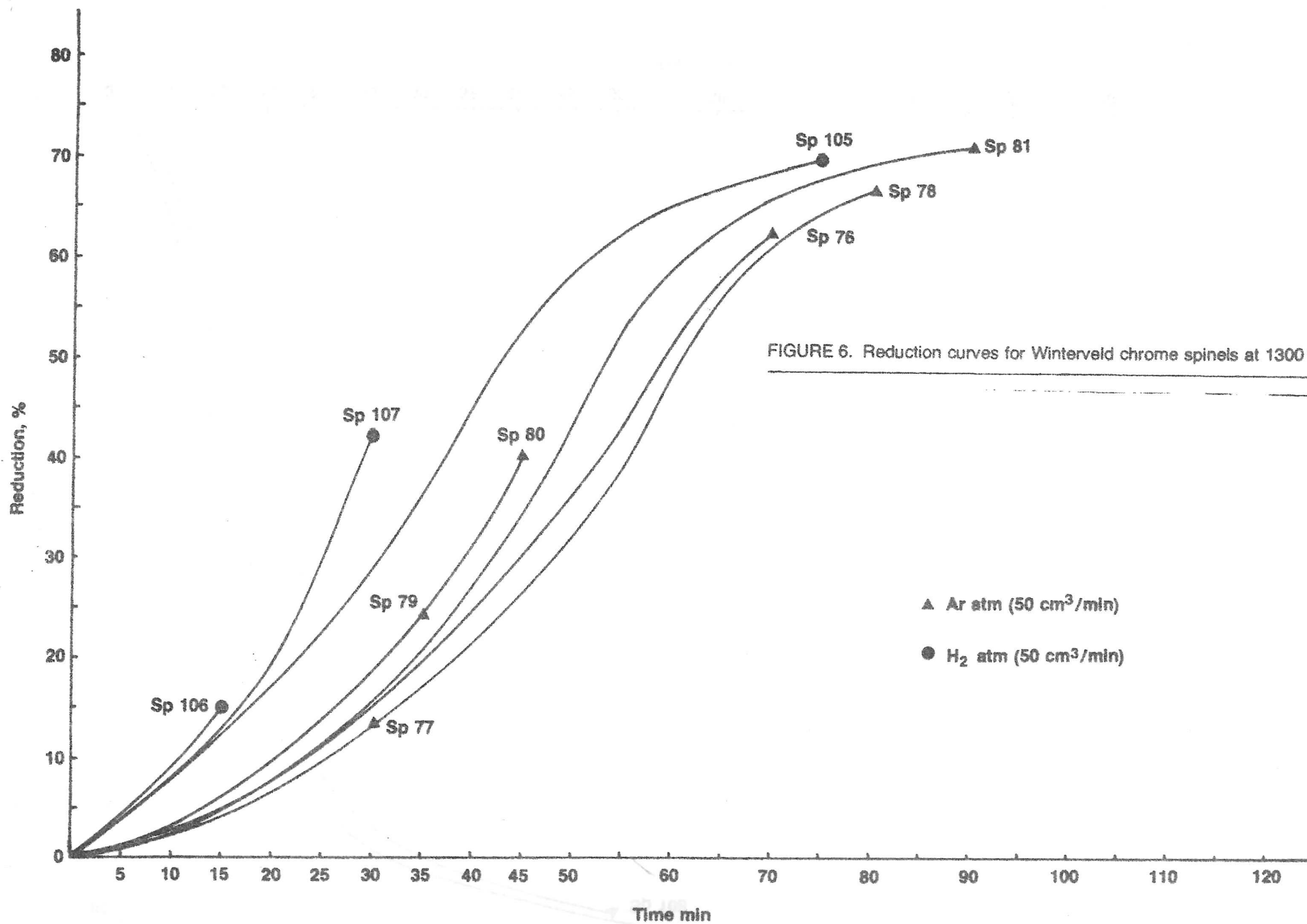


FIGURE 6. Reduction curves for Winterville chrome spinels at 1300°C

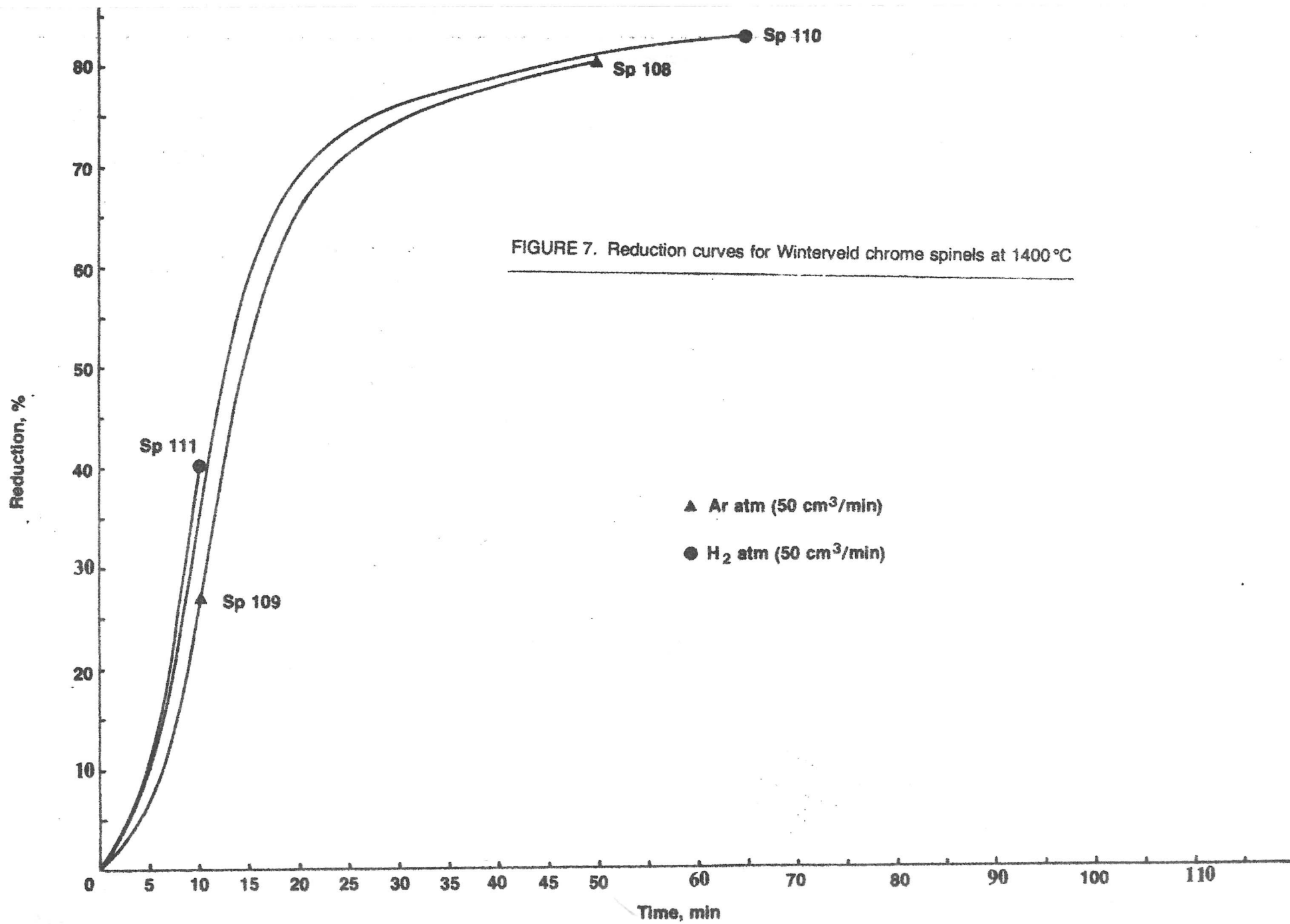
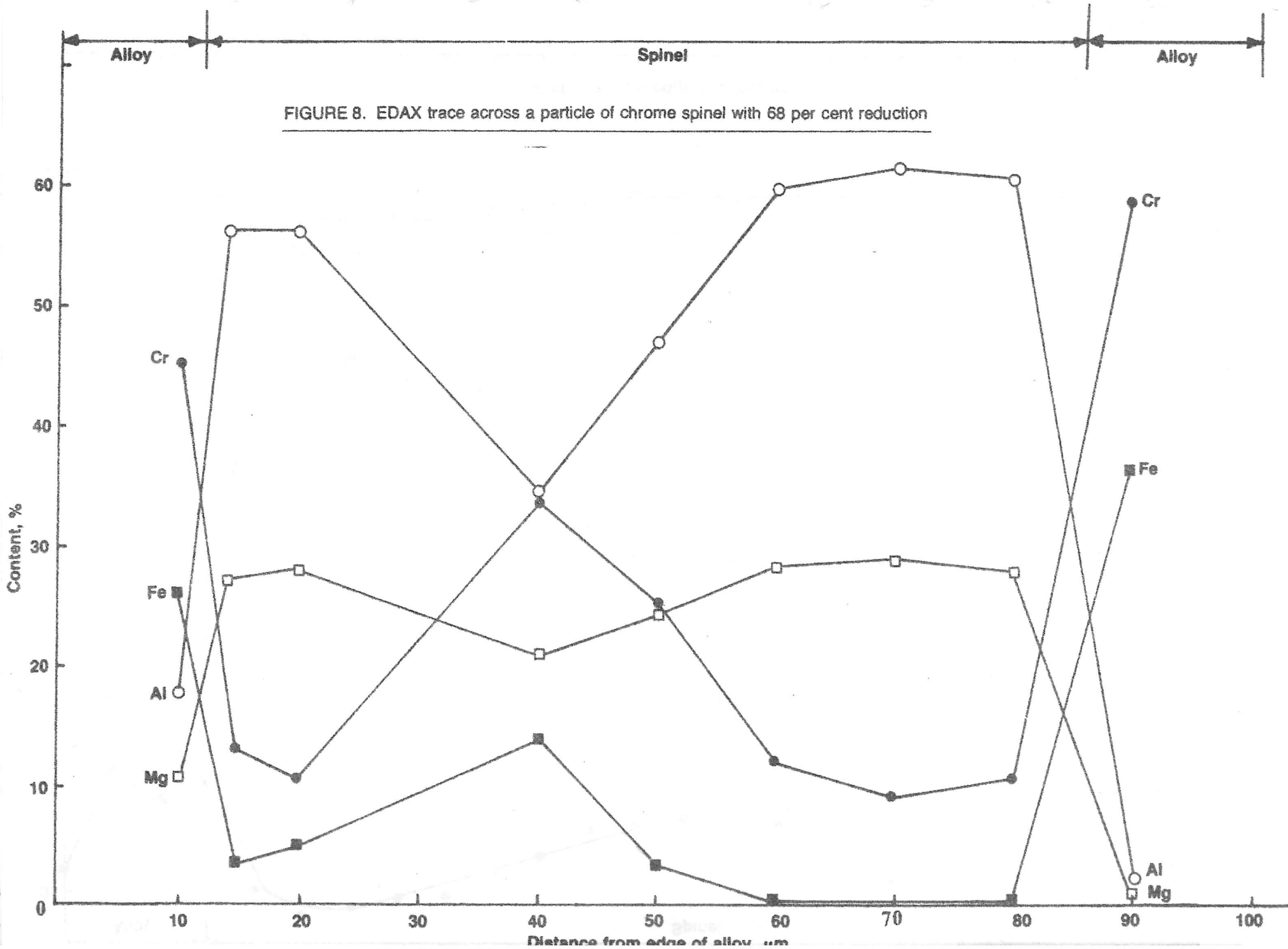


