GPLUS Final Report for OSRAM Sylvania[1]

Roberta A. Peascoe , Ted Besmann , Evan K. Ohriner, Sudarsanam S. Babu and Camden R. Hubbard

Oak Ridge National Laboratory
Dec. 31, 2002

Problem

Currently the major cause for shutting down a quartz melter is the growth of metallic crystals that disrupt the flow of molten quartz and the formation of a continuous quartz tube. These unwanted metallic crystals nucleate on the bottom of the orifice and near the stream of extruded molten quartz. Several factors determine when the metallic crystals will intercept the quartz tubing and consequently halt production. These factors include the location of crystal nucleation within the cooling chamber, the growth direction and the rate of crystal growth. A GPLUS study for OSRAM Sylvania was undertaken at ORNL to investigate the nucleation, growth and source of the metallic crystals in hopes of determining methods for controlling crystal growth and extending the lifetime of the quartz melter.

One potential means of reducing or eliminating crystal growth in quartz melting furnaces is to coat the internal components with another refractory metal such as rhenium or iridium. These materials have been reported to be useful as coatings in reducing metallic impurity contents in melted quartz. The purpose of this analysis is to obtain a rough estimate of coating thickness needed for long-term service at 2000° C. The coating thickness requirement is controlled by diffusion of the coating material into the molybdenum base metal.

There area few possible mechanisms by which a coating could reduce or eliminate crystal growth. Each of these would have somewhat different requirements for coating thickness. The first mechanism relies on the coating to prevent any underlying molybdenum metal from reaching the surface and reacting with the molten quartz and being transported into the vapor phase. Iridium and rhenium coatings may have much lower oxide partial pressures and would be less susceptible to the vapor phase transport responsible for crystal growth. A second mechanism would rely on the coating or its reaction products to have a different crystal structure than the molybdenum itself and thus impede the nucleation of molybdenum crystals. A third mechanism might be that the coating material would become incorporated into any nucleated molybdenum crystals which in turn would slow the growth of unwanted crystals.

---

[1] Research sponsored by the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Glass Industry of the Future, GPLUS. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

Experimental

In a prior GPLUS project, samples from two types of quartz melters, types 1 and 2, were shipped to ORNL for examination. In this study, samples from a third type of quartz melter (labeled OSRAM '02) were examined. The OSRAM '02 melter was formed using some tungsten components which were expected to reduce the rate of metallic crystal formation. Samples from the third quartz melter included: pieces from the molybdenum orifice, the tungsten skirt, and the tungsten container tube. Quartz, solidified after melter shutdown, was found on the inside of the orifice and container. Metallic crystals were found on the bottom of the orifice and on the walls of the skirt.

Samples were cut and mounted in epoxy and polished for examination using X-ray diffraction (XRD), optical microscopy and scanning electron microscope (SEM). SEM examinations were carried out on a Hitachi S4100 with computer interfaced energy dispersive spectrometer (EDS) with digital imaging, and image analysis capabilities. XRD examinations were carried out on a Scintag PAD V powder diffractometer with Cu K radiation ($\lambda_{K\alpha_1}$ = 1.5406 Å).

Thermodynamic calculations were undertaken using the FactSage™ program package to help determine possible mechanisms for refractory metal transport and crystal formation and growth.

Diffusion controlled growth calculations were performed for W-Ir and Mo-Ir diffusion couples at 2000°C for 100h. This simulation used published binary phase diagrams available for W-Ir, Re-W and Mo-Re (Fig. 1). However computational thermodynamic data for these systems are not established, thus computations used only solid solution end members and ignored the formation of intermetallics.

In addition, an experiment was undertaken at 2000°C to examine the rate of diffusion of molybdenum into a coating layer and the development of intermatillic species. A molybdenum sheet of 0.062" (1.5 mm) thickness was cut to produce three pieces, 2" (51 mm) square. Iridium alloy (containing 0.3% W) foil of 0.005" (0.13 mm) thickness was cut to 0.5" (12 mm) square. Rhenium metal sheet of 0.015" (0.4 mm) thickness was also cut to 0.5" (12 mm) square. All materials were cleaned in acid solutions. The materials were then stacked with the rhenium and iridium foils between the molybdenum sheets. The assembly was heated in vacuum (10^{-5} torr) for 8 hours under the load of a 20 lb (9 kg) weight of molybdenum bar and the assembly was thus diffusion. The assembly was cut and a cross section of the diffusion couple was polished using standard metallographic methods.

