

Microscopic rods in metallurgical slags

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ABSTRACT. Microscopic rods of wüstite and sulphide phases have been observed within silicate crystals from metallurgical slags. The rods, which are distinct from acicular crystals of accessory minerals, tend to be orientated perpendicular to the faces of the host crystal. These rods, and their constant orientation, are a product of the crystallization environment. It is proposed that they result from saturation of the melt with the relevant phase at the growth front of the silicate crystals. This microstructure is compared with known examples of microscopic rods and tubes in rocks.

MANY metallurgical slags have compositions within the system CaO-(Fe oxide and/or MgO)-Al₂O₃-SiO₂. From these slags, minerals such as melilite, pyroxene, olivines, spinels, and plagioclase crystallize, all of which occur in igneous rocks, as well as other phases which are not naturally occurring. The petrography of slowly cooled metallurgical slags can be interpreted in the same way as the petrography of an igneous rock.

During a study of metallurgical slags from the ferrous, tin, and copper extraction industries (Wearing, 1981), a common mineralogical feature was the presence of opaque, microscopic rods within silicate minerals. These rods, which are distinct from acicular inclusions of accessory minerals such as rutile, tend to be orientated perpendicular to the faces of the host crystal. Although this microstructure has been described before (e.g. Edwards, 1949; Nurse and Midgely, 1951; Riley, 1979), no explanation has been offered for its origin.

Description of the microscopic rods

The microscopic rods develop in a variety of slags, each with its own characteristic mineral assemblage. The rod-forming phases were identified by (i) X-ray diffraction, using a Gandolfi single-crystal camera, and (ii) qualitative analysis by a CSI Microscan 9 electron microprobe. The microscopic rods, which tend to be restricted to certain minerals, are composed of sulphide phases and wüstite (FeO) in the following forms: (1) CaS

rods occur in melilite, merwinite (Ca₃MgSi₂O₈) and monticellite (CaMgSiO₄) in ferrous reducing slags; (2) ZnS rods occur in pyroxene from a zinc-rich tin slag; (3) wüstite rods occur in melilite phenocrysts in tin slags; and (4) wüstite rods occur in the fayalite of a FeO-SiO₂-rich copper slag. All the rods are thus compositionally different from their host minerals.

The morphology of the microscopic rods was determined by an ISI-40 scanning electron microscope, at an accelerating potential of 30 kV. They are nearly circular in cross-section, of variable diameter (not greater than 10 μm) and several hundreds of μm in length. Thin section examination suggests that the rods are usually tubular and completely filled with a solid phase, and this appears to be supported by evidence from scanning electron microscopy. However, in the melilite of ferrous reducing slags, some rods have gaps in their filling. This feature is probably a result of insufficient material being supplied to the growing rods.

When the host mineral is a phenocryst phase, the microscopic rods are orientated perpendicular to the faces of the crystal. The centre and diagonals of the host crystals are always rod-free, forming a Maltese Cross pattern (fig. 1). Often these rods increase in concentration away from the centre of

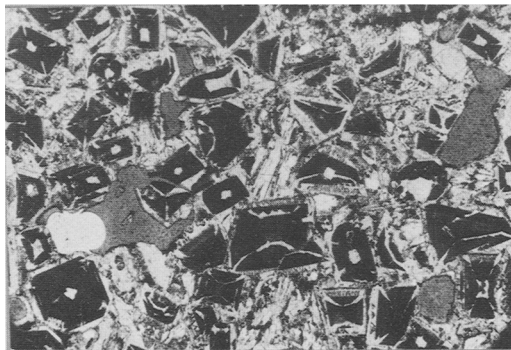


FIG. 1. Maltese Cross pattern formed by CaS rods (black) within melilite crystals of ferrous reducing slags. Plane polarized light; field of view is 1.5 mm across.

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the host mineral, by progressive bifurcation. Dendritic rosettes of CaS and wüstite sometimes form amongst the microscopic rods. They are always surrounded by a rod-free zone, up to 0.03 mm across. Dendritic rosettes also crystallize within the groundmass of the slags.