FIGURE 7. Reduction curves for Winterveld chrome spinels at 1400 °C



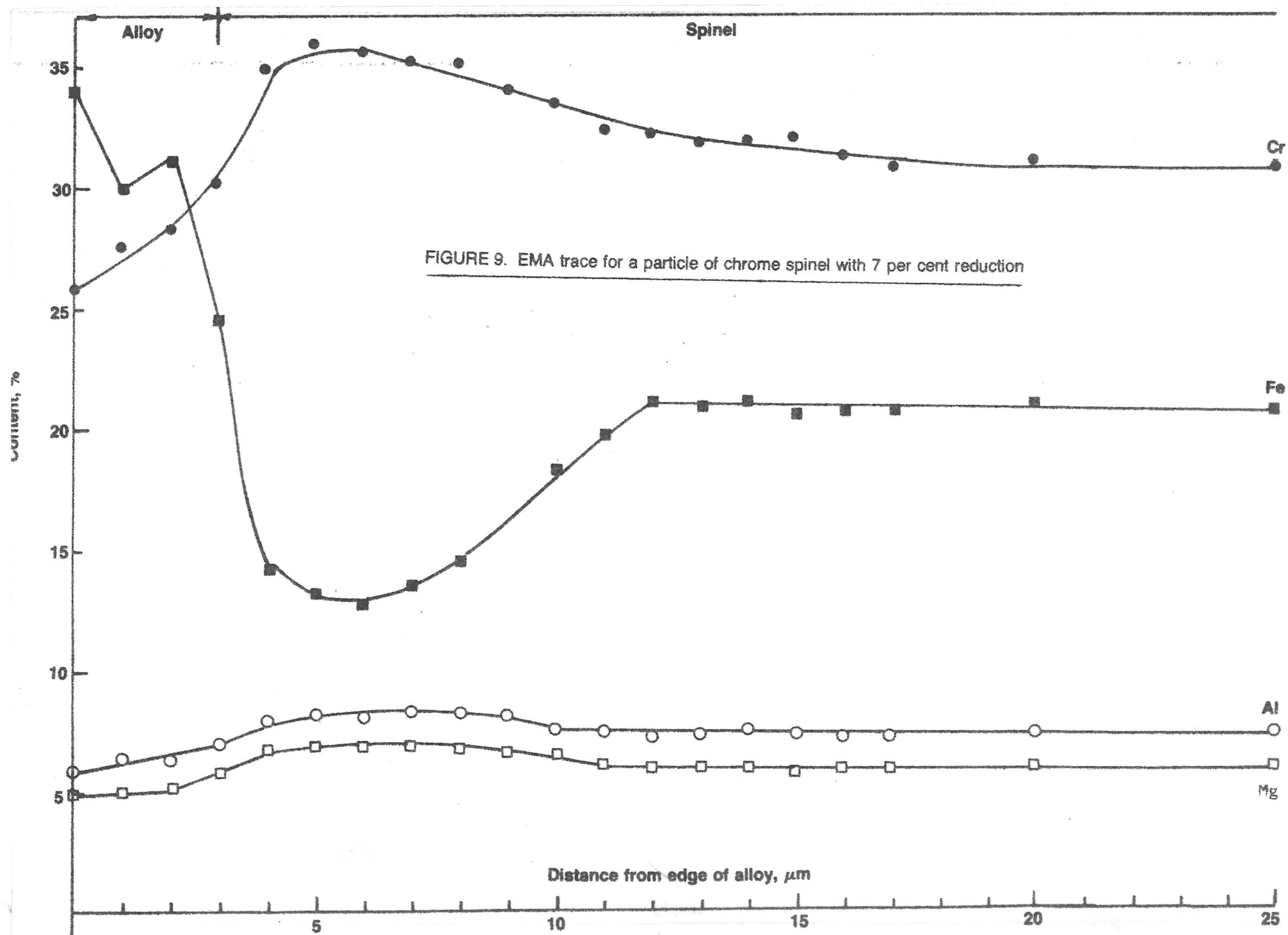


FIGURE 9. EMA trace for a particle of chrome spinel with 7 per cent reduction

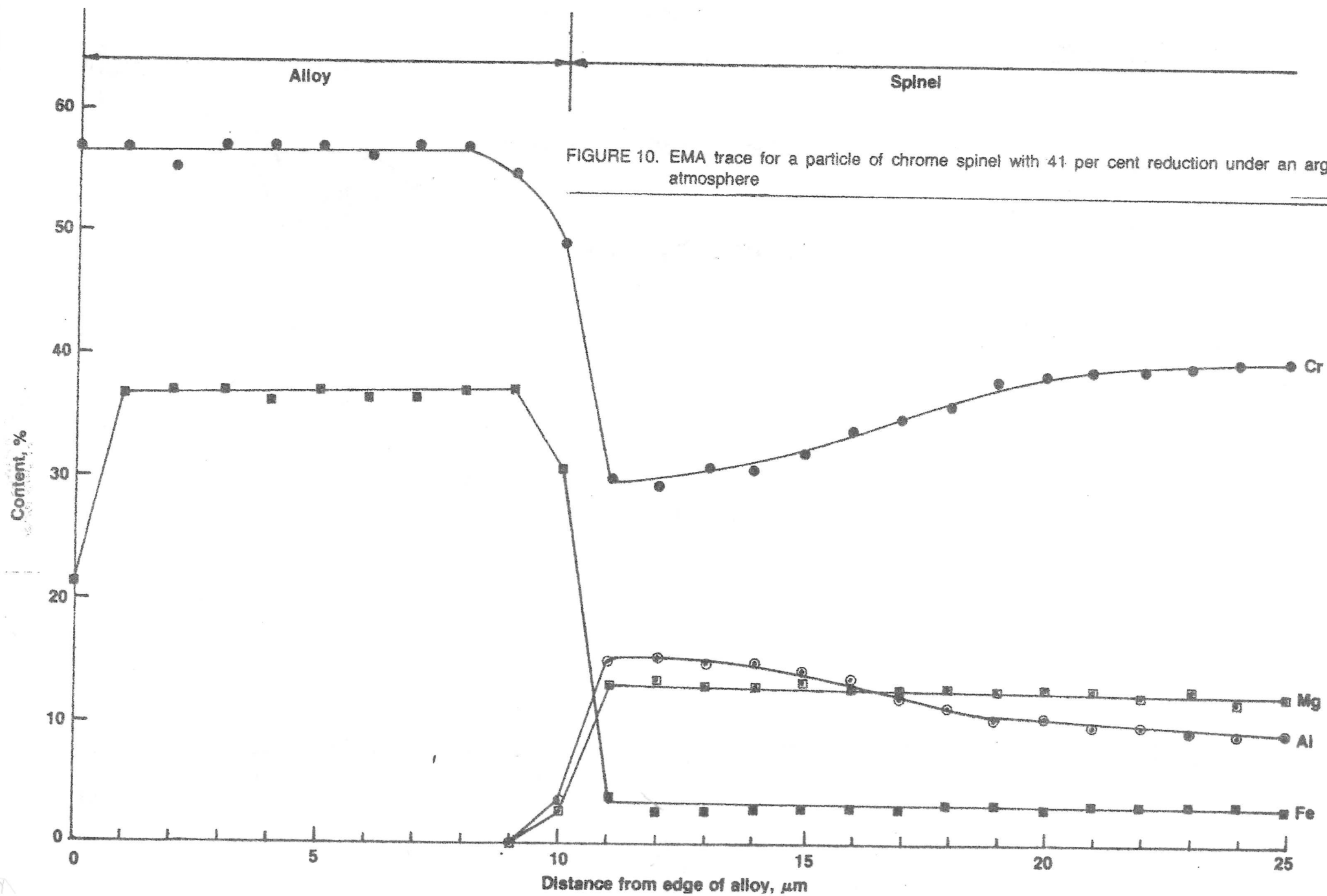
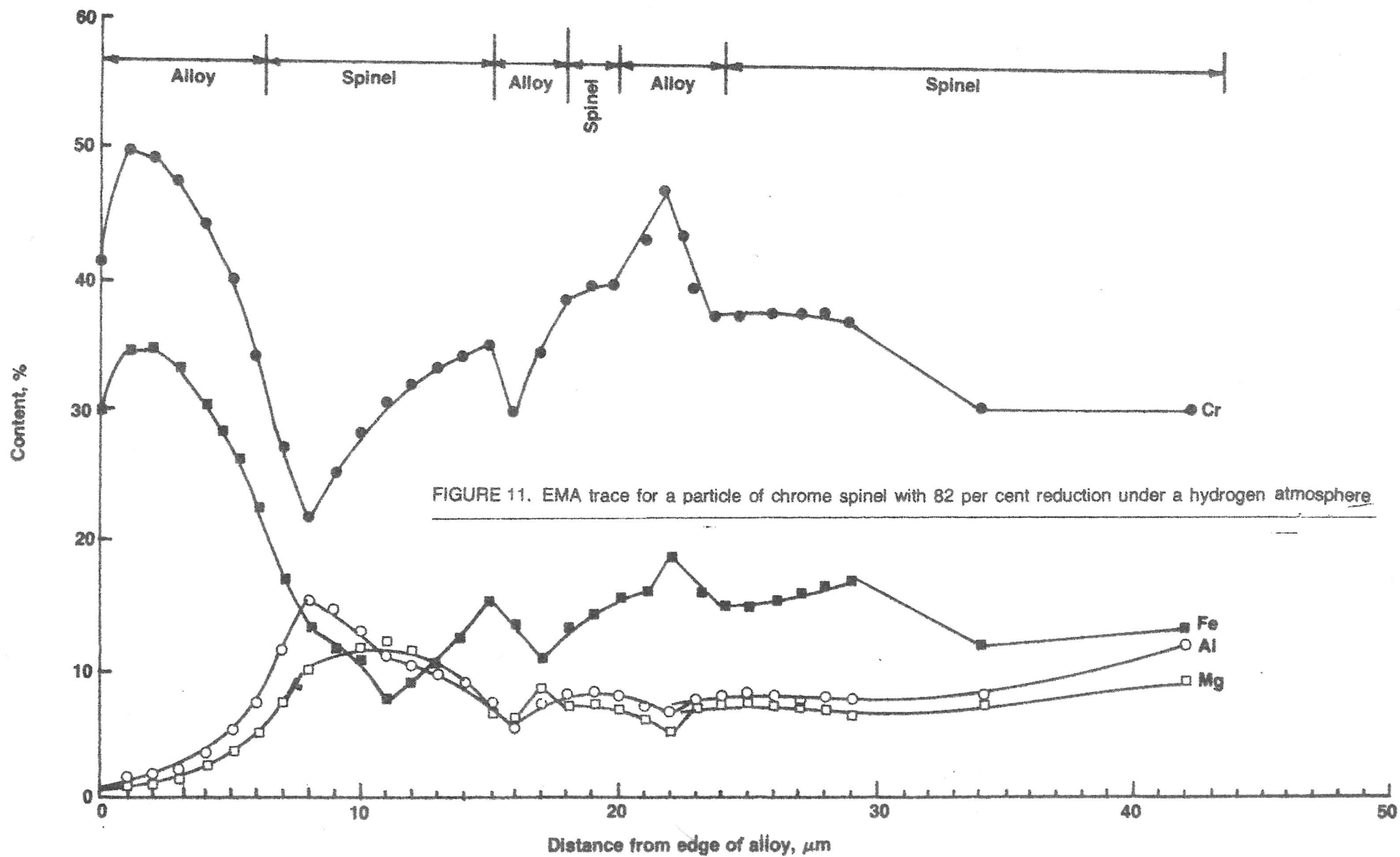
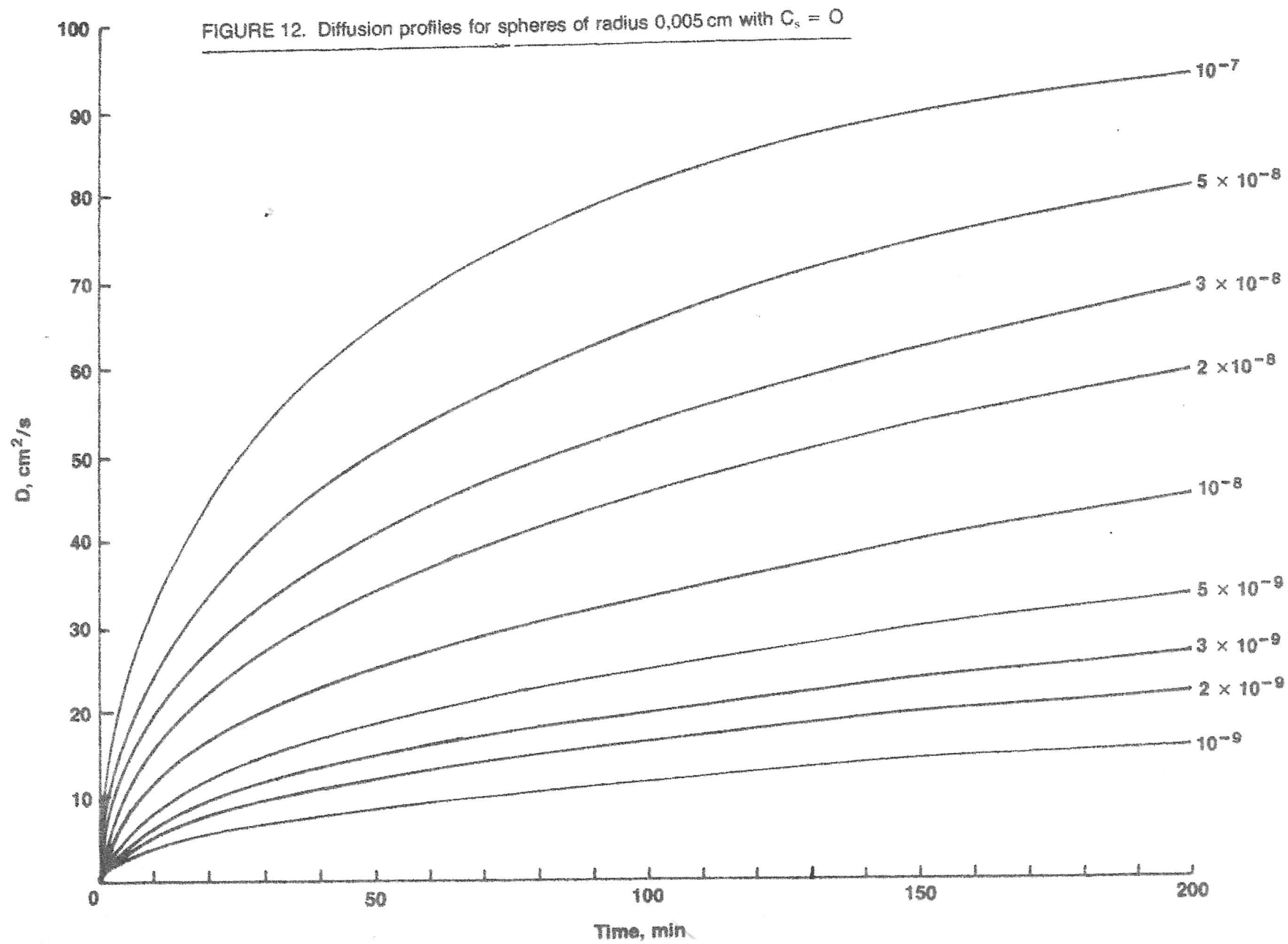
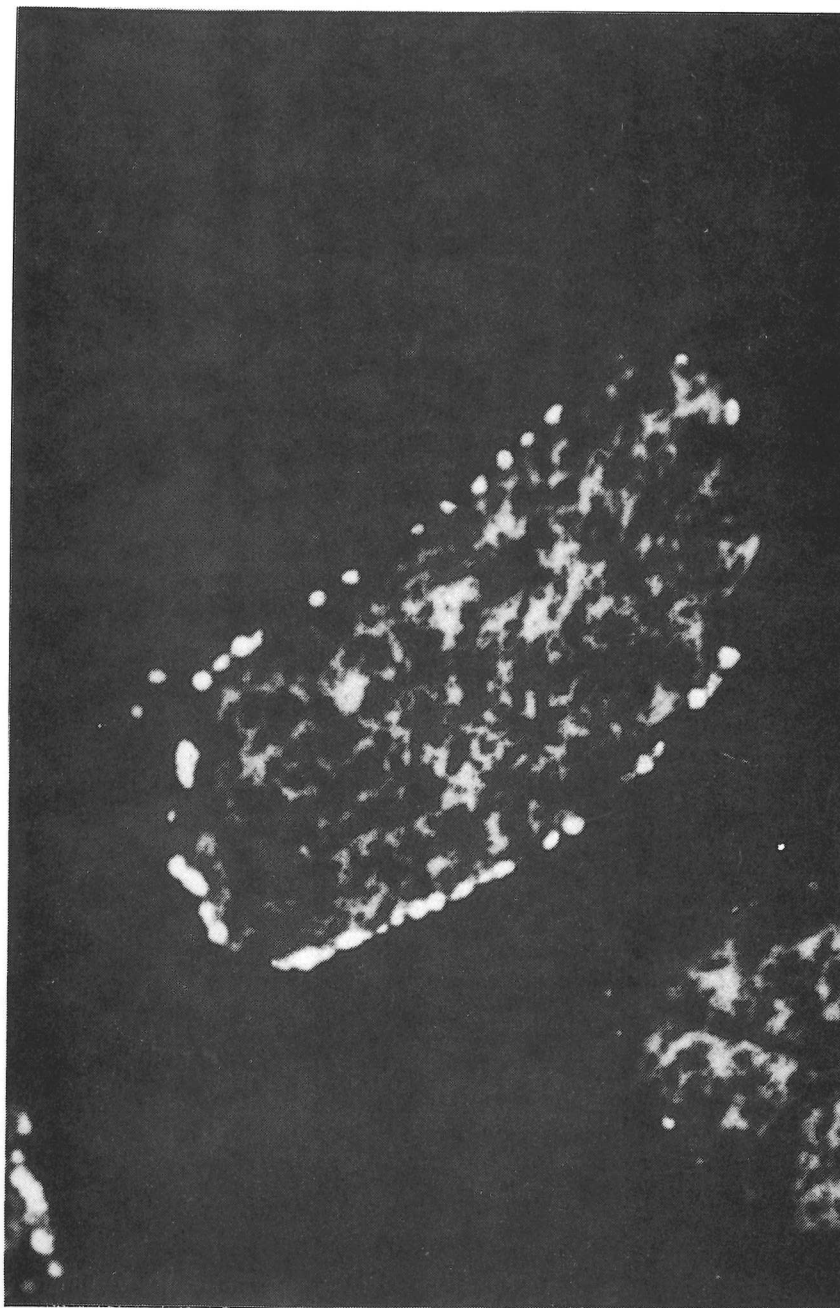