Sample Analysis

Analysis of the quartz melter included samples from the orifice and skirt. A slice taken from the orifice was cut into four pieces, and three of them along with a sample from the container and skirt were mounted in epoxy for examination (Fig. 2). Sample 5 was cut from the bottom of the orifice where it was attached to the skirt. On this sample, EDS measurements were taken at six locations across the sample from the outer edge of the container to the inner surface of the molybdenum ring

at the bottom of the orifice, as labeled in Figure 3. Crystals covered the inside surface exposed to the gases cooling the extruded molten quartz tube. EDS spectra of the skirt revealed the presence of both molybdenum and tungsten on the outer surface of the skirt where a molybdenum flame spray had been applied to the melter. Only tungsten was present on the interior sheets that composed the rest of the attached skirt. The interior of the ring at the base of the orifice was molybdenum, but the crystals growing on the bottom of the orifice were a combination of molybdenum and tungsten.

Orifice sample 4 (see Figs. 2 and 4) was cut from bottom of the orifice at the opening for molten quartz extrusion. Crystals attached to the bottom of the orifice were a mixture of molybdenum and tungsten, while the interior of the orifice was Mo.

A small sample of the skirt with an attached crystal was also examined (see Fig. 5). EDS spectra revealed the presence of only tungsten in the interior sheets. Tungsten and some molybdenum were present in the spectra from the attached crystals.

Three samples, 1 to 3, of skirting and the attached crystals growing on the tungsten skirt were cut from a single large piece of skirting, as seen in Figure 6. These three samples were then cut where clumps of crystals were found on the skirt material at different locations and distances from the orifice (see Fig. 6). EDS spectra were taken on each sample starting at the interior of the skirt material then moving to were the crystals were attached to the skirt surface (see Fig. 7-9). Measurements then continued along the crystals to the outer surface. The crystals on sample #1, located near the orifice, were predominately tungsten with an indication of the presence of molybdenum (see Fig. 7). The indication of molybdenum increased near the outer edge of the crystal. Only tungsten was observed in the crystals growing on the two samples further away from the orifice (see Figs. 8 & 9). This can be seen by comparing the EDS spectra from the outer-most crystal for the three samples, 1-3, where the presence of molybdenum occurred only in the sample closest to the orifice (Fig. 10).

Modeling Results

Several thermodynamic calculations were performed similar to analysis used in the prior study of molybdenum transport in a quartz melter. This time molybdenum, tungsten, rhenium and iridium were included to compare various refractory metals that could have potential applications in the quartz melter. The mole fraction for each element in the gas phase was determined in the same environment and is summarized in Figure 11.

Calculations for molybdenum, in a SiO_2-H_2-Ar environment are graphed in Figure 11. At 2000°C, the total partial pressure of all the molybdenum oxide gas species had reached a mole fraction of $3x10^{-5}$. Previously, based on the supplied gas flow rates, we calculated that this transport level was potentially sufficient to account for the observed crystal growth.

Thermodynamic calculations for tungsten oxide species in the same SiO_2-H_2-Ar environment are graphed in Figure 11. By 2000°C, the tungsten oxide vapor pressure in the gas had reached the

$3x10^{-5}$ level as well. Thus, tungsten transport is also possible by tungsten oxide species and the predicted equilibrium levels are sufficient to explain the observed tungsten crystal growth.

To consider if other refractory metals could be used in the melter the modeling was extended to include rhenium and iridium. The thermodynamic data available for rhenium or iridium calculations is not as extensive as for molybdenum and tungsten. Further the lack of high temperature data for some possible oxide species along with the unknown data's reliability make predictions uncertain. We feel further assessment of the data quality is outside the scope of the project.

For iridium the estimated vapor pressure is higher than that seen for rhenium. This is still quite low (10^{-6} range at the highest temperature) when compared to molybdenum and tungsten. Thus, rhenium and even iridium should be stable in the molten SiO2-H2-Ar environment.

Before considering either rhenium or iridium, thermodynamic calculations need to extend to the range from below 1800°C but above the melting point of quartz. This range was not investigated, and it is possible that rhenium or iridium has stable oxide phases at these lower temperatures and partial pressure conditions.

Diffusion Results

Diffusion controlled simulations for W-Ir and Mo-Ir at 2000°C for 100h were calculated using solid solution end members and ignored the formation of intermetallic precipitation or σ phase development. They showed cross diffusion and interface movement between the W-Ir phases (Fig. 12). Extensive cross diffusion was predicted but with limited interface movement between the Mo-Ir phases (Fig. 13).

The diffusion between the Mo-Ir phases was next experimentally tested along with Mo-Re at 2000°C, and the microstructures of the Mo-Ir and Mo-Re diffusion couples, viewed with interference contrast, are shown in Figures 14 and 15 respectively. The likely phases present are identified in the micrographs based on the equilibrium phase diagrams (Fig. 1). The approximate average thickness values of the various layers were measured from the micrographs of both diffusion couples and are listed in Tables 1 and 2. The value for the iridium and rhenium layers are tabulated as the half thickness value since the centerline of these layers are symmetry planes. This analysis is equivalent to two coated molybdenum plates pressed into contact, with the coating thickness as half the original foil thickness.

