The hot corrosion of metals and alloys has normally been investigated in the laboratory using simplified sulfate melts. These have not contained aluminum, employing rather added lithium cations to lower the melting point to plant operational temperatures. Lithium is not found in superheater deposits and a consideration of deposit analyses indicated that the next most abundant cation, after sodium and potassium, was aluminum: only 15 mol% is needed to lower the melting point to 550°C. Corrosion tests with this melt have shown little difference in the rate of hot corrosion determined using the lithium-containing melts, but a very different mechanism. The generation of oxide ions in the melt upon oxidation of nickel (the metal studied in most detail) caused an aluminum-rich layer, 0.2 mm thick, to build up within the melt, adjacent to the scale, and the later precipitation of an insoluble residue within the bulk melt. This residue contained no nickel and, surprisingly, could not be identified by X-ray analysis as one of the 14 known modifications of alumina. The rate determining step for the dissolution of scale into the melt was found to be that of the passage of nickel-sulfato complexes through the aluminum-rich layer. Suggestions are made for the incorporation of the implications of this finding into future hot corrosion research.
1. Introduction

Corrosion by molten salts contributes significantly to the cost of electricity generation from fossil fuels. In coal-fired boilers, the molten salts are principally alkali metal sulfates, while in oil-fired furnaces, vanadates are additionally found. Hot corrosion also occurs in gas turbines, particularly on the first stage nozzle guide vanes and rotor blades. The aggressive liquid deposits derive from impurities in the fuel and the combustion air and form on metal surfaces at temperatures of 550°C and above. Since it is not economically practicable to use impurity-free fuels hot corrosion must be investigated, and minimized to the best of our ability.

In such investigations it is obviously important to employ a molten sulfate mixture which is representative of that occurring in practice. Analyses of deposits for the cations present do not reflect the relative proportions found in the fossil fuel used. Some cations are concentrated in the molten deposit by one or more orders of magnitude: the concentration of the vanadium present in fuel oil is one well known example. In this study we focus on deposits, containing aluminum cations, expected on superheater and reheater tubes in coal fired power plants. However, the presence of very similar deposits are expected at those sites in gas turbines where hot corrosion occurs. Thus our findings can apply equally in this area.

2. Composition of the Deposit

Hot corrosion deposits are generally described, rather than fully identified, as alkali metal sulfates. The deposits are formed from the impurities in coal, and in this context the impurities may be defined as any inorganic constituent and any element other than carbon, hydrogen and oxygen.

Inorganic constituents of coal are primarily ash-forming, and can be sub-divided into inherent or extraneous mineral matter. Inherent mineral matter, generally less than 2% by weight, comprises those inorganic compounds once part of the original plant substance. The main elements are Fe, Ca, Mg, P, K, Na, Si, Al and Mn.

The remainder of the ash-forming substances are extraneous mineral matter, having been mixed with the plant material during coal-formation, or introduced later by contamination with mineral-laden water. They may also be derived from the roof of the seam during mining.

The mineral matter in coal may be classified into six main groups (1,2), and these are shown in Table 1. (A large number of associated minerals are also present in coal, but in negligible amounts in this context.) Of the minerals listed, kaolinite, pyrites and calcite comprise around 95%.
| Group     | Examples                                                                 |
|-----------|--------------------------------------------------------------------------|
| Shale     | muscovite \((K,Na,H_3O_3,Ca)_2(Al,Mg,Fe,Ti)_4^-\)  
            | hydromuscovite \((Al,Si)_8O_{20}(OH,F)_4\)  
            | illite \(\text{Al}_2O_3.2\text{SiO}_2.x\text{H}_2O\)  
            | bravaisite \(\text{Al}_2O_3.2\text{SiO}_2.x\text{H}_2O\)  
            | montmorillonite \(\text{Al}_2O_3.2\text{SiO}_2.x\text{H}_2O\)  
            | biotite \(\text{Al}_2O_3.2\text{SiO}_2.x\text{H}_2O\)  
| Kaolin    | kaolinite \(\text{Al}_2O_3.2\text{SiO}_2.x\text{H}_2O\)  
            | livesite \(\text{Al}_2O_3.2\text{SiO}_2.x\text{H}_2O\)  
            | metahalloysite \(\text{Al}_2O_3.2\text{SiO}_2.x\text{H}_2O\)  
| Sulphide  | pyrite, marcasite, FeS\(_2\)  
| Carbonate | ankerite, Ca\((\text{Fe,Mg,Mn})(\text{CO}_3)_2\)  
            | calcite, Ca\text{CO}_3  
            | siderite, Fe\text{CO}_3  
| Chloride  | sylvite, KCl  
            | halite, NaCl  
| Oxide     | quartz, Si\text{O}_2  
            | haematite, Fe\text{O}_3  
            | magnetite, Fe\text{O}_4  

