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Preparation and Characterisation of High Surface Area Semiconducting Oxides

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The conventional method of preparing doped semiconducting oxides involves solid state sintering at elevated temperatures and the resultant products have a very low surface area (< 1 m^2 g^{-1}). This severely limits the activity of semiconducting oxide catalysts, such as lithiated NiO. A cryochemical method based on the freeze drying of mixed salt solutions, followed by low temperature calcining has yielded lithiated NiO of over 60 m^2 g^{-1}. DTA, conductivity measurements and chemical analyses confirmed that under these conditions, very uniform mixing between Li_2O and NiO is achieved and that Li_2O can diffuse into the NiO lattice at about 400° C, as compared to 950 to 1000° C for products prepared by conventional means.

1. Introduction

In 1948, Verwey, Haaijman and Romeijn [1], showed that the conductivity of non-stoichiometric transition metal oxides could be controlled by doping them with cations of lower or higher valency. When NiO, an insulating, metal-deficient, non-stoichiometric transition metal oxide is doped with 10 at. % Li_2O, the conductivity at 25° C increases from 10^{-8} ohm^{-1} cm^{-1} to 1 ohm^{-1} cm^{-1}. The incorporation of Li^+ into the NiO lattice creates an equivalent number of Ni^{3+} in order to preserve electroneutrality. The increased number of Ni^{2+}–Ni^{3+} couples enhances the electrical conductivity, since electron hopping could occur by $Ni^{2+} - e \rightleftharpoons Ni^{3+}$. This system provides an ideal model for the study of the influence of magnetic, electronic, thermo-electric and crystallographic properties on the catalytic and electrocatalytic behaviour of semiconducting oxide catalysts [2-4]. The usual preparation method involves the thermal decomposition of mixed metal salt solutions, followed by heat treatment at 950 to 1000° C to ensure the complete diffusion of Li_2O into the NiO lattice. Winter [5] suggested that oxygen is dissociatively chemisorbed above the Néel point of NiO and that the particle size of NiO affects the Néel point - for 1 m^2 g^{-1} NiO, the Néel point is 220 to 250° C; 220 m^2 g^{-1} NiO, below room temperature. Since the O–O bond is very stable, any catalysts which could dissociatively chemisorb O_2 should be very active. This was confirmed by Tseung, Hobbs and Tantram [6], who showed that when low surface area (1 m^2 g^{-1}) lithiated NiO powder was used as electrocatalyst for the reduction of oxygen in 75% KOH solution at 220° C, over 300 mA cm^{-2} at 900 mV could be obtained, as compared with only 160 mA cm^{-2} at 900 mV for a commercial platinum black electrode. However, the performance of the lithiated NiO electrode was very poor at lower temperatures. Though higher surface area could be produced by the vacuum decomposition of $Ni(OH)_2$, it is not suitable as an electrocatalyst since it has a high resistivity and its surface and bulk properties are strongly influenced by oxygen partial pressure, making it unstable in use [8]. Thus, a study of novel methods for preparing high surface area semiconducting oxide catalysts is of fundamental and practical interest.

1.1. Review of Possible Methods

Since the formation of NiO–Li_2O solid solution is the most important step in the preparation of high surface area lithiated NiO, any potential method must be capable of forming oxide solid solutions with the minimum amount of sintering and grain growth. The following methods are therefore of interest:

(i) Flame reaction method [9], whereby mixed metal salt, water, and methanol solution is sprayed through a fine nozzle to a ring of oxygen-acetylene or oxygen-hydrogen flame. The resultant powder is then collected in an electrostatic precipitator. The temperature of the flame is over 2000° C, and therefore, interdiffusion between the oxides will be rapid; since the particles are suspended in a gaseous medium, very little grain growth can take place. Ferrite powders of over 30 $m^2 g^{-1}$ have been produced by this method.