FIGURE 10. EMA trace for a particle of chrome spinel with 41 per cent reduction under an argon atmosphere

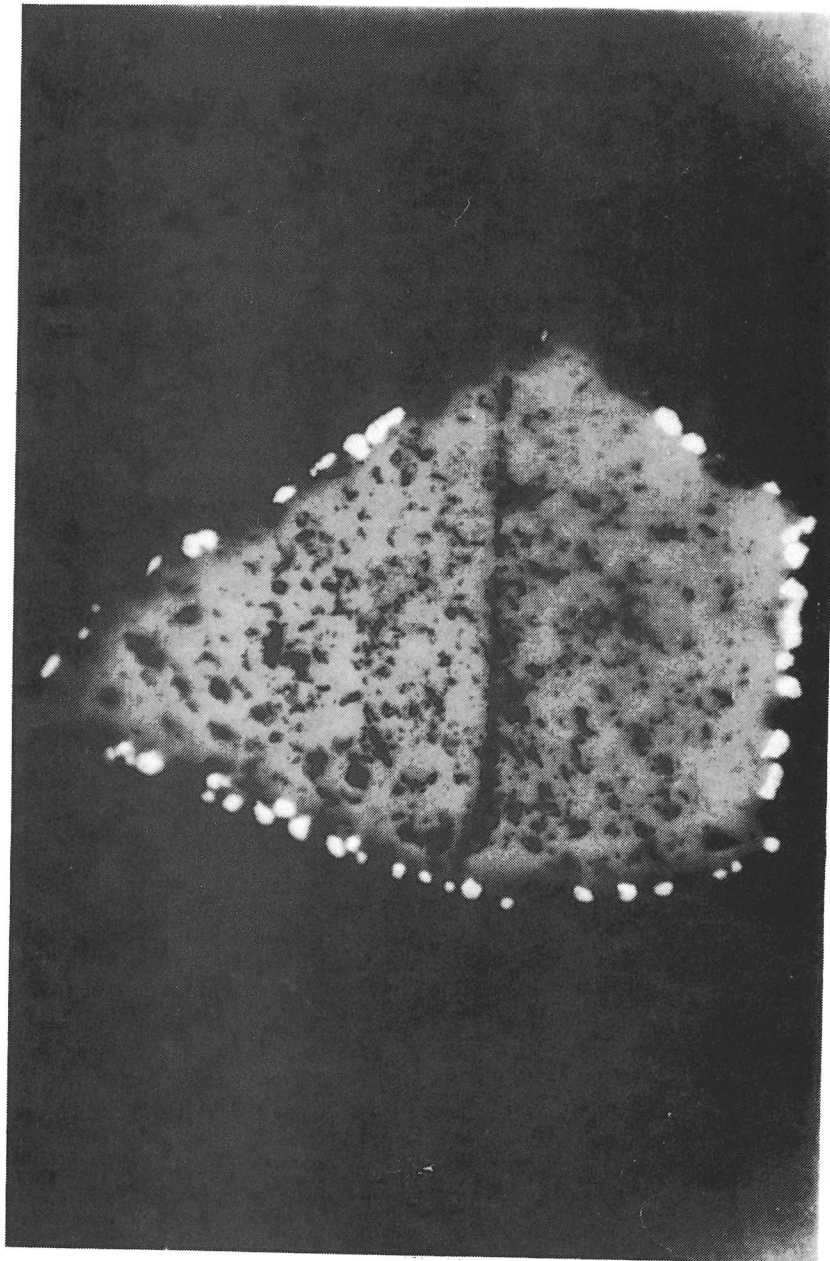






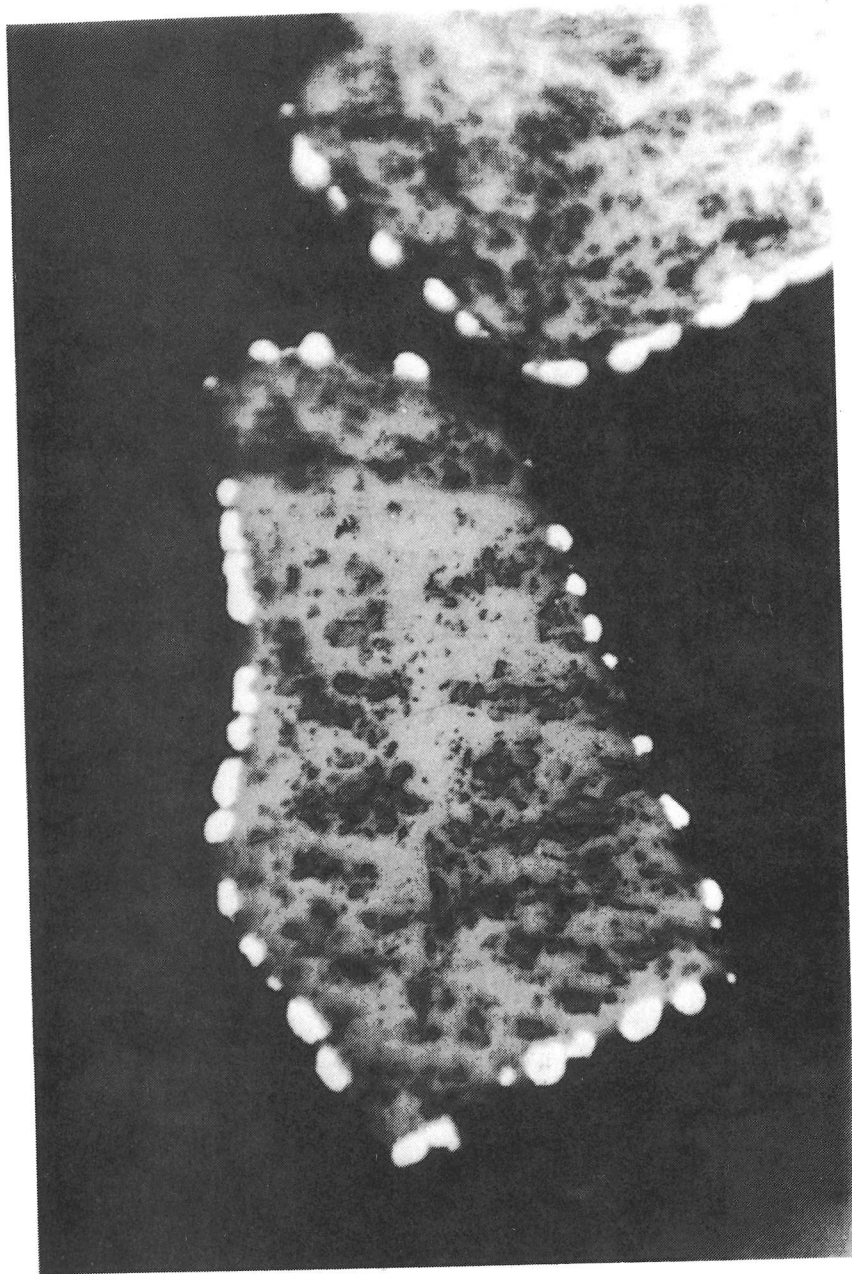
100 μm

PLATE I



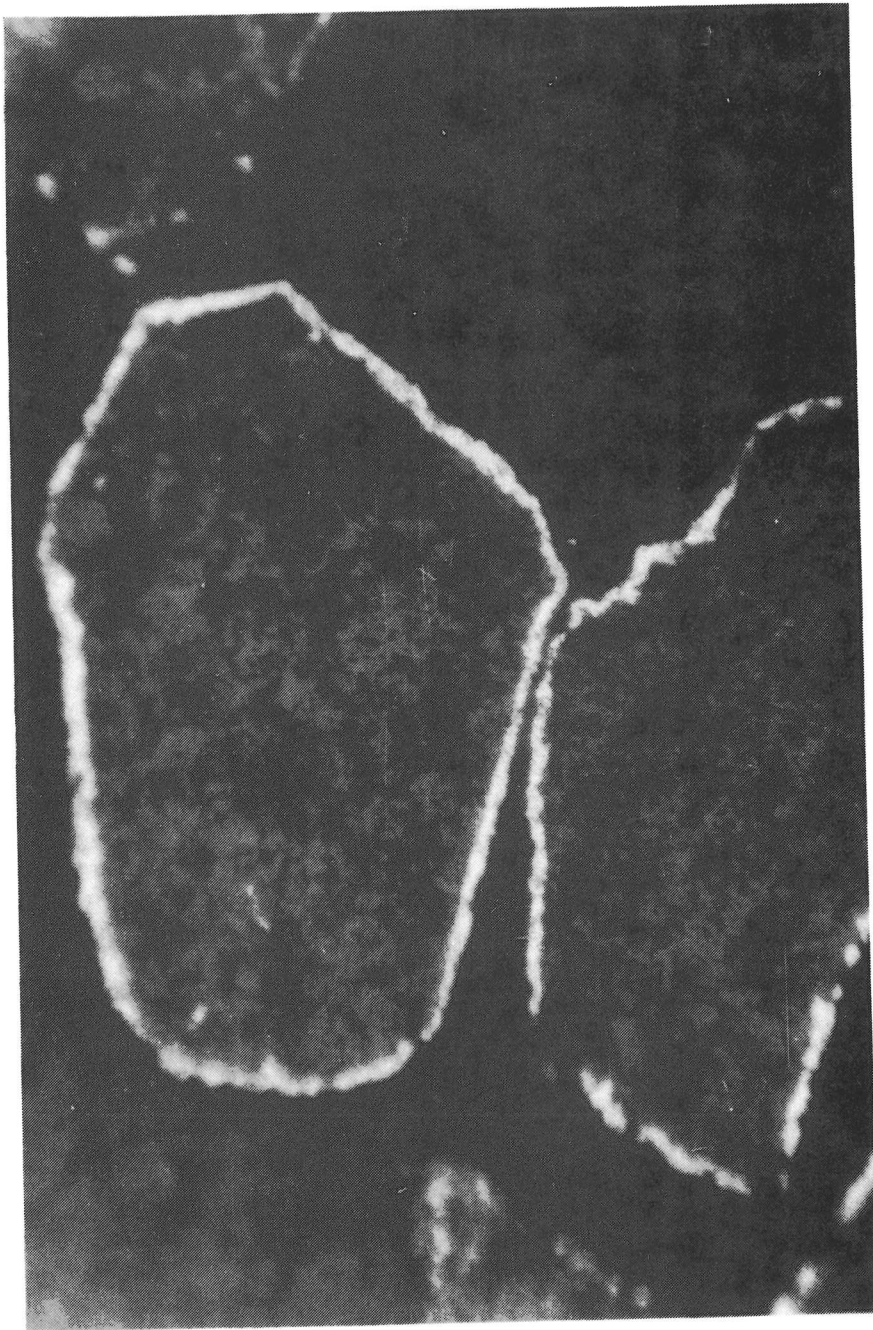
100 μm