Nurse and Midgely (1953) found that small additions (0.2%) of Ca_2SiO_4 or $\text{CaMgSi}_2\text{O}_6$ to åkermanite caused exsolution of the impurity during crystallization runs below 1200 °C, to form a peg structure (i.e. microscopic rods). The similarity of this structure to that of the CaS rods observed by these workers (1951) in melilite of ferrous reducing slags, led to the suggestion that exsolution was the probable origin of the CaS rods. Ivanov and Lapin (1972) described microscopic MnS rods in the melilite of Mn-rich ferrous reducing slags, which exhibit similar features to the CaS rods. Edwards (1949) described a lead slag with hardystonite ($\text{Ca}_2\text{ZnSi}_2\text{O}_7$) crystals which had opaque rod-like inclusions: the rods were thought to be produced by exsolution. Riley (1979) described hardystonite from lead slags which have orientated wüstite rods. From the photomicrographs, the hardystonite is the primary phase.

Origin of microscopic rods

Sulphide rods. In some quenched ferrous reducing slags, where melilite crystals are set in glass, CaS rods which had grown in front of the host mineral were observed optically (fig. 2). Chemical gradients were detected in the residual liquid (now glass) near the liquid-melilite interface, by electron microprobe step-scans. Sulphur is strongly enriched in front of the melilite crystals, since melilite does not accept sulphur into its structure. The sulphur would eventually reach a saturation limit and so precipitate solid CaS, as observed.

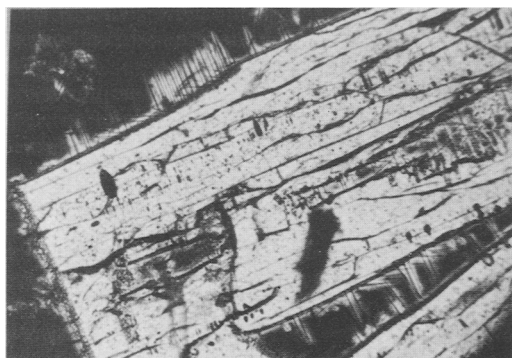


FIG. 2. CaS rods growing ahead of melilite, into the surrounding glass, in a ferrous reducing slag. Plane polarized light; field of view is 1.0 mm across.

In some ferrous reducing slags, globular CaS has precipitated between the melilite crystals. This intercrystalline precipitation appears to have precluded the formation of microscopic rods. The melilite of these slags is of small size, which suggests a slow growth rate. In the samples where there are no CaS globules, but which have a similar crystallization time, the melilites have numerous rods and a larger crystal size, which implies a much faster growth rate. Therefore, the growth rate of a possible host mineral appears to be an important factor in determining the presence of microscopic rods.

The MnS rods described by Ivanov and Lapin (1972) probably have the same origin. The Mn-rich character of the slags probably resulted in Mn being more readily available than Ca to combine with S at the time of sulphide saturation.

In the hand specimen, the sample with ZnS rods shows evidence of the ZnS segregating into sulphide areas, distinct from the silicate slag. This feature may represent sulphide immiscibility, although the ZnS segregations show no relationship to the ZnS rods. The absence of residual liquid precludes any knowledge of the chemical gradients. However, a similar situation to that in ferrous reducing slags probably occurred, and in this case Zn was the most readily available element to combine with S.

Wüstite rods. The entry of wüstite rods in tin slags coincides with the FeO enrichment of the melilite, which must reflect an increase in the concentration of this oxide in the melt. The crystallization of FeO as a phase indicates that there is an excess of this oxide during the formation of melilite and magnetite. The liquid trend of such slags is towards iron enrichment. The absence of wüstite as a phase elsewhere suggests that its formation may be directly related to melilite crystallization, as already shown for the CaS rods. Iron enrichment of the residual liquid would probably produce an increasing chemical gradient in front of the growing melilite crystal.

The possibility of FeO immiscibility in an iron-rich melt is not feasible as an explanation. However, as the interface liquid was becoming enriched in FeO then the saturation level for this oxide in the melt could be reached. This would result in the crystallization of wüstite, and explain its absence within the groundmass. Therefore, the wüstite growth would be controlled by the melilite to produce the constant rod orientation.

The bulk composition of the copper slag can be plotted in the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ (Osborn and Muan, 1960), from which wüstite is an expected product of crystallization. In the groundmass the wüstite has only the dendritic rosette habit, which suggests that this is the equilibrium (i.e. free grow-

ing) habit. Therefore, the growth of wüstite and the host mineral together is an important factor in the development of microscopic rods.