(ii) Radio-frequency oxidising plasma [10], whereby pure, mixed, single-phase halides are passed through an induction plasma torch to produce the respective oxides with considerable solid-solution formation, e.g. up to 6 at. % Cr in δ-alumina from CrO_2Cl_2 and $AlCl_3$, free from problems of contamination, sintering and irreproducibility. Powders with specific surface areas up to 100 $m^2 g^{-1}$ (particle size diameter between 0.01 and 0.15 μm) have been prepared by this means.

(iii) Cryochemical method: if a solution containing two different metal salts is frozen rapidly enough to prevent the precipitation and segregation of the solutes, and if there is no melting of the ice during the subsequent vacuum drying, the resultant dried product should retain the state of subdivision and degree of homogeneity of the original solution, since the solutes are effectively immobilised by the ice crystals during the freeze drying process. In recent years, freeze drying has been used successfully in the preparation of high surface area cermet and alloy powders [11] and $MgO.Al_2O_3$ [12] powder.

Both the flame reaction and radio-frequency plasma methods involve the use of high temperatures and are therefore not likely to be suitable, since the vapour pressure of Li_2O is very high compared with NiO and considerable segregation might occur. In theory, if mixing on an atomic scale is achieved by freeze drying then high surface area lithiated NiO could be produced, since the distance that NiO and Li_2O need to interdiffuse would be very short and hence there will be no need for sintering the powder at elevated temperatures for long periods. Freeze drying therefore appears to be the more appropriate method.

2. Experimental

2.1. Uniformity of Mixing

No previous work has been done on the uniformity of mixing that can be achieved on freeze drying. Direct chemical analysis is rendered impractical by the fact that we are considering mixing on the atomic scale. The surface area of the freeze dried powder is usually too high for accurate X-ray powder diffraction studies since line broadening invariably occurs. Furthermore, in the preparation of mixed oxides from mixed metallic salt solutions, it is difficult to ascertain to what extent the freeze dried mixed salt solution is truly homogeneous on an atomic scale and to what extent the subsequent solid solution oxide results from a more rapid migration during the decomposition of the oxysalts. Since there appeared to be no way of checking this easily for the above case, consideration had to be given to other salt systems capable of forming solid solutions, for which some other suitable criterion for assessing the uniformity of mixing is available (e.g. conductivity measurements). $AgCl$-$CdCl_2$ solid solution was chosen as the model system. If a solid solution is formed, each Cd^{2+} replaces two Ag^+ ions in the lattice. In order to preserve electroneutrality there must always be at least as many vacant Ag^+ cation vacancies as there are Cd^{2+} ions. The existence of cation vacancies will increase the ionic conductivity of AgCl substantially.

For example Koch and Wagner [13] have measured the conductivity of AgCl and AgCl doped with cadmium at 210° C and found that as little as 1 % $CdCl_2$ in AgCl increased the conductivity by more than 100 times. Therefore, an increase in the conductivity of AgCl after freeze drying a solution of AgCl and $CdCl_2$ can be attributed to the formation of $CdCl_2$-AgCl. This can only occur if mixing on an atomic scale is achieved, since no heat-treatment has been provided for the diffusion of Cd^{2+} into the AgCl lattice.

AgCl is of course insoluble in water, but soluble in conc. NH_4OH. $CdCl_2$ is only sparingly soluble in conc. NH_4OH. It was found that a large excess of 50% aqueous NH_4OH satisfactorily dissolved the mixtures used. Bearing in mind the large differences in solubility of each component, it can be seen that this presents a fairly rigorous test of the effectiveness of the freeze drying process.

2.2. Preparation of Freeze-dried Samples

2.2.1. Lithium-Doped Nickel Oxide

The starting materials were Analar grade lithium acetate and nickel acetate. Aqueous solutions of these soluble salts were mixed. The solution was then made as dilute as practicable (e.g. for an ultimate 5 g batch of oxide, the mixed acetates were dissolved in 500 ml of distilled water). A high pressure nitrogen supply was connected to the Buchner flask containing the solution and the solution was sprayed as a fine jet through a nozzle into a dish containing liquid nitrogen, thus enabling the liquid droplets to be frozen instantaneously. The solid sample was then transferred to a vacuum bell-jar which formed a part of the freeze drying equipment, and subjected to a vacuum of 0.1 torr, until all traces of water had been removed, such a point being indicated by a reduction of pressure to 10^{-3} torr.