PLATE II



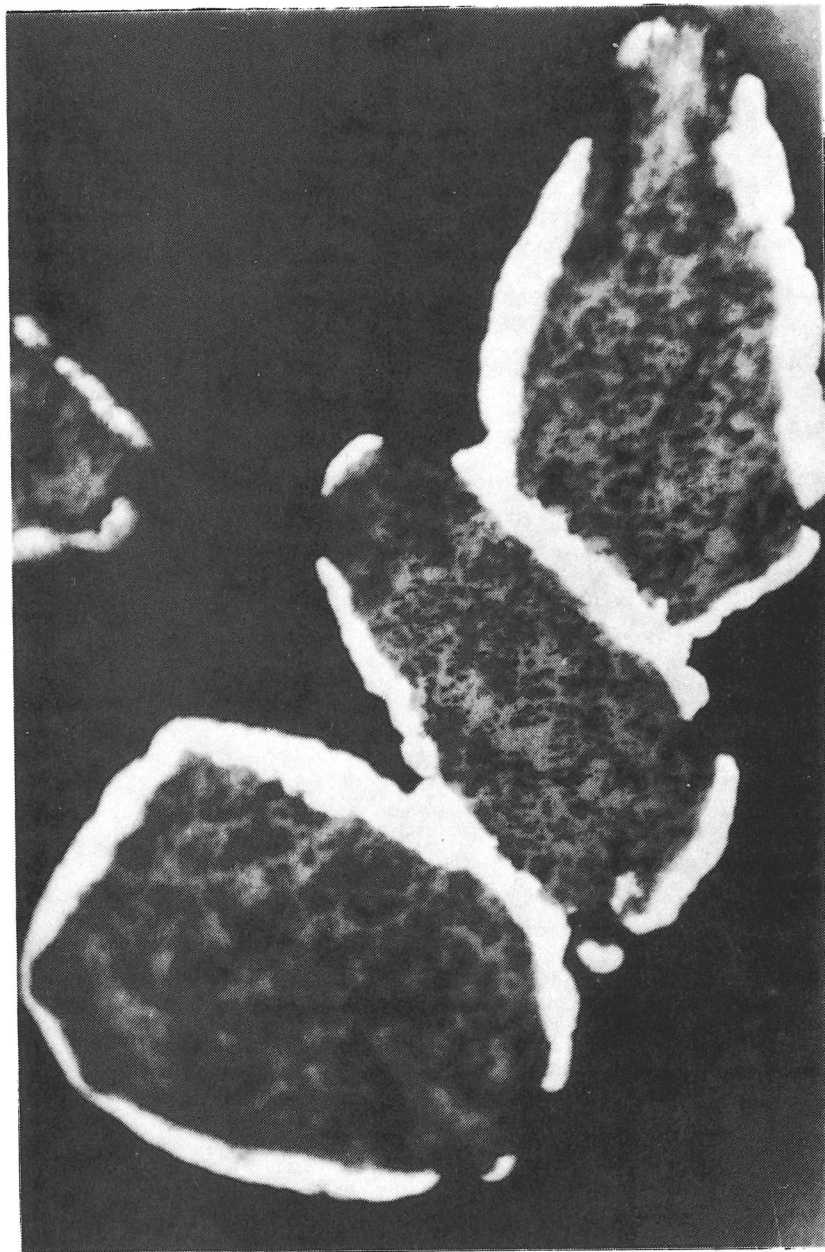
100 μm

PLATE III



100 μ m

PLATE IV



100 μm

PLATE V



100 μm

PLATE VI



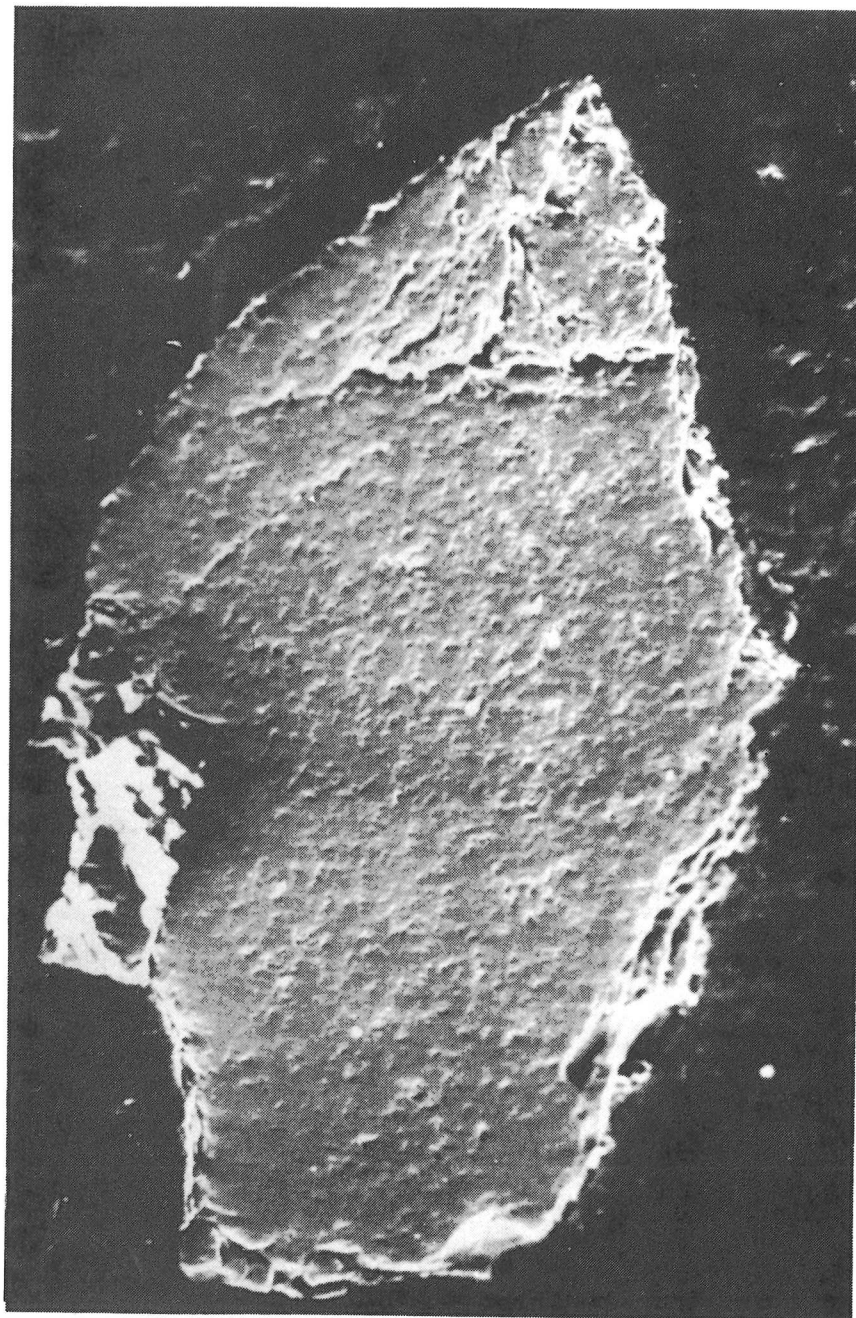
100 μm

PLATE VII



100 μm

PLATE VIII



100 μm

PLATE IX

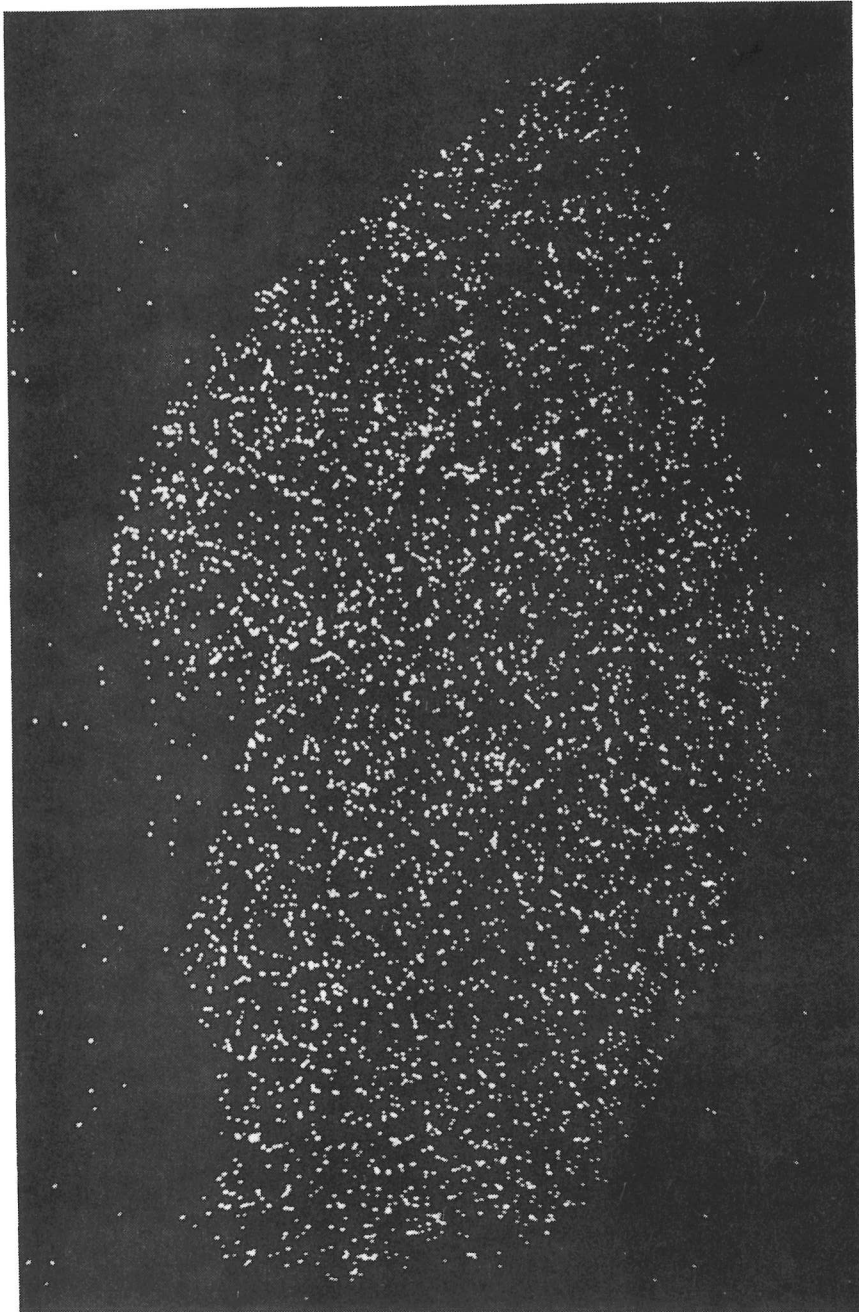