(a) See Refs. 1 and 2.
Sulfur and chlorine are the two most important impurities which are not ash-forming. The normal weight percent range for sulfur is 1-4%, but up to 10% has been found. Chlorine levels in coal are normally 0.2-0.4%, but there is currently a trend towards the use of higher chlorine coals (up to 0.8 weight%), and this has focussed interest on the possibility of chloride ions being present in superheater deposits and thus participating in the corrosion process.

Chlorine occurs in the mineral form mainly as NaCl, with very little KCl, and this form probably accounts for around one half of the chlorine content. The form of the remainder is not clear. In the combustion zone NaCl is volatilized, and an exchange mechanism has been proposed (3) whereby potassium is replaced by sodium in the alumino silicates, allowing the formation of KCl vapor. The temperatures in the combustion zone are also sufficient to volatilize silica from shales and kaolins, and decompose carbonates to give CaO and MgO.

Table 2 gives reported chemical analyses for the fused inner white layer of superheater and reheater deposits. The year associated with the various reports is given because we believe the latest ones reflect improved analysis techniques and procedures. However, a considerable scatter of the data is readily seen. This arises in part from the difficulties inherent in obtaining representative samples, but also from variations between power station fuel supplies, and operating temperatures and conditions.

The earlier analyses refer to the now older, and less efficient, 220 megawatt boilers, and show sodium and potassium cations generally predominating over the alkaline earth cations. The iron in these deposits originates from both the coal and the superheater and reheater tubes and its concentration is thus expected to be time-dependent. Since (Na,K)SO₄ eutectic melts above 800°C, and the operating temperatures of these tubes is around 600°C, another cation has to be added to produce a lower melting eutectic. That cation has in the past been lithium, but the (Li, Na, K)SO₄ eutectic, while melting around 550°C, contains 78 mole% lithium, not a major component of superheater deposits. Laboratory tests using this eutectic have provided insight into hot corrosion, but we wished to use a more typical melt.

The later analyses, reflecting the coming on-line of the larger 660 megawatt generating plant, show generally some increase in the sodium and potassium levels in the deposits, but larger increases in aluminum levels. The calcium and magnesium levels are possibly now somewhat lower.

These conclusions are not clear cut from the data in Table 2, which contains only a selection of analyses of inner fused deposits. (It is traditional to give the constituents as their oxides: it does not imply they are present in that form.) A total analysis means that...
Table 2
Chemical Analyses of Fused Inner Layer of Superheater and Reheater Deposits
(expressed as percentages, by weight of air-dried sample)

| Analysis          | SiO₂ | Al₂O₃ | FeO | Fe₂O₃ | CaO  | MgO  | K₂O  | Na₂O  | SO₃ | Ref | Year |
|-------------------|------|-------|-----|-------|------|------|------|-------|-----|-----|------|
| Total             | 9.7  | 3.2   | 5.9 | 15.0  | 5.8  | 1.4  | 7.4  | 3.3   | 38.9| 7   | 1960 |
| Water Soluble     | 0    | 2.9   | 0   | 1.8   | 4.0  | 1.0  | 5.0  | 5.7   | 35.1| 7   | 1960 |
| Water Insoluble   | 15.6 | 5.9   | 1.1 | 8.5   | 3.0  | 0    | 0.1  | 1.3   | 5.4 | 7   | 1960 |
| Total             | 52.4 | 7.2   | I   | 8.6   | 2.4  | 2.7  | 2.5  | 0.6   | 15.6| 8   | 1960 |
| Water Soluble     | 0.1  | 6.2   | 0.9 | 3.8   | 1.7  | 0.6  | 10.5 | 2.0   | 37.2| 9   | 1963 |
| Water Soluble     | 0.8  | 3.2   | 2.77| 2.26  | 1.6  | 0.3  | 5.9  | 6.4   | 29.7| 10  | 1962 |
| Total             | 14.8 | 13.6  | I   | 9.5   | ½    | ½    | 15.0 | 39.4  | 11  | 1952|
| Total             | 15.8 | 9.0   | ½   | 11.8  | 3.9  | 0.8  | 9.0  | 5.9   | 43.3| 12  | 1955|
| Total             | 11.5 | 8.0   | -   | 10.0  | 3.9  | 1.1  | 6.8  | 8.6   | 45.5| 13  | 1968|
| Water Soluble     | 0.08 | 33.89 | I   | 4.36  | 0.91 | 10.5 | 1.63 | 34.1  | 14  | 1968|