In all cases, the salts were decomposed *in vacuo* at 250° C and cooled to room temperature before admitting air to complete the oxidation:

$$\tfrac{1}{2}x\,.\,Li_2O + (1-x)\,.\,NiO_{1+\lambda} + \tfrac{1}{4}(x + 2\lambda x - 2\lambda)O_2 \rightarrow Li_x\,Ni_x^{3+}\,Ni_{1-2x}^{2+}\,O\,.$$

where λ represents the proportion of excess oxygen. The samples (either 5 at. % or 10 at. % Li-doped NiO) were then subsequently heat treated for 3 h at 300° C, 400° C, 500° C, 600° C, 800° C or 1000° C. In all cases, the product was a fine black powder, except for those treated at 1000° C where the decrease in surface-excess oxygen as a result of grain growth produced a grey-green colour.

In order to compare the effectiveness of freeze drying with conventional solid state sintering techniques, an analogous series of lithiated NiO was prepared by evaporating a solution of mixed acetates in an oven and subjecting them to a similar heat-treatment subsequently.

2.2.2. Cd-Doped AgCl

Identical freeze drying procedures were adopted but using 50 % aqueous ammonia as the solvent. The product was analysed immediately after the completion of the drying stage. The white powders obtained faded in daylight to pale mauve over a period of a few weeks. Samples were also prepared by vacuum drying of the solution or straightforward evaporation over a bunsen burner.

2.3. Chemical Analysis of the Product

The atomic ratio of nickel to lithium in the original stock solution was carefully controlled in all cases. However, after decomposition at elevated temperatures, the lithium itself can either be: (i) incorporated as Li^+ in the NiO lattice; (ii) as free Li_2O, existing as a separate phase; (iii) lost by evaporation due to the volatility of Li_2O.

Li-doped NiO is extremely resistant to dilute acids and dissolves only in concentrated acids. However, by boiling under reflux in aqua regia, it can be completely dissolved. Free lithium oxide on the other hand is freely soluble in dilute acetic acid at 60° C. Thus by using flame photometry to analyse the lithium concentration in the various solutions, it is possible to determine indirectly the amount of lithium incorporated into the NiO lattice. Thus,

% of available lithium
incorporated into NiO lattice

$$= \frac{\text{total lithium} - \text{free lithium}}{\text{lithium in original solution}} \times 100\,\%$$

2.4. Surface Area Measurements

The surface areas of the powders were determined by a gravimetric method using the basic BET equation [14], with nitrogen as the adsorbate at 77° K. A CI Electronics Mark 3 microbalance with a sensitivity of 10^{-6} g was used for all adsorption measurements. Corrections were applied to all results for inherent imbalance, buoyancy and thermomolecular flow over the whole pressure range used; a cross-sectional area of 16.2 Å^2 was assumed for the nitrogen molecule.

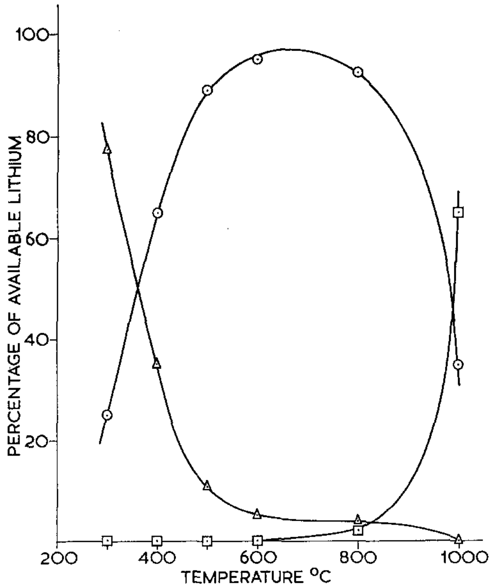


Figure 1 Variation of lithium content with calcining temperature for a nominally 5 at. % lithium-doped, freeze dried nickel oxide sample. ○ — ○ lithium in solid solution; △ — △ free lithium (as oxide); □ — □ lithium lost by evaporation.