PLATE X

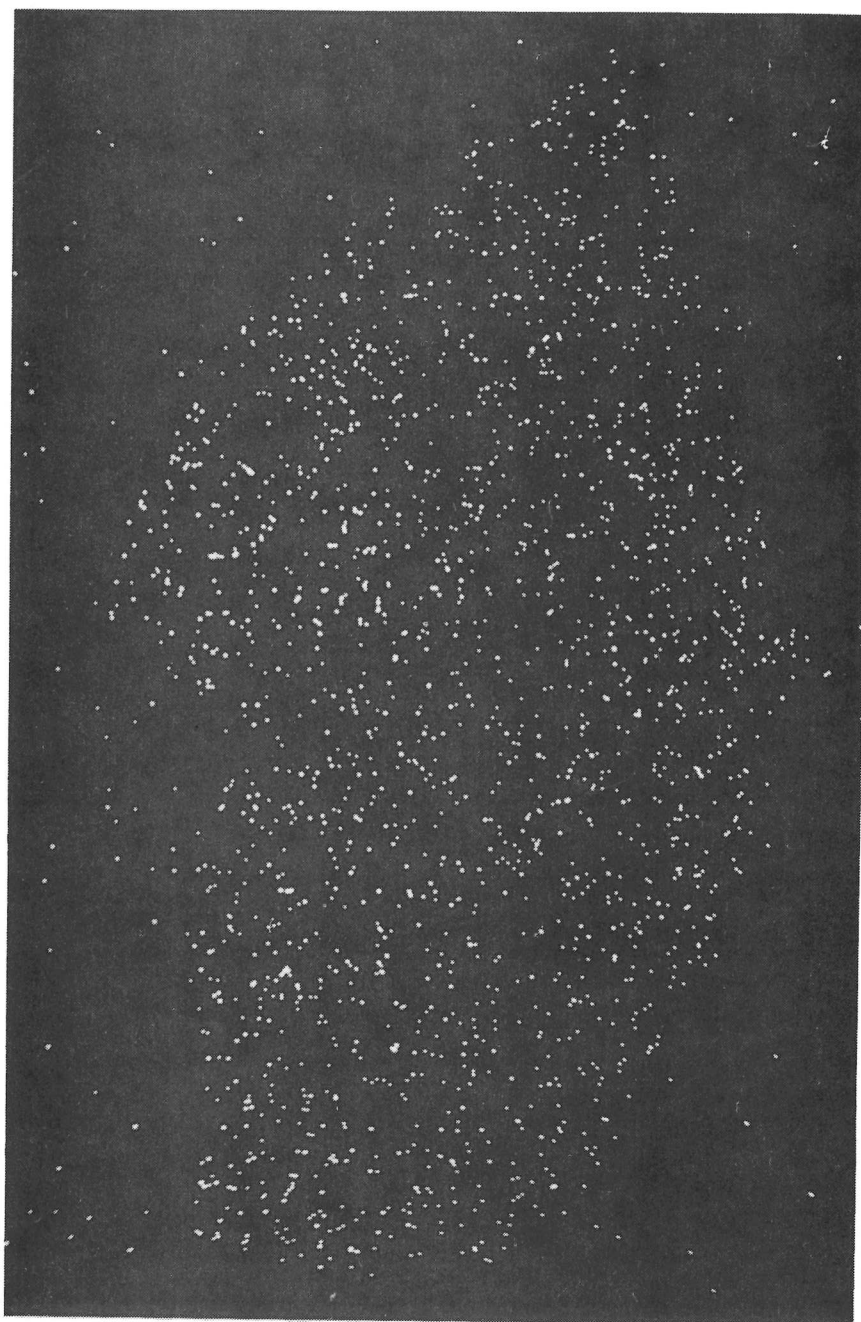


PLATE XI

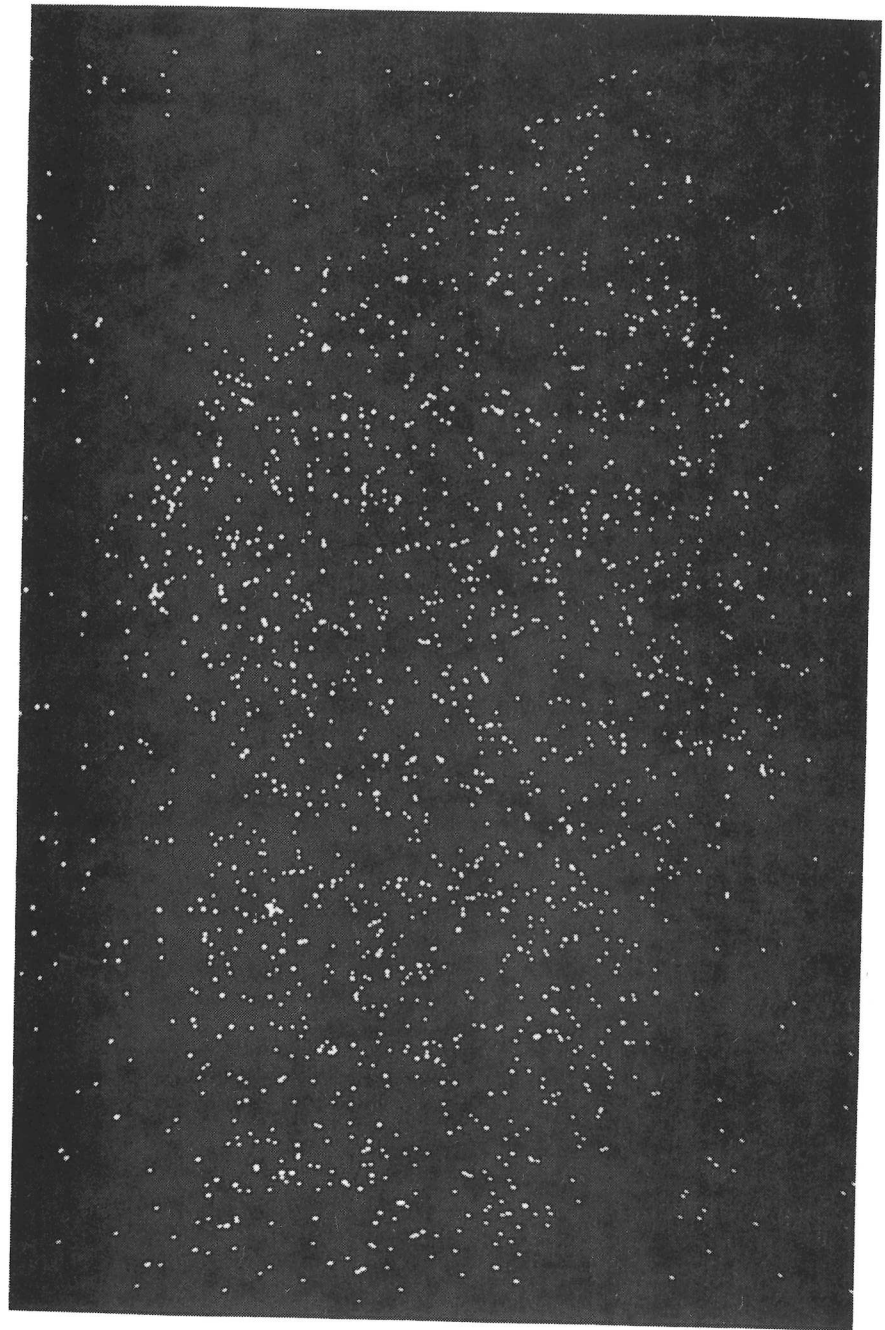


PLATE XII

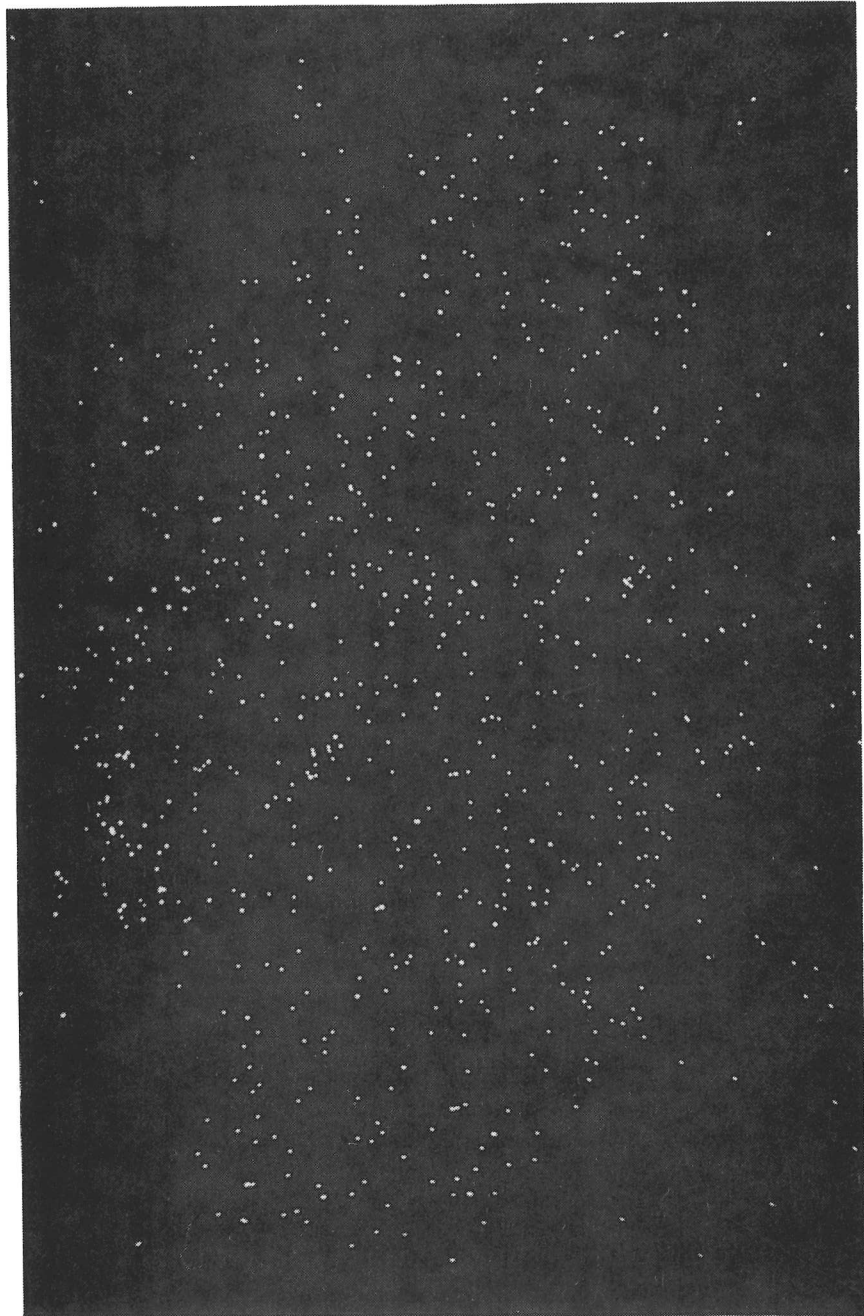


PLATE XIII

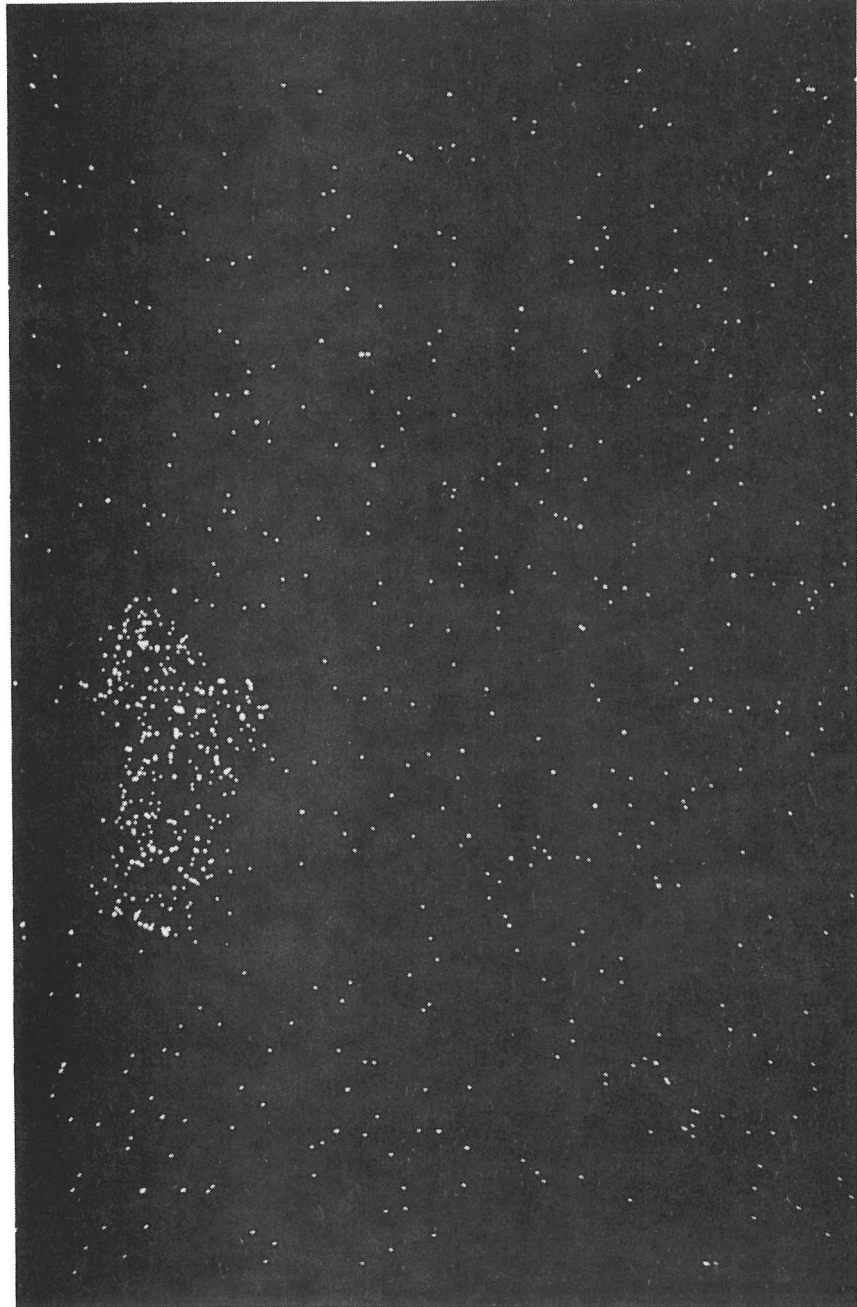
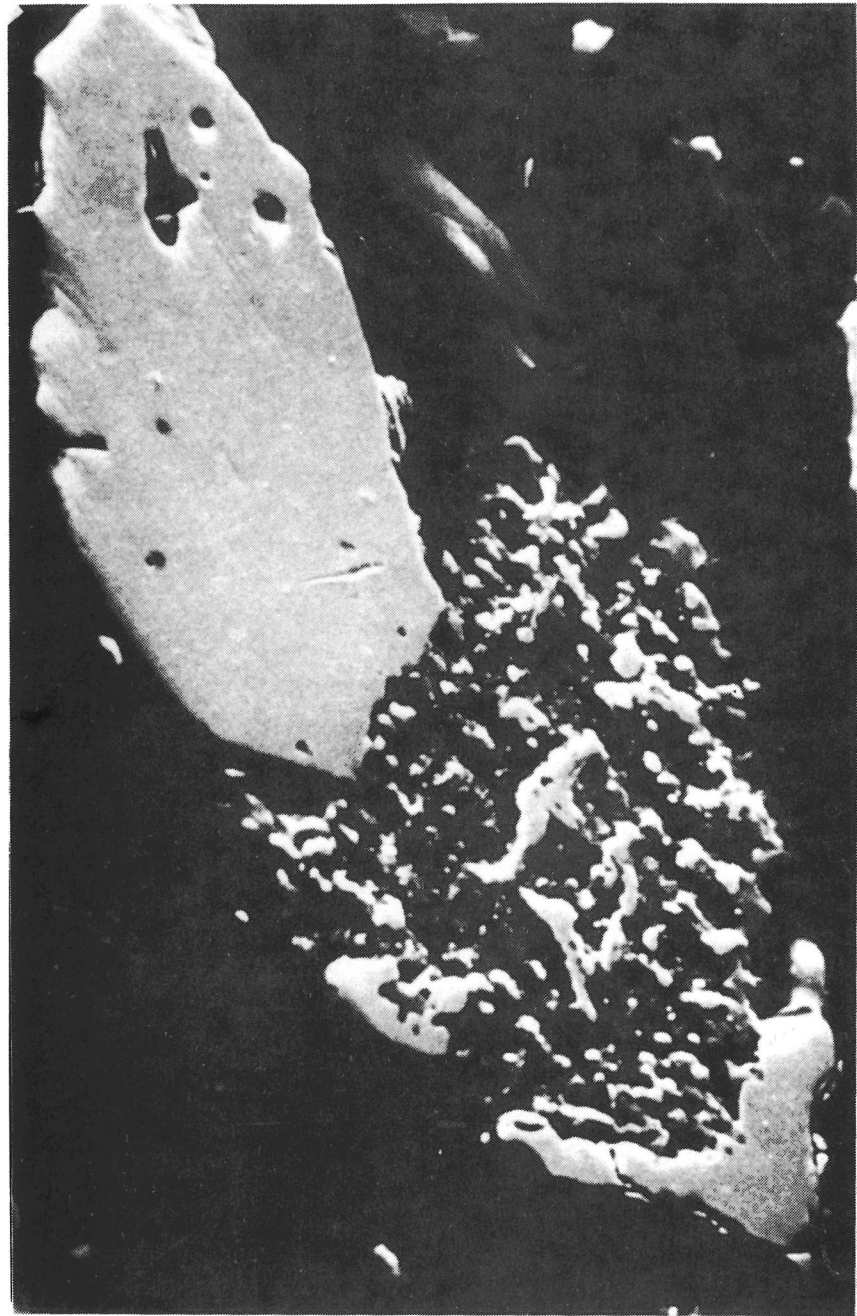