I not given

* expressed as combined percentage
the figures represent the combined water-soluble and -insoluble contents. Analyses for chloride are infrequently reported, and are thus not included. Table 3 contains similar analyses of the outer, mainly fly-ash, layers of deposits. A comparison of Tables 2 and 3 shows, as expected, more silica in the outer layer, and an enrichment of the inner layer in the alkali metals with respect to the fly-ash composition. However, there seems to be no common Na to K ratio within the fused layer, and we therefore based our search for an appropriate, simplified, yet representative melt using a ratio of unity, i.e. upon the (Na, K)SO₄ eutectic.

We thus investigated the effect of added aluminum upon the melting point of (Na, K)SO₄ eutectic (4). Only relatively small additions of aluminum were needed to produce dramatic reductions in the observed melting point. The composition chosen for this work contained 15 mole % aluminum, and equal portions of sodium and potassium. This mixture melted around 550°C, and was stable under a synthetic flue gas atmosphere. The important component of the gas was the small concentration of SO₃, which prevented decomposition of the melt, (and the appearance of Al₂O₃), seen when the mixture was held molten in air.

An infrared investigation of the differences in structure and cation interactions within (Na, K, Al)SO₄ and (Li, Na, K)SO₄ (solified) melts has been published (4), and we here now examine the interaction of the aluminum-containing melt with metals and alloys, considering initially in detail melts containing nickel coupons.

3. Experimental

A coupon, approximately 8 mm x 8 mm x 1 mm, of metal or alloy is placed in an optical silica cell (Fig. 1) containing molten sulfate. The cell is located in a specially designed furnace (5), heated largely from above to create a known, representative thermal gradient down the melt, and a synthetic flue gas mixture is passed over the upper surface of the melt. The furnace is sited in the large cell compartment of an Applied Physics Cary 14 H spectrophotometer, the optics of which are essentially reversed to prevent any light emitted by the hot sample affecting the pen position on the recorder. The conventional record of light absorbed by only the sample as a function of wavelength is thus obtained. The optical path of the instrument is modified with masks so that only a horizontal slot of light (1-2 mm high) passes through the molten salt. Consequently the spectra, and hence the concentration, of dissolved species are recorded as a function of time and distance from the coupon in the melt experiencing the thermal gradient. In addition, periodic visual inspections of the corrosion process can be made.

At the end of various exposure times to both lithium- and aluminum-containing sulfate melts, including some standard crucible tests, the melt was quenched and the metal coupon, with adhering melt,
Table 3

Chemical Analyses of Outer Friable Layer of Superheater and Reheater Deposits
(expressed as percentages, by weight, of air-dried sample)

| Analysis     | SiO₂  | Al₂O₃ | FeO | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | SO₃ | Ref | Year |
|--------------|-------|-------|-----|-------|-----|-----|-----|------|-----|-----|------|
| Water Soluble| 0.06  | 3.02  | †   | 1.69  |      | 1.02*| 5.0 | 1.57 | 16.7| 14  | 1968 |
| Total        | 45.9  | 18.7  | †   | 23.1  | 2.5 | 1.9 | 2.2 | 1.1  | 0.8 | 8   | 1962 |
| Total        | 41.4  | 16.8  | †   | 24.3  | 7.4 | 0.5 | 2.6 | 3.4  | 3.0 | 12  | 1955 |
| Total        | 38.8  | 17.2  | 0.0 | 16.9  | 6.5 | 1.3 | 3.4 | 2.2  | 11.5| 7   | 1960 |

† not given

* expressed as combined percentage
was separated from the remaining solidified melt. The coupons were prepared by conventional metallurgical procedures for subsequent electron micrograph (EM) and electron probe microanalysis (EPMA) studies. The quenched melt was subjected to elemental analysis and X-ray powder investigations.