2.5. Conductivity Measurements

A Wayne-Kerr AC Bridge was used (1592 Hz) for all conductivity measurements.The procedure was to introduce a weighed amount of the powdered sample into a specially designed cylindrical steel die which has a 1 cm diameter inner teflon sleeve. The height of the pressed powder bed was monitored and its conductivity measured. Specific conductivities were then computed and plotted against pellet density. For comparative purposes, the specific conductivity at 75% density was arbitrarily taken as representing the specific conductivity of the powder. All the measurements were carried out at 25° C.

2.6. Differential Thermal Analysis

A Grimshaw-Roberts DTA [15] apparatus was used to monitor the changes in freeze dried nickel-lithium acetate and a mechanically mixed nickel acetate and lithium acetate, on heating from room temperature to 700° C. If Li_2O diffuses into NiO vigorously, it should be detectable as an exothermic peak in the DTA curve. The rate of heating was 150° C h^{-1} in all cases.

3. Results

3.1. Lithium Distribution

Figs. 1, 2 and 3 show the ultimate distribution of the added lithium in a nominal 5 at. %, 10 at. % Li sample, prepared by freeze drying and a 5 at. % Li sample prepared by the conventional method, as a function of calcining temperature. (3 h at each temperature.)

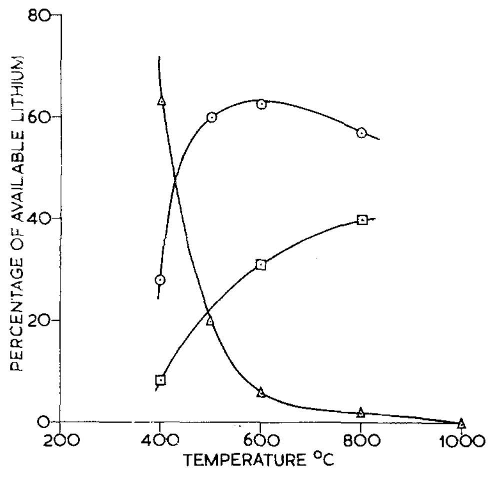


Figure 2 Variation of lithium content with calcining temperature for a nominally 10 at. % lithium-doped, freeze dried nickel oxide sample. ○ — ○ lithium in solid solution; △ — △ free lithium (as oxide); □ — □ lithium lost by evaporation.

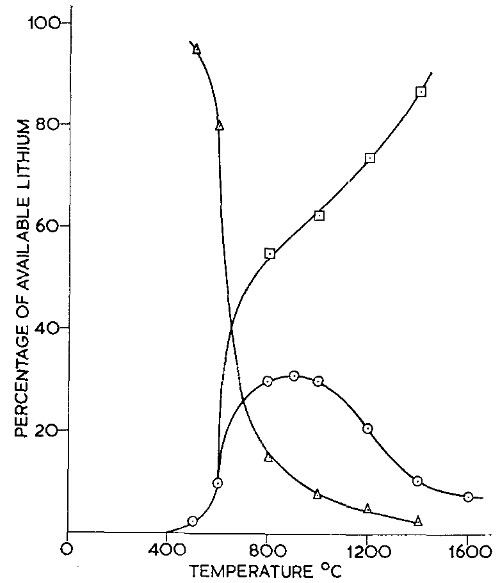


Figure 3 Variation of lithium content with calcining temperature for a nominally 5 at. % lithium-doped nickel oxide sample prepared by direct heat-treatment of mixed salts. ○ — ○ lithium in solid solution; △ — △ free lithium (as oxide); □ — □ lithium lost by evaporation.