PLATE XIV



100 μm

PLATE XV

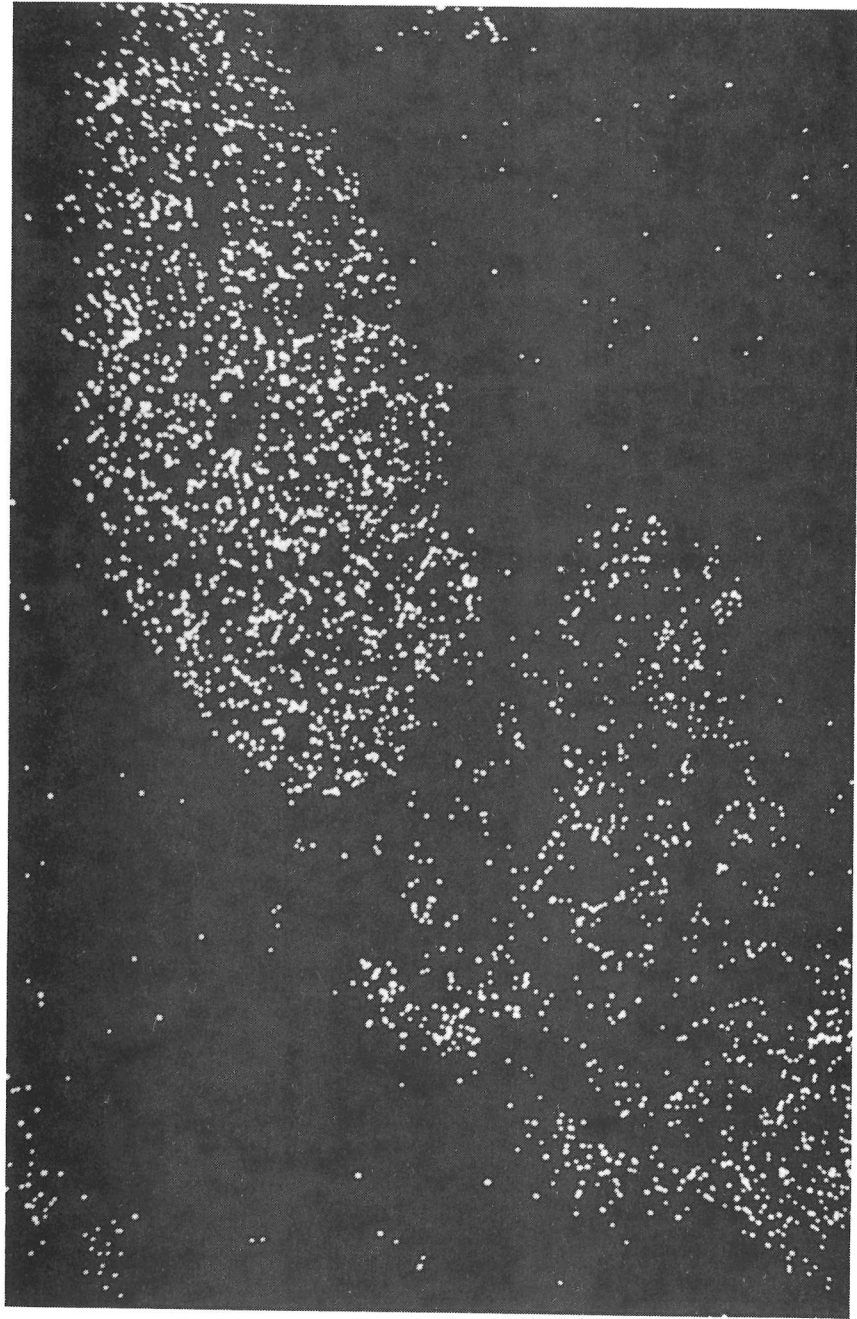


PLATE XVI

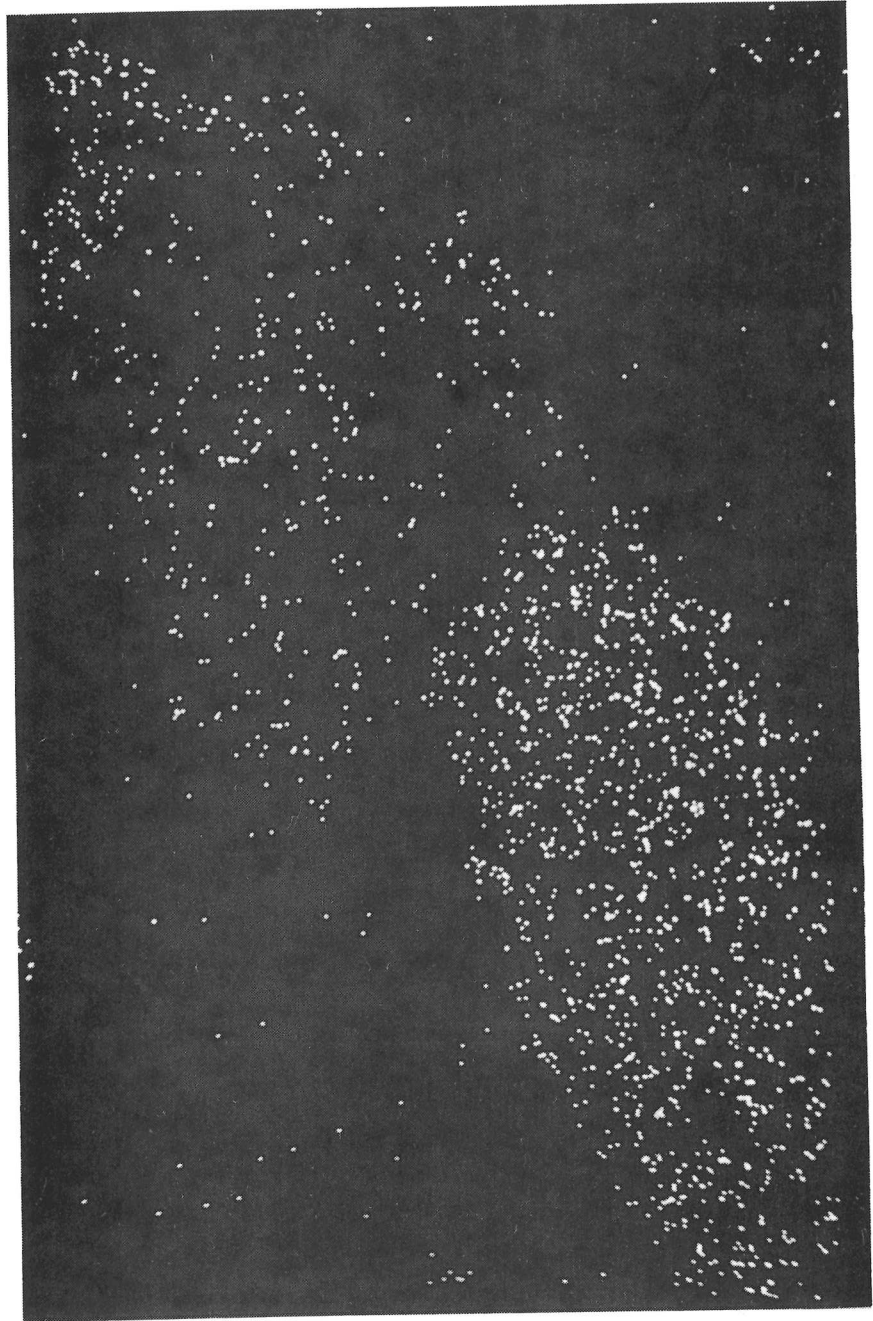


PLATE XVII

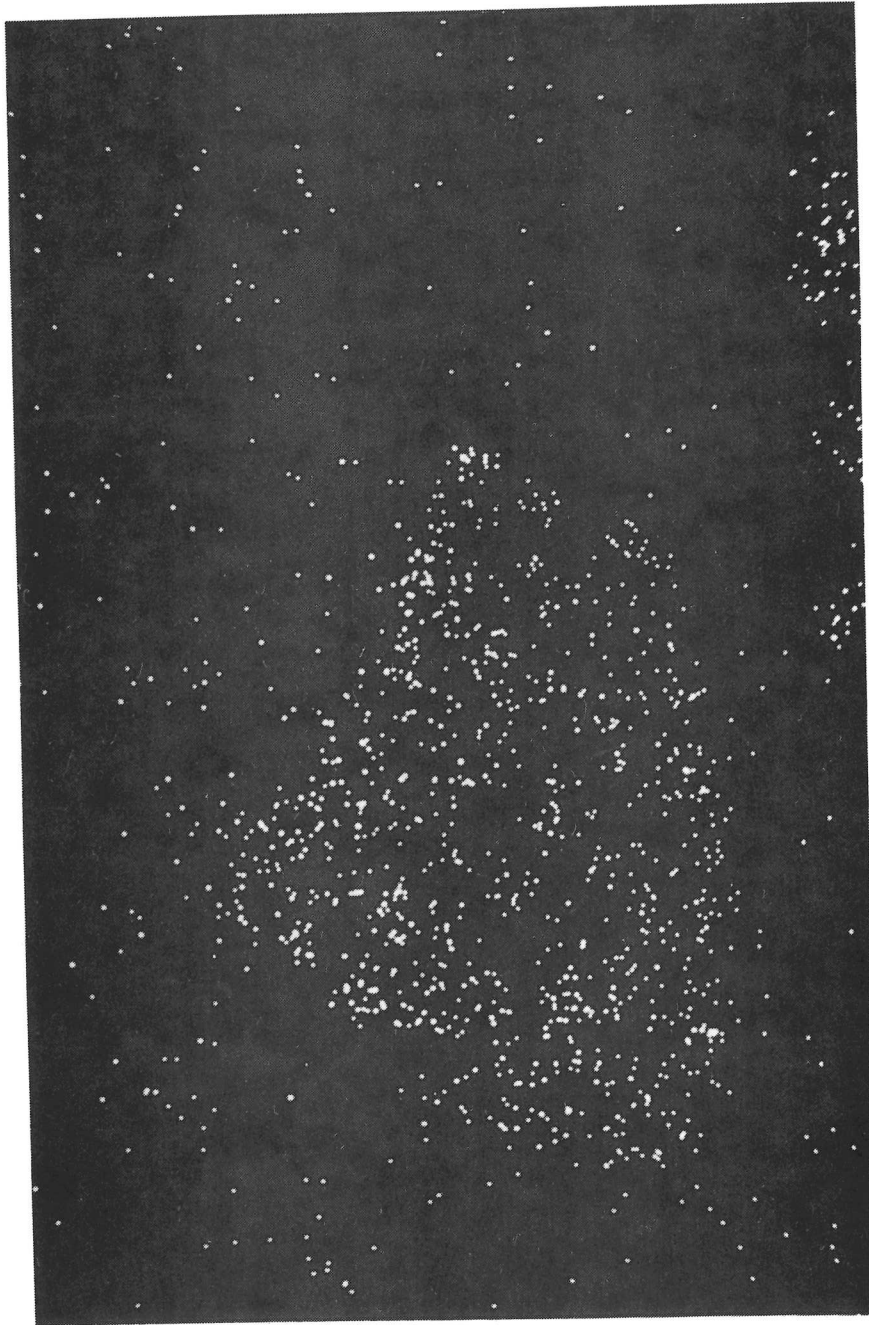


PLATE XVIII

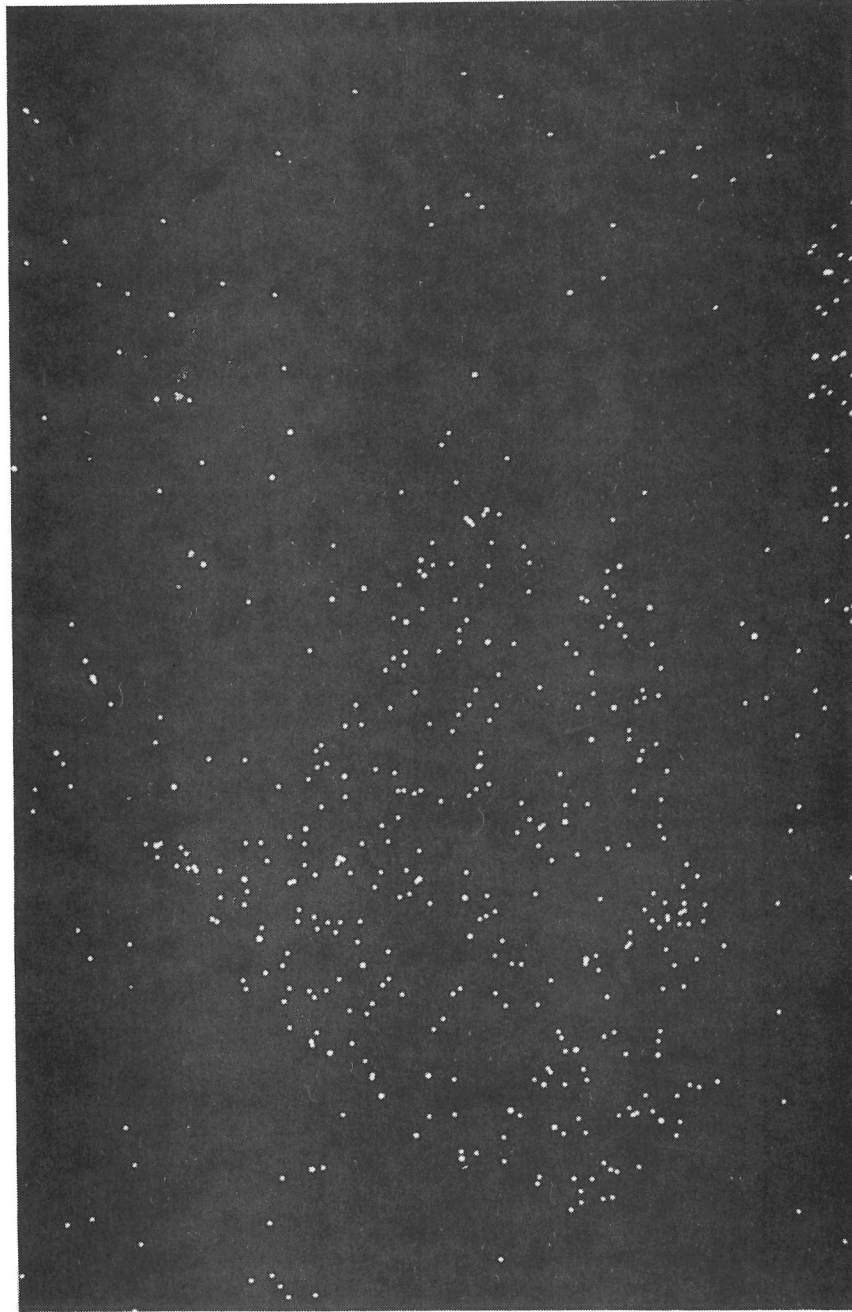
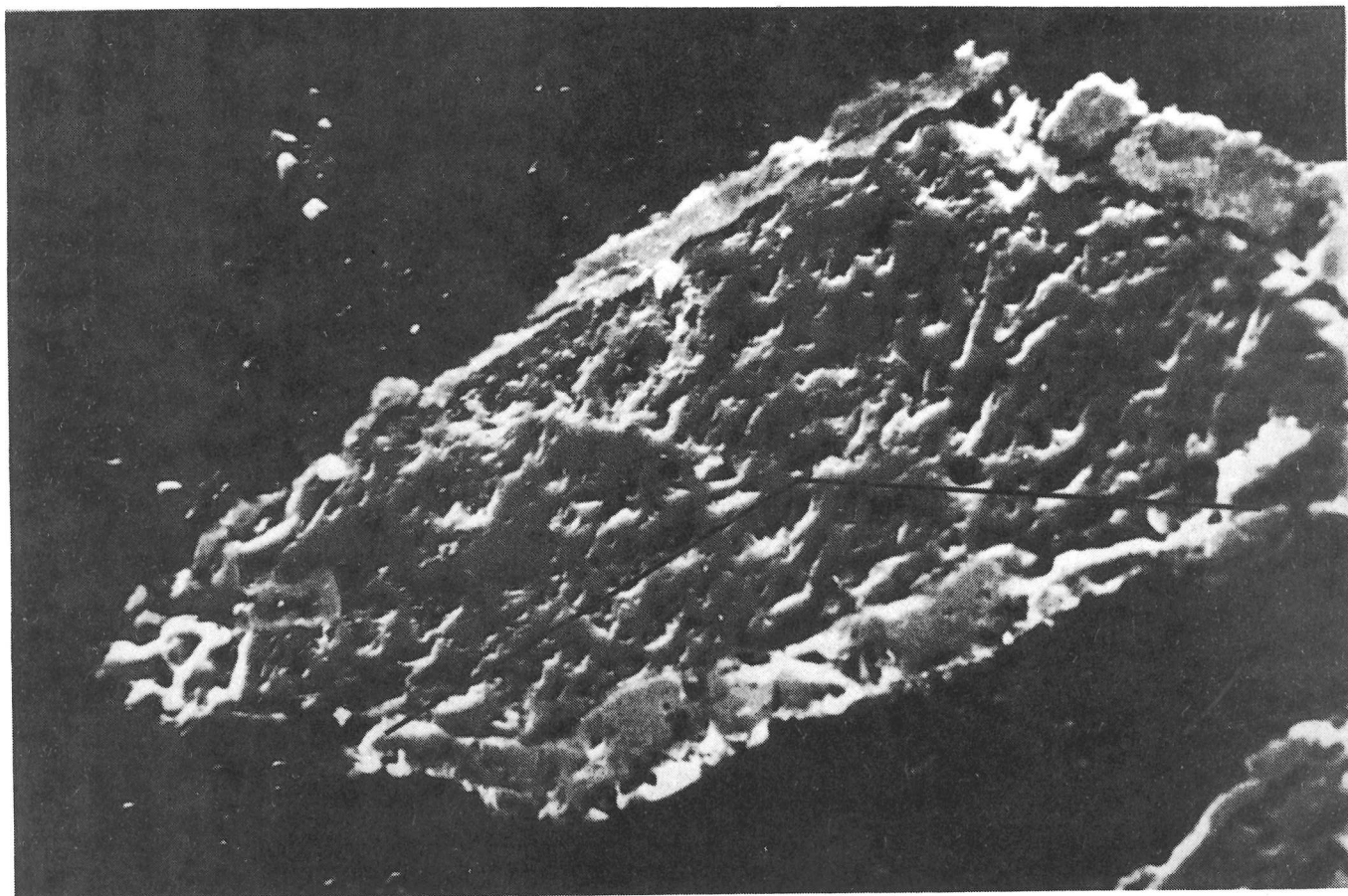