4. Results and Discussion

The main finding concerning the crucible tests was that the aluminum-containing sulfate melt was somewhat more aggressive than the lithium-containing melt. The extent of corrosion appeared to be increased by a factor of around two, from weight loss measurements.

The main difference in the mode of behavior showed up as the slow appearance of an insoluble white material after several hours in aluminum-containing melts in the presence of, particularly, nickel coupons. Initially this solid was considered as alumina, from the interaction of the aluminum cations in the melt with the oxide ions generated in the corrosion process. No oxide of lithium is expected to be insoluble under these conditions.

The white solid was observed as a fine uniform dispersion throughout the melt at the end of experimental runs. We have not been able to identify it as exclusively Al₂O₃, or even majorly as having an alumina structure from X-ray diffraction measurements.

4.1. Examination of Quenched Melts

Of the various metal specimens investigated, the white solid appeared in greatest quantity and in the shortest time in the presence of nickel coupons, and thus we have concentrated on this system.

After removing the corroded coupon the solidified melt was tested for water-solubility. In each case, a white insoluble residue was obtained, approximately 5% (by weight) of the initial sample. To ensure no soluble material remained with or within the solid, extensive heating and leaching, using large volumes of distilled water and an ultrasonic bath, were performed. Upon X-ray diffraction, the residues produced extremely complex patterns, and no clear identification was possible.

The results are summarised in Table 4 for the X-ray powder analysis for the residues obtained after corrosion runs at various nickel coupon temperatures, and contained in silica cells (Fig. 1). The thermal gradient in all cases had been close to 130°C, and synthetic flue gas (16% CO₂, 4% O₂, 0.4% SO₂, balance N₂) had passed continuously over the melt surface. The apparent presence of water-insoluble mixed-sulfates is thus surprising. We stress that nickel compounds were entirely absent from the precipitate.
Table 4
X-Ray Powder Diffraction Analysis of Water-Insoluble Residues from Melts After Corrosion Runs

| Metal Temperature (°C) | Major Constituents                      | α-Al₂O₃ Component* |
|------------------------|----------------------------------------|-------------------|
| 587                    | Possibly NaAl(SO₄)₂ + some unidentified | Minor             |
| 606                    | Possibly KNaSO₄                        | Minor             |
| 616                    | Unidentified pattern                   | Minor             |
| 632                    | Similar to 606°C                       | Minor             |

* JCPDS 10-173; b JCPDS 27-631; c JCPDS 20-927

The infrared spectra of solidified melts were therefore recorded, using the KBr-disc technique. The spectra of four solidified melts, from the corrosion runs at the four coupon temperatures (Table 4), were measured and compared with the spectrum of a "pure" sample. This was one that had been held in the molten state for several hours, but with no nickel coupon (and thus no corrosion products) present, and in which no precipitate was observed to form. No significant differences were seen between the four coupon-containing melts: some differences were noted between these and the pure melt spectrum, but none helped definitively to identify the precipitate. However, information upon the melt structure, and the effect thereon of corrosion product dissolution, was obtained, and the results published (4).

The appearance of the precipitate in the (Na, K, Al)SO₄ melt only in the presence of metals, particularly nickel, is interesting. The addition of oxide ions (as Na₂O) to the pure melt causes the immediate formation of α-alumina, but a corroding metal brings about a different reaction. X-ray diffraction analysis here failed to identify the solid as primarily alumina. Fourteen different Al₂O₃ structures are contained in the NCPD file, and of these only α-Al₂O₃ was observed as a minor constituent. Possibly Al₂O₃ can adopt an unlisted structure when formed under these conditions, or have a complex combination of modifications which make identification impossible. The presence of diffraction patterns attributable to mixed sulfates implies inclusion or incorporation of such species during precipitate formation in the melt. In our view, however, this is unlikely, because of the extensive leaching treatment. The alternative we favor is that the precipitate either contains, or may be (related to), an insoluble aluminum-sulfate mineral, several of which are known to exist.
4.2. Metallographic Examination of Corroded Specimens

EM (electron microscopy) and EMPA (electron microprobe analysis) were used to examine the corroded coupons. In general there were no significant variations between coupons exposed at different temperatures. The micrographs of a nickel coupon corroded at 616°C are typical (Fig. 2). The specimen was ground to 600 grit silicon-carbide paper along one edge to expose the bare metal, and is thus viewed with adherent solidified melt on both faces.