3.2. Surface Area of Nickel Oxide, Lithiated NiO and Cd-Doped AgCl Samples

Table I shows the area of various NiO and lithiated NiO samples after heat-treatment for 3 h at different temperatures. The results for the various Cd-doped AgCl samples are shown in table II.

3.3. Conductivity Measurements

From the plots of relative density against specific conductivity points of comparable density (75% of the theoretical density) were read off and used for direct comparisons of the conductivities of the powders.

3.3.1. Lithium-Doped Nickel Oxide

The specific conductivity for each sample at 75% density are plotted against at. % Li in fig. 4a.

3.3.2. Cd-Doped AgCl

Table III compares the specific conductivity of Cd-doped AgCl prepared by freeze drying, vacuum drying and evaporation to dryness.

TABLE I Surface area of nickel oxide samples prepared by different methods

Calcining Temperature (° C)	Specific surface area (m^2 g^{-1})			
	Freeze-dried samples. Nominal lithium content			Samples prepared by direct heat-treatment of mixed salts
	0%	5%	10%	
300	76	95	102	
400	—	70	65	8.5
500	—	28	30	
600	—	10	12	
800	$\sim$2	$\sim$2	$\sim$2	< 1
1000	< 1	< 1	< 1	< 1

TABLE II Surface area of cadmium-doped silver chloride samples prepared by different methods

Cadmium doping level (% cations)	Special surface area (m^2 g^{-1})		
	Freeze-dried by normal method	Vacuum-dried at room temp.	Solution boiled to dryness
0	30	$\sim$5	< 1
0.1	35		
1.0	38		
10	27	$\sim$5	< 1

TABLE III Specific conductivity of cadmium-doped silver chloride samples prepared by different methods

Cadmium doping level (% cations)	Specific conductivity (mho cm^{-1}) at 25° C		
	Freeze-dried by normal method	Vacuum-dried at room temp.	Solution boiled to dryness
0	1.125×10^{-9}	2.0×10^{-9}	5.0×10^{-9}
0.1	8.5×10^{-8}		
1.0	1.6×10^{-7}		
10	1.26×10^{-6}	8.0×10^{-9}	1.05×10^{-8}

3.4. DTA

Fig. 5 shows the DTA curves for a 10 at. % lithium-nickel acetate sample prepared by freeze drying. This shows an exothermic peak at 425° C, which is not detectable on a mechanically mixed 10 at. % lithium acetate-nickel acetate sample.