Nurse and Midgely (1953) and Edwards (1949) have proposed that microscopic rods like those described in this paper are formed by exsolution. However, the microscopic rods here described are considered not to be an exsolution effect, because their volume is too large for such an origin. The evidence suggests, rather, that they are a product of the crystallization environment, resulting from saturation in the relevant phase at the growth front of silicate crystals.

Growth as a rod-form is energetically advantageous, since it involves both a minimum diffusion distance and necessitates no further nucleation. The rod mineral appears to crystallize in front of the advancing interface of the host crystal, and so the rods must have initially nucleated heterogeneously against this interface.

Since the rods grow ahead of the host mineral's interface, their growth must be continued by the chemical gradients. Since the chemical gradients are perpendicular to the advancing interface, such longitudinal growth by the rods (i.e. along chemical gradients) would explain their constant orientation relative to the host crystal. The chemical gradients developed in the liquid by the growth of the host mineral. Any subsequent transverse growth of the rods will be terminated by the advancing face of the host crystal.

The clear core of the host mineral represents the period of growth prior to saturation at the interface. The clear diagonal zones are a result of the rods growing in front of, and perpendicular to, the faces of the host mineral: subsequent growth at the edge regions of the host crystal will be a completely new area, and so no rods will be present for inclusion.

The CaS rods within the merwinite and monticellite of ferrous reducing slags are disorientated relative to the crystal faces of these two minerals. This suggests that the subsequent growth of merwinite and monticellite, adjacent to the melilite, did not modify the chemical gradients associated with melilite which control the rod orientation. Thus, the microscopic rods grew at an angle to the crystal faces of the merwinite and monticellite.

The innermost wüstite inclusions of some fayalite crystals in the copper slag are of the dendritic rosette type. They represent free growing wüstite which has been subsequently included by the fayalite. Towards the rim, these rosettes are replaced by coarse and poorly orientated rods of wüstite, which in turn are replaced by thinner, well-orientated rods. Comparison with the ferrous reducing slags suggests that the well-orientated

rods probably formed under conditions of chemical gradients, and their thinness suggests fast growth of the fayalite, so reducing the rod diameter. The coarser and poorly orientated rods must have developed when the chemical gradients were insufficient to produce the constant orientation.

Microscopic rods in rocks

Microscopic rods (and tubes) have been observed in many rocks, although little comment has been made about them. The so-called 'peg structure' of natural melilite is similar in appearance to the microscopic rods of melilites from slags. However, El Goresy and Yoder (1974) analysed numerous pegs in a melilite nephelinite with the electron microprobe, which indicated the presence of at least three phases (mostly alteration products of melilite, with some kalsilite and nepheline). It was concluded that kalsilite- and nepheline-bearing pegs probably exsolved from a high-temperature åkermanite, rich in the soda-melilite molecule and its potassium analogue, and were subsequently altered. Thus, these pegs which consist entirely of the silicate alteration product, bear no relationship to the rods of slag melilites.

Richter and Simmons (1977) studied microtubes in granite, monzonite, syenite, granodiorite, anorthosite, dolerite, gabbro, and lunar basalts. As with slags, this microstructure occurs in single crystals, although in cross-section they are either elliptical or circular. Their size is similar, and they may be hollow or partially or completely filled with another phase. These 'microtubes' form in quartz, K-feldspar, plagioclase, muscovite, biotite, pyroxene and olivine. Richter and Simmons suggest that they form by at least three different processes: (1) the partial annealing of microcracks; (2) the natural etching of dislocations; and (3) the primary inclusion of fluid material during crystal growth.

Nockolds *et al.* (1978, pp. 358 and 359) describe an andalusite crystal (chiastolite variety) from a schist in the aureole of the Skiddaw Granite, in which spindlets of quartz run parallel to the direction of growth of the {110} sectors. It is considered that the growth of the quartz spindlets is energetically advantageous, and the supply of SiO₂ is in front of the growing andalusite. Therefore, these spindlets appear to form in a similar way to the microscopic rods of slags.

Roedder and Weiblen (1972) describe microscopic tubes in plagioclase crystals from Lunar Mare basalts. These tubes are parallel to the direction of growth, and are considered to contain late magmatic immiscible silicate glass. Since immiscibility does not occur in the slags, there is

no comparison between wüstite and the iron-rich 'microtubes' of lunar basalts.

The compositions of all these rocks differ from the compositions of the slags which have been studied and in most of them the cooling rate is slower, which accounts for the differences between the microscopic rods in the rocks and those in the slags.

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