The feature which we believe is unique to aluminum-containing melts is the presence of a pronounced layered structure in the melt at the scale-melt interface. This inner layer, approximately 0.2 mm thick, is rich in aluminum and nickel, but deficient in potassium, relative to the outer layer, which is assumed to be representative of the bulk melt. EMPA studies of iron and chromium samples (6) revealed a thin aluminum-rich layer with iron, but not with chromium. However, the extent of scale formation with chromium was too small to be detected, and the mechanism for producing an aluminum- and chromium-rich layer within the melt may have been absent. At the time of writing, similar analyses on various nickel-based alloys and stainless steels are incomplete, but will be presented at the meeting.

4.3. Nature of the Inner Layer

In the hot corrosion of metals by molten sulfates the oxide layer on the metal surface is continuously being dissolved into the molten salt. The stabilities of the dissolved corrosion products, (largely transition metal-sulfato complexes), decrease with increasing temperature, and these species migrate outwards across the temperature gradient resulting from the heat flux. At the higher temperatures at the melt-ash interface most of these species, notably the iron and chromium complexes, decompose, being removed from solution as the insoluble oxides.

The rate-controlling step for hot corrosion has generally been considered as the rate of transport of the various sulfato complexes across the molten salt layer. Using our new technique (5) for the continuous monitoring of hot corrosion, termed EASE (Electronic Absorption Spectroscopy Experiments), we have recently shown (6) that the rate of migration across the thermal gradient is relatively rapid, and cannot therefore always be the rate controlling step, especially in the case of nickel. We now here propose and examine the idea that, where the inner layer is seen, the rate controlling step is the transport of transition metal-sulfato species across this layer.

That this layer is involved is almost inescapable, since the rate of scale buildup on nickel is rapid, and often faster than the rate of concentration increase of nickel within the melt (6).
4.4 Initial Reactions

All our metal specimens were pre-oxidized, generally in air for 24 h at 550°C, before being exposed to the melt. This was done to make the experiments representative of boiler conditions, in which oxidation of tube surfaces occurs before molten deposits form. Thus the first reaction is the interaction between oxide and the melt and, in the case of nickel, rapid penetration of the oxide scale by the melt.

Anodic oxidation of nickel,

\[ \text{Ni} \longrightarrow \text{Ni}^{2+} + 2e, \]  

then occurs, and a corresponding reduction of sulfate ions,

\[ \text{SO}_4^{2-} + 8e^{-} \longrightarrow S^{2-} + 40^{2-} \]  

Sulfur trioxide will also be present in the melt, having been formed in the synthetic flue gas via the platinized Kaowool catalyst (Fig. 1), (in generating plant by the catalytic action of Fe\(_2\)O\(_3\) in fly-ash). It will be transported through the sulfate melt as a consequence of the sulfate-pyrosulfate equilibrium, viz.

\[ \text{SO}_4^{2-} + \text{SO}_3 \pm \text{S}_2\text{O}_7^{2-} \]  

Sulfur trioxide may also be reduced to give sulfide and oxide ions,

\[ \text{SO}_3 + 8e^{-} \longrightarrow S^{2-} + 30^{2-} \]  

Oxide ions can also arise from the acid-base equilibrium that exists in molten sulfates,

\[ \text{SO}_4^{2-} \pm \text{SO}_3 + \text{O}^{2-} \]  

and from partial reduction of sulfate to yield sulfur dioxide, which is essentially insoluble in molten sulfates,

\[ \text{SO}_4^{2-} + 2e^{-} \longrightarrow \text{SO}_2 + 20^{2-} \]  

The dissolved oxide ions from the scale, and generated oxide ions at the solid-liquid interface, react with the aluminum cations in the melt to form Al\(_2\)O\(_3\), and thus displace these reactions to the right, thereby enhancing the oxidation (corrosion) of the metal, and producing SO\(_2\) gas at the solid-melt interface.