4. Discussion

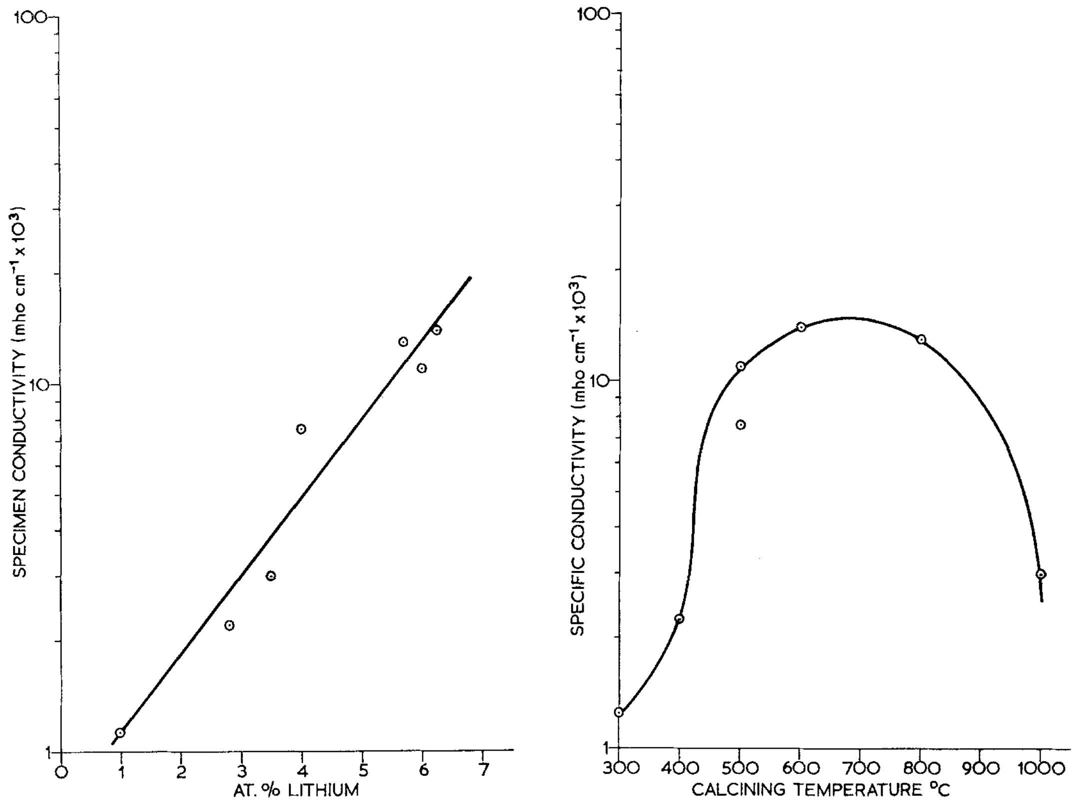
The 100-fold increase in electrical conductivity of 10 at. % Cd-doped AgCl powder prepared by freeze drying, together with the progressive increase of the conductivity over the range between 0-10 at. % Cd clearly indicates that solid solution can be achieved at room temperature for this system. This substantiates the claim that homogeneous mixing on a molecular scale can be achieved by freeze drying. On the other hand, in the case of vacuum drying, even though the solution is frozen after a few minutes of evacuation, the resulting 10 % $CdCl_2$-90 % AgCl powder is not a $CdCl_2$–AgCl solid solution, suggesting that unless the solution is frozen instantaneously, precipitation and segregation of the solutes is unavoidable.

The chemical analyses of the Li-doped nickel oxide system show that Li^+ ions begin to enter the NiO lattice at temperatures below 400° C and by 600° C optimum lithiation conditions have been reached. The DTA results confirm this, showing the presence of an exothermic peak between 400 and 450° C for the freeze-dried sample, which is absent from other samples prepared by conventional methods.

Within the limits of experimental error, the conductivity followed the expected relationship with respect to lithium content. The absolute values appear to be somewhat different to those reported by other workers, but since there is such a great diversification in technique of both preparation and measurement, this is not surprising.

The measurements were carried out primarily to ensure that the lithiation figures obtained by chemical analysis reflected the true extent of bulk lithiation and were not simply due to a high degree of surface lithiation over the first few atomic layers. If this inhomogeneity within a single particle in fact existed, it would adversely affect the bulk conductivity to such an extent that the controlling parameter would be sintering temperature rather than analysed lithium content. As can be seen, no such relation exists between temperature and conductivity (fig. 4b) providing further confirmation of good distribution of Li^+ in the lattice. The conductivity-temperature relationship in fact shows a remarkable similarity to the lithium content-temperature relationship (figs. 1, 2).

Whereas all surface areas obtained on the freeze-dried samples were higher than the corresponding values obtained, using the more usual solid state diffusion methods, it was not possible to achieve the kind of surfaces obtained



(a) (b)

Figure 4 (a) Electrical conductivity of polycrystalline lithium-doped nickel oxide as a function of lithium content. (b) Electrical conductivity of polycrystalline lithium-doped nickel oxide as a function of calcining temperature.

by El Shobaky, Gravelle and Teichner [7] who made pure NiO with a specific surface area of 200 m^2 g^{-1} by the vacuum decomposition of nickel hydroxide. However, the present results appear to be the first successful preparation of Li-doped NiO in high surface area form which has a distribution of cations comparable with those preparations requiring far more vigorous thermal treatment, which could only yield a low surface area product.