Table 1. Approximate thickness of layers measured for Mo – Ir diffusion couple after 8 hours at 2000° C.

Label	thickness, μm
Iridium solution [a]	40
Ir_3Mo	25
IrMo	10
Mo_3Ir	80

Iridium foil original [a]	65

[a] half thickness

Table 2. Approximate thickness of layers measured for Mo – Re diffusion couple after 8 hours at 2000° C.

Label	thickness, μm
Rhenium solution [a]	150
Chi	10
Sigma	50
Rhenium foil original [a]	190

[a] half thickness

Discussion

Analysis of specimens from the three OSRAM Sylvania quartz melters examined at ORNL leads to the following findings. Molybdenum or tungsten crystals form on the bottom of the orifice and skirt when molybdenum or tungsten oxide vapors (MoO_X or WO_X) are reduced to solid molybdenum or tungsten by the Ar/H_2 cooling gases circulating below the orifice. Upon cooling, molybdenum or tungsten condenses out of the vapor phase and deposits on the relatively cooler surface of the orifice or skirt. This is especially apparent at the gas inlets on the skirt. A preferred (111) growth direction was observed for both tungsten and molybdenum crystals.

Thermodynamic modeling shows that WO_X species, have sufficient vapor pressure to explain the tungsten removal from the inside of the tungsten lined melter and redeposit on the skirt and lower surface of the orifice as seen in the OSRAM '02 quartz melter. In addition, molybdenum transported from the upper surface of the orifice and possibly from the mandrel in the OSRAM '02 melter despite the greater surface area of tungsten present in the melter relative to molybdenum. The lack of tungsten crystals in a prior study of a similar tungsten / molybdenum melter maybe due to a difference in operating temperatures.

The changes in crystal composition in different location of the cooling chamber may reflect temperature gradients and the relative mole fraction of the metallic gas species. In the OSRAM '02 case, tungsten crystals tended to form preferentially on the skirt while molybdenum crystals tended to form on the orifice. Variations in mole fractions with temperature in conjunction with temperature gradients between the orifice and skirt as well as in the circulation of the cooling gases may direct the preference in crystal composition.

Diffusion controlled simulation for Mo-Ir predicts extensive cross diffusion but limited interface movement of the phases after 100 h at 2000°C (Fig. 13). Looking at micrographs from the 8 hr diffusion experiments (Fig. 14), it is possible to extrapolate the diffusion to longer times by making a number of simplifying assumptions. Assuming that diffusion of molybdenum into the foil (or coating) is negligible in comparison with diffusion into the molybdenum and that the kinetics are parabolic, then the thickness of the coating as a function of time will follow:

$X = Xo - Kt^{1/2}$ uints of K=□m/hr$^{1/2}$.

In which X_O is the original coating thickness at t=0 and K is a constant. The values of X=40 and X_O=65 for the iridium diffusion couple result in a value of K of 8.8 □m/hr$^{1/2}$. From this, it can be calculated that a foil or coating that thick would be consumed in 54 hours. A coating that would not be consumed in one year would have a thickness of 2.2 mm. The values of X=150 and Xo=190 for the rhenium diffusion couple result in a value of K of 14 μm/hr$^{1/2}$. From this, it can be calculated that the 190 μm foil or coating would be consumed in 180 hours. A coating that would not be consumed in one year would have a thickness of 3.5 mm.

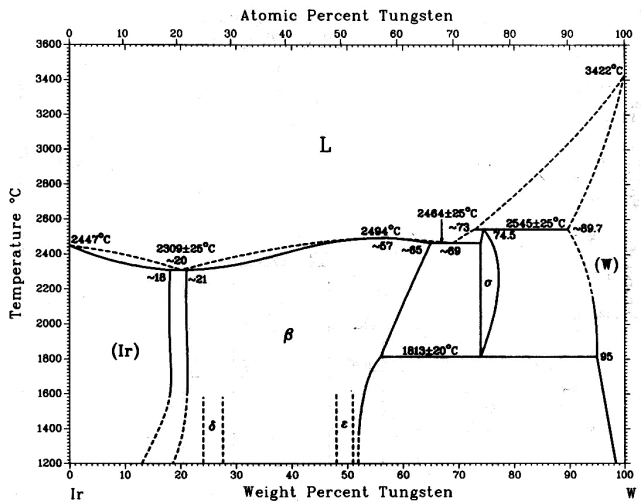
The above calculations indicate that coating thickness values needed to maintain an Ir or Re coating for a one-year life are quite thick, and are similar to the values from the calculated simulations. In practice, it may not be necessary to maintain a composition at the surface near that of the original coating, as intermetallic phases will remain with substantial content of the coating material after the coating itself is consumed. It is possible that coating thickness values of half those calculated above could provide substantial benefit even after the coating layer itself diffuses into the subsurface.