PLATE XIX



50 μm

PLATE XX

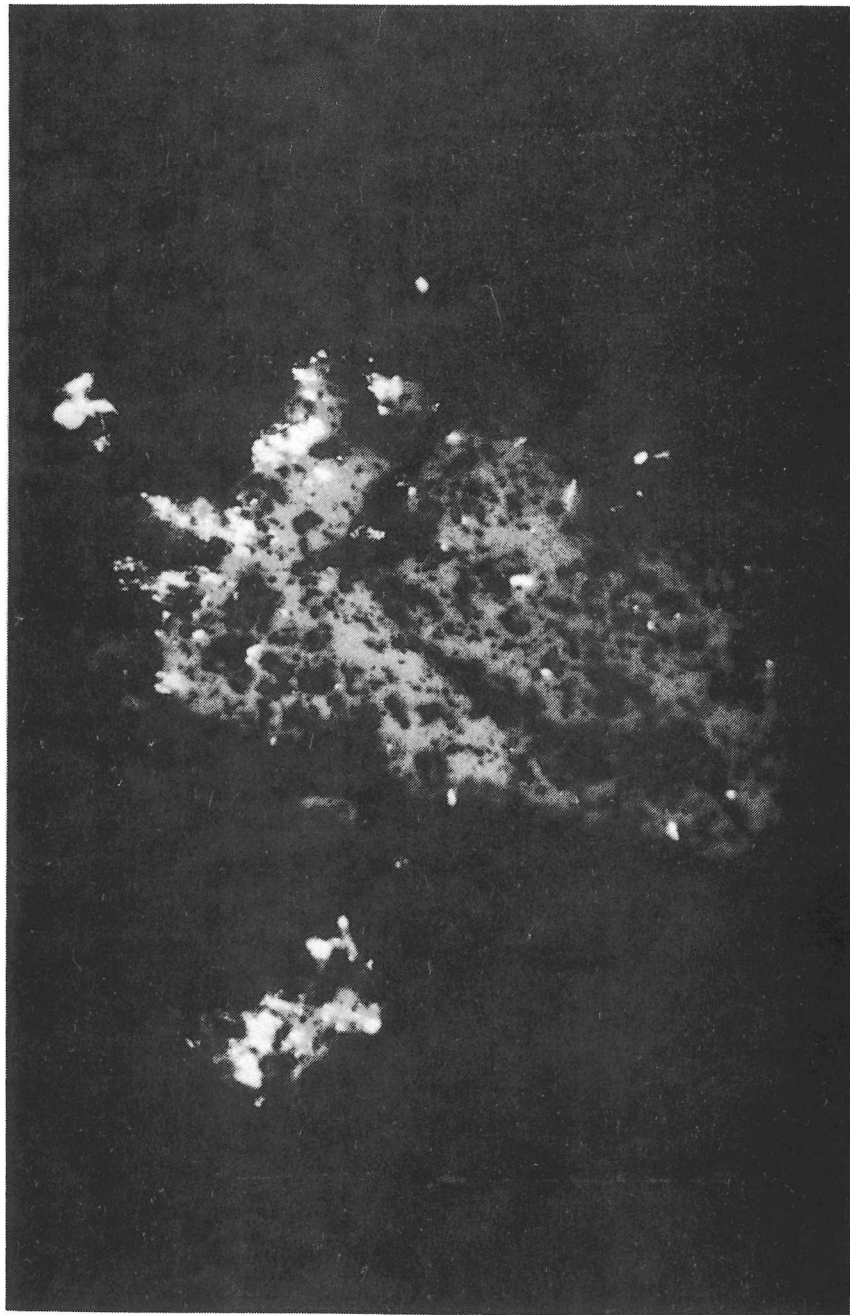
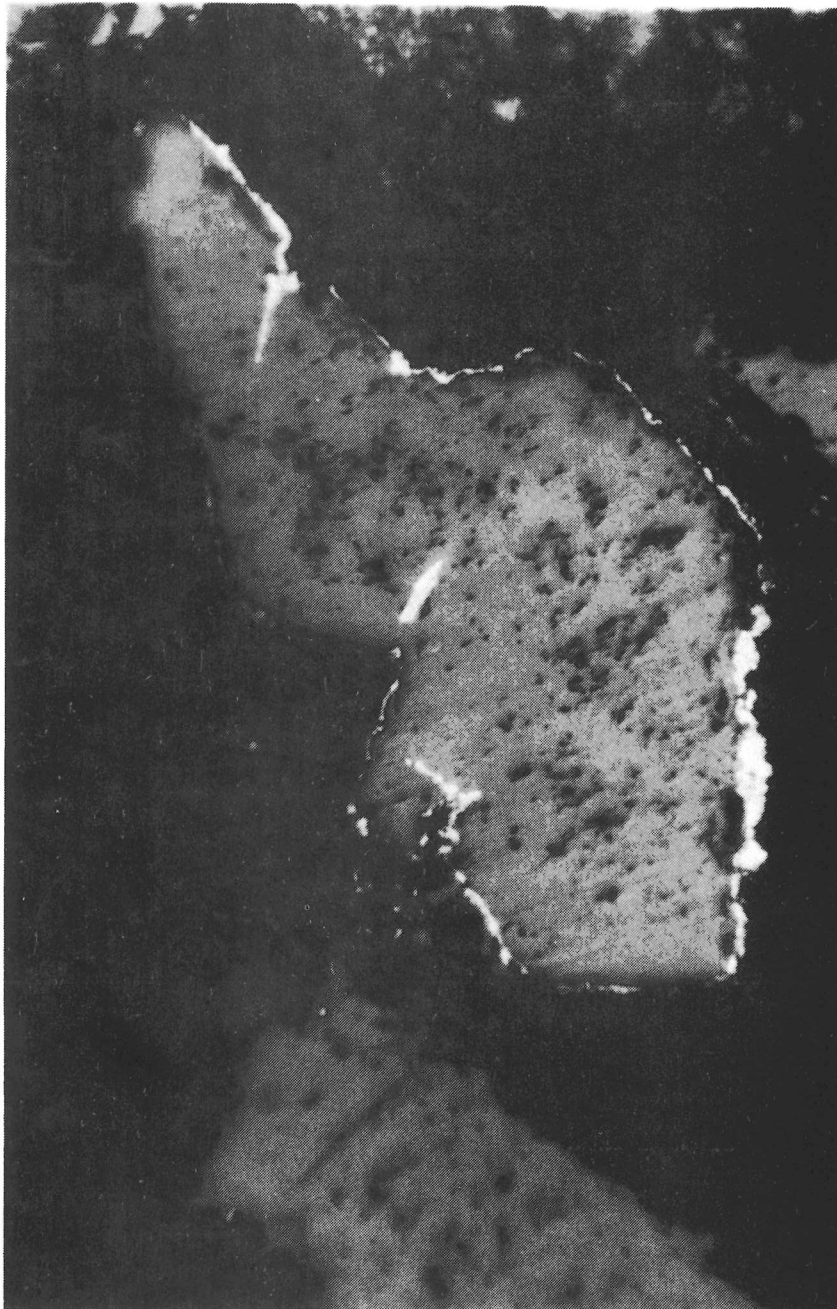
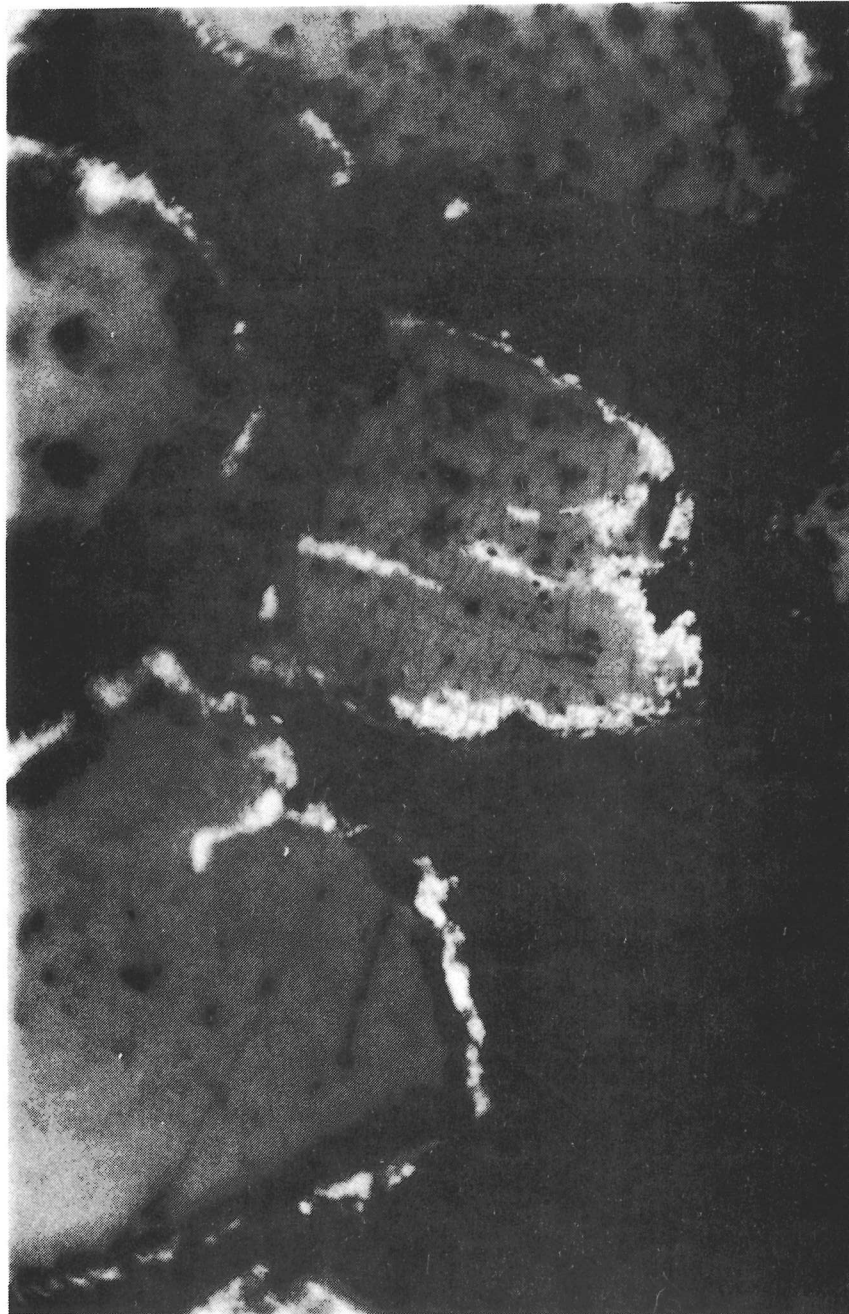


PLATE XXI



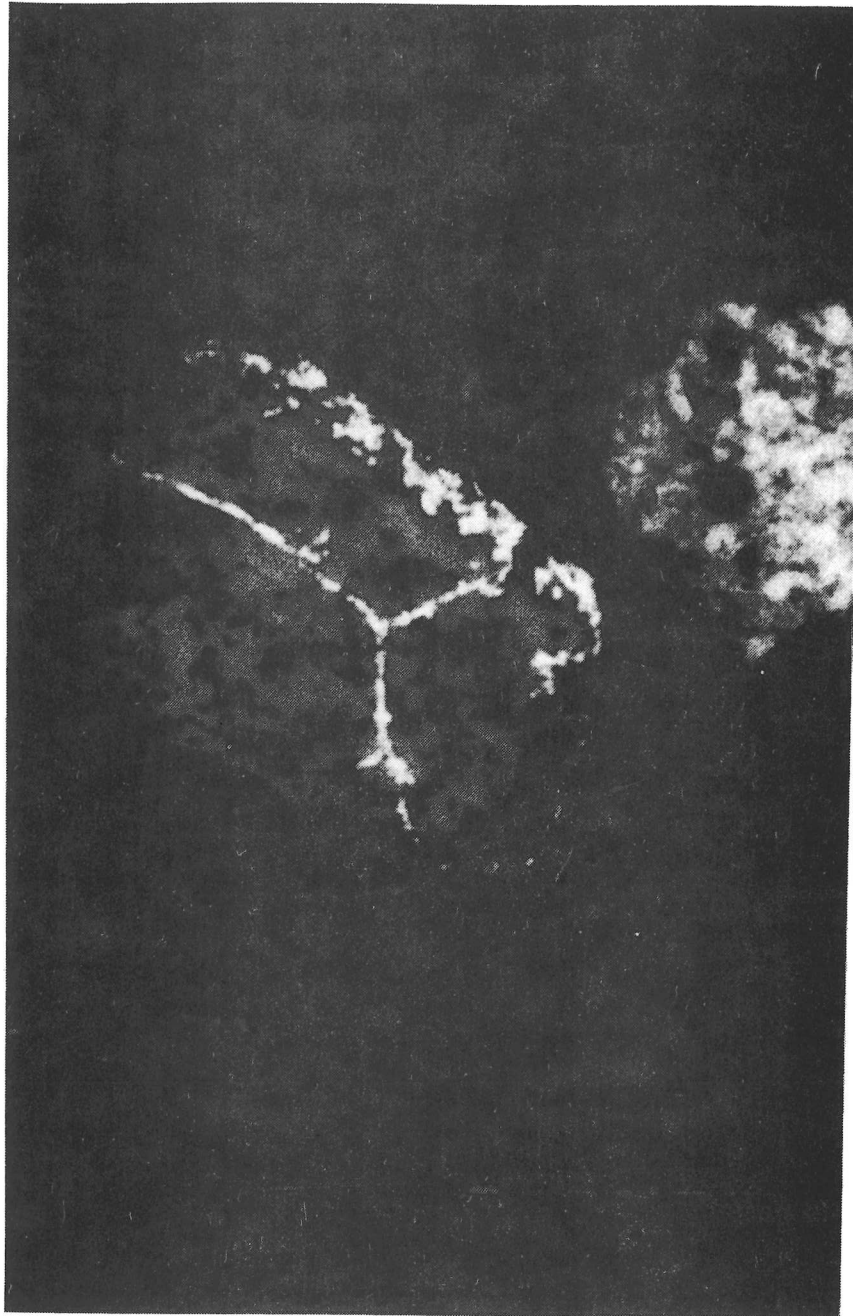
100 μm

PLATE XXII



100 μm

PLATE XXIII



100 μm

PLATE XXIV

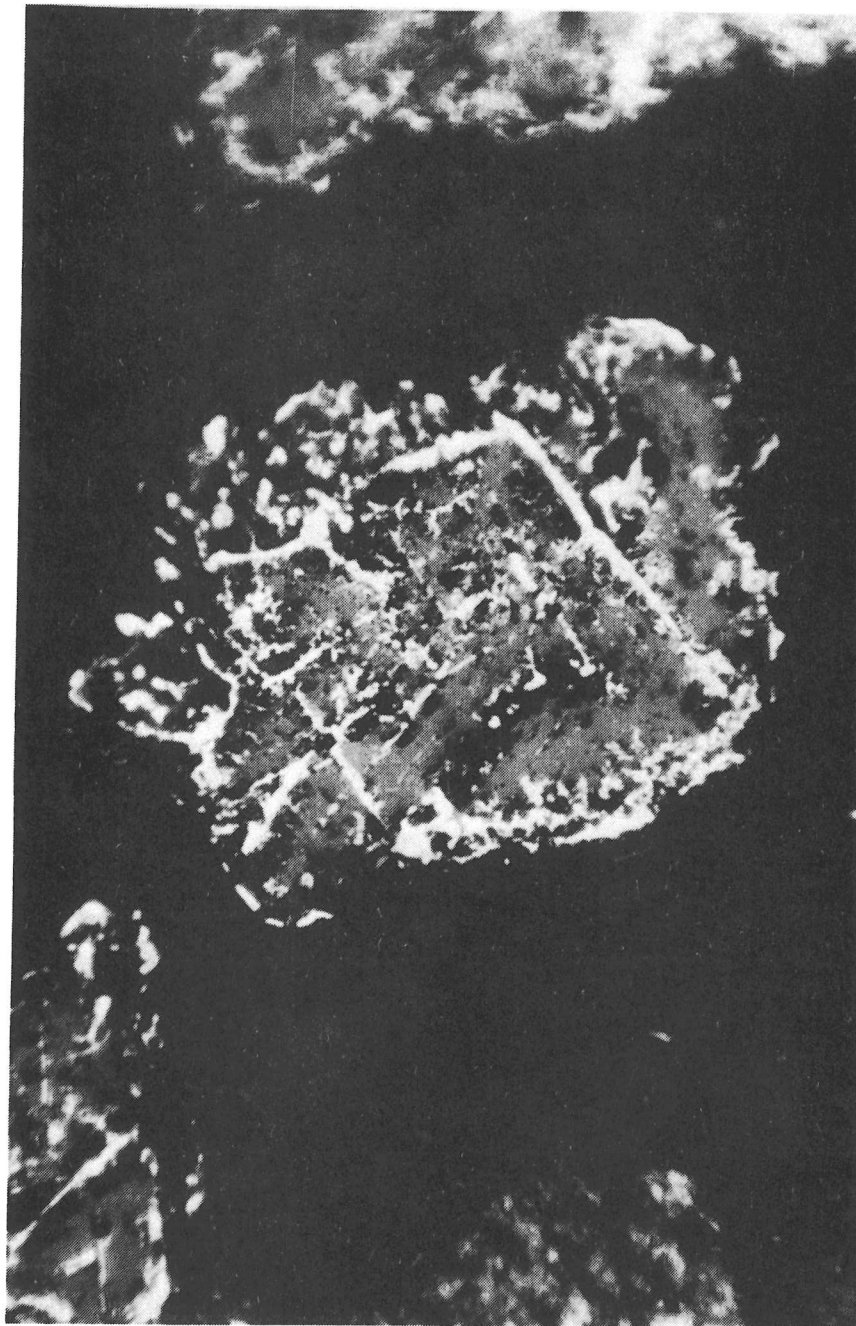
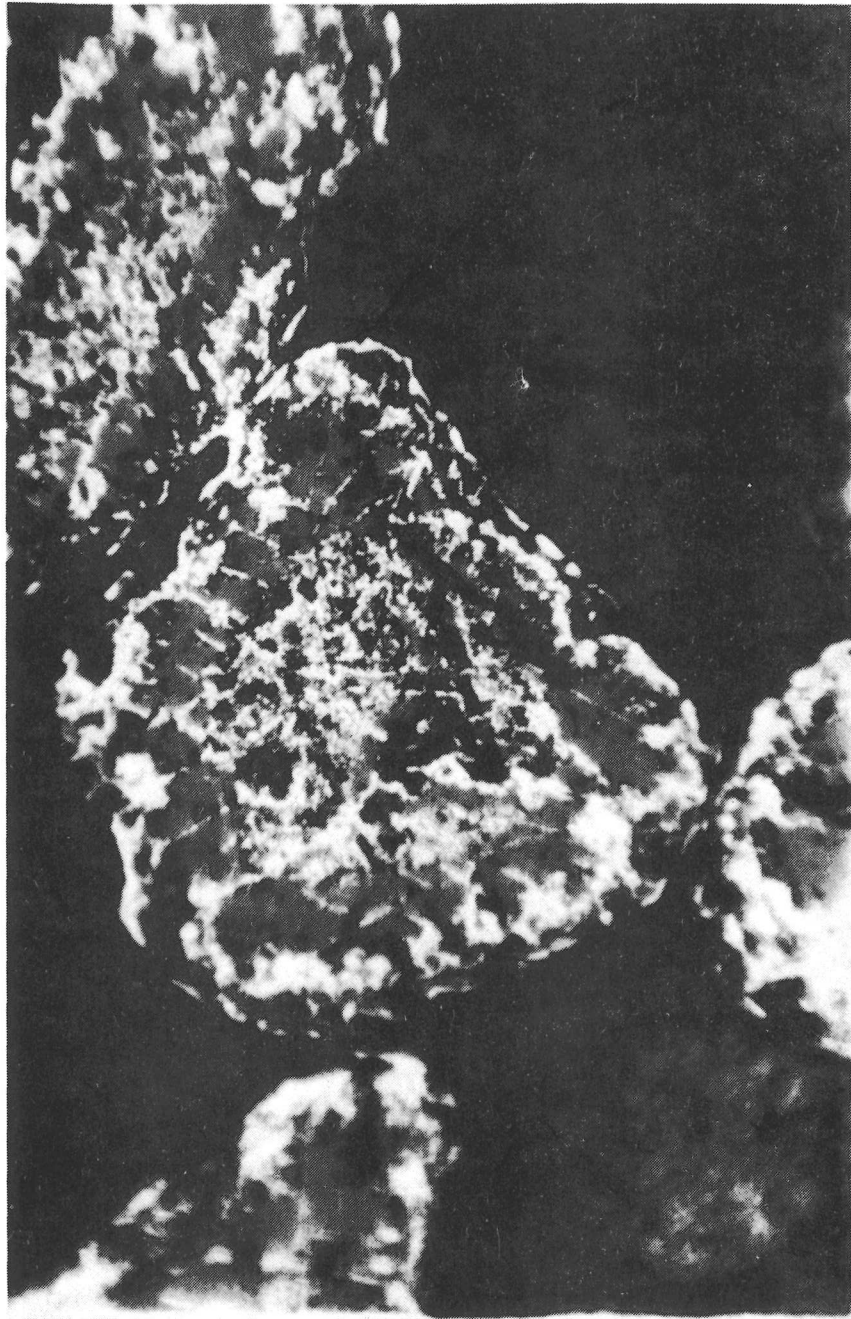
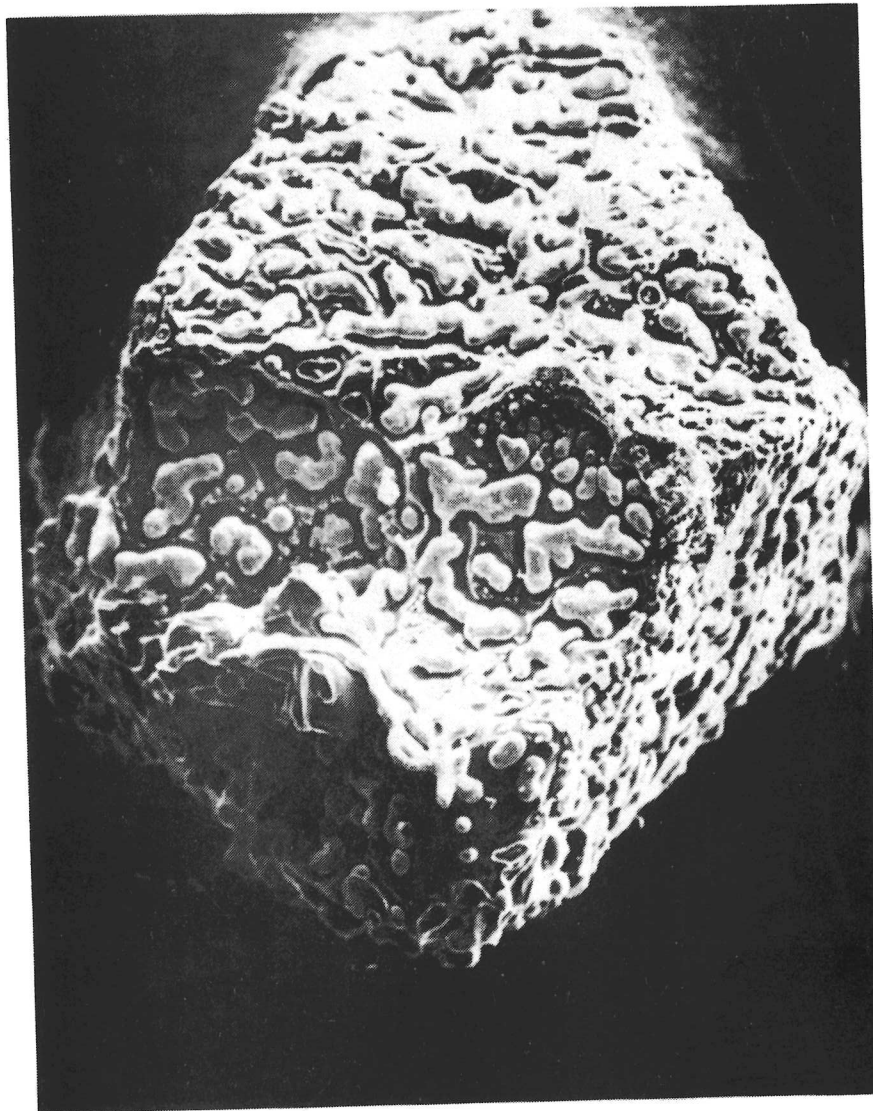


PLATE XXV



100 μm

PLATE XXVI



500 μm

PLATE XXVII

DISCUSSION

Dr. D. Slatter*

I would like to know whether Dr. Finn has done any subsequent tests to see whether his very interesting model for the reduction of the Winterveld ore can be fitted to the reduction of other types of chrome ores with different compositions?

Dr. C. Finn:

Thank you for the opportunity to tell you that we are continuing with our research on chromite. We now have another student who is using very similar techniques looking at a very exciting new chrome ore body. This is the UG2 chrome body which will probably be exploited for its platinum reserves producing chromite spinel as a tailing material. The reaction model that fits the Winterveld spinel fits the UG2 spinel as well.

* University of Zimbabwe, Zimbabwe