Finally, the chemical analyses show quite clearly that measurable quantities of lithium are present in solid solution even at 300° C, considerably below the NiO Tammann temperature. Lithium oxide, with a lower Tammann temperature, must therefore enable lithium ions to diffuse more readily than their host cations, and it would be expected that further lithiation could be achieved at this temperature by extending the time interval beyond 3 h, with little sacrifice of surface area, which is predominantly controlled by the bulk diffusion of the more concentrated host species.

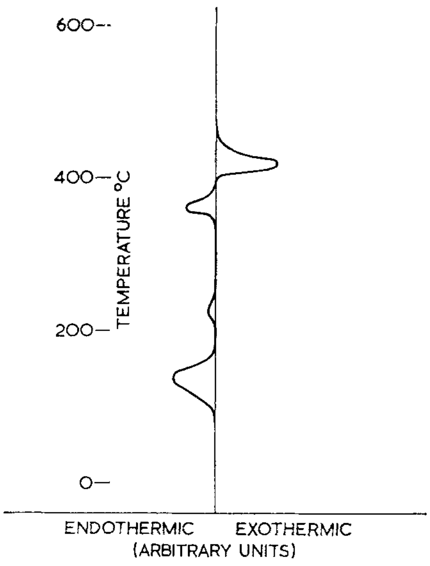


Figure 5 Differential thermal analysis curve for a nominally 10 at. % lithium-doped nickel acetate prepared by freeze drying mixed acetates.

Acknowledgement

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Letters

Rosette-like Precipitates of Silica

A rosette-like structure has often been observed in metallurgical slags. Whiteley and Hallimond [1] seem to be the first to have published in 1919 a micrograph of this structure, fig. 1, which they found in spoon samples withdrawn from acid slags with approximately the following composition: 55% SiO_2, 30% FeO, 15% MnO. From its appearance under the microscope, its refractive index and its response to various etching reagents, they concluded that it is a form of silica and suggested that it is cristobalite.

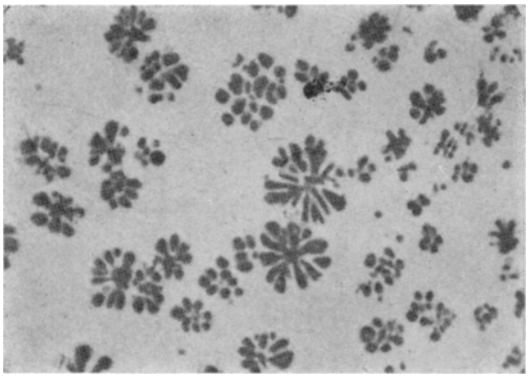

Figure 1 Rosette-like precipitate, observed by Whitley and Hallimont in acid slag (× 625).

The same rosette-like structure was later observed in spherical inclusions found in solidified steel. Urban and Chipman [2] reported that these rosettes are glassy in appearance and have a refractive index that is near that of quenched cristobalite.

Later authors have accepted that the rosettes consist of cristobalite and Kiessling [3] in his 1968 review of non-metallic inclusions in steel states that cristobalite is easily recognised by its rosette morphology.

When investigating various glasses Greig [4] in 1927 noticed the separation of clusters of little "dots" which were occasionally seen to form a unit composed of rods radiating from a common centre. They were observed in the systems CaO-SiO_2 and MgO-SiO_2. From their appearance in the micrographs it seems certain that they are identical to the rosettes already discussed. Greig discussed whether they could consist of a second liquid, presumably very siliceous, formed in a two-liquid region but he finally concluded that they consist of cristobalite.

Barry, Clinton, Lay, Mercer, and Miller [5] recently reported on the same structure found in a glass of the following composition: 56% SiO_2, 23% Al_2O_3, 21% Li_2O. They suggest that it is a