4.5. Transport Characteristics

With aluminum-containing melts there is thus a ready mechanism
for providing a precipitate at the solid-melt interface, within the melt, which might be expected to hamper the diffusion of nickel sulfato complexes into the bulk melt. Under conditions of rapid corrosion, oxide ions would later be able to diffuse into the bulk melt and in due course alumina or, as we now know, an insoluble aluminum-containing compound will appear in the melt. We have not yet been able to determine if the solid appears further and further from the solid-melt interface with increasing time, or if it appears uniformly within the melt after certain criteria are attained. The former is difficult to observe, and the latter could seem like the former, under the combined effects of appropriate particle size and gravity. Our periodic inspections indicated a uniform distribution of the insoluble material throughout the melt after several hours, but more experiments are required, and under isothermal conditions.

However, the aluminum-rich inner layer in the melt may be of different composition or structure to that of the bulk precipitate, and further work regarding this layer is planned. At present we can note that the bulk precipitate contains no nickel, or any originally present was leached out. Thus, assuming the same composition for bulk precipitate and inner layer, the transport of nickel through this material can be expected. The criteria for a different composition for the inner layer would have to include an open structure or pore size which would permit transport through the material, and in addition the capacity to contain, and possibly also retain, large concentrations of nickel, and other transition metal-sulfato complexes. We note that alumina has been used successfully in the chromatographic separation of transition metal complex ions in molten salts (15).

This inner layer must also allow through it sulfate and pyrosulfate ions, and sulfur dioxide (and possibly trioxide) gas. This is to enable the scale formation process, in the case of nickel, to continue. However, the evolution of gas, seen apparently at the solid-melt interface, any arise at the scale-melt interface, or within the melt, at the inner layer-bulk melt junction. In the former case, some disruption of the inner layer would be expected, and possibly erratic metal dissolution rates as a function time, but this was not found (6), and currently we favor the latter site.

4.6. Dissolution Rates

The rate of transport of corrosion products (transition metal-sulfato complexes), the rate controlling step, across the inner layer is obtained by determining the total concentration of these species in the bulk melt as a function of time (6). The concentration, at any time, of these corrosion products in the inner layer may be determined using the Tyrell equation (16) for the flux of corrosion products in a medium. This requires chemical diffusion and Soret coefficients, but these are not known for our conditions, but suitable alternatives are available (17,18). For nickel, dissolution rates
obtaining after 2.5 h at 632°C and 5 h at 587°C coupon temperatures were determined (6) as approximately 3.72 and 0.51 mg cm⁻² h⁻¹ respectively, (equivalent to 4200 and 570 nm h⁻¹, 9350 and 1250 mil year⁻¹ respectively). Fitting these rates into the Tyrell equation for a 0.2 mm layer gives a concentration difference equivalent to 16% (by weight) of nickel at 632°C and 2% (by weight) at 587°C. These would relate to values which an open net-work aluminum-containing material might reasonably be expected to hold.

5. Conclusions and Implications

(1) It is reasonable, and appropriate, that laboratory tests of the hot corrosion of metals and alloys by molten sulfates should, in the future, particularly for superheater corrosion studies, employ melts containing aluminum ions.

(2) The generation of oxide ions by the corroding metal causes an aluminum-containing layer within the melt and adjacent to the metal scale. Transport of corrosion products into the bulk melt is limited by this layer. Its composition is uncertain, and it is not, as might be expected, a common form of alumina.

(3) We propose that this finding may lead to economic benefits. We suggest that instead of seeking for better corrosion-resistant metals or coatings to withstand hot corrosion, the interaction between the metal surface and the corrodent could be tailored to produce within the melt an inner layer which has a very slow rate of transport of corrosion products across it into the melt, and retards scale formation. This could be achieved by either the use of an appropriate surface metal treatment or coating, or by addition of an appropriate chemical to the fuel, particularly during start-up.

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Fig. 1 Optical cell and insert. The inset shows the position of the insert and metal coupon during an experimental run.
Figure 2  Electron microprobe analysis of a corroded nickel coupon and adhering melt, showing nickel-rich and aluminum-rich regions in the melt. Clockwise, (A) nickel; (B) potassium; (C) aluminum; (D) electron image. Arrow indicates upper coupon surface. Coupon temperature 616°C, magnification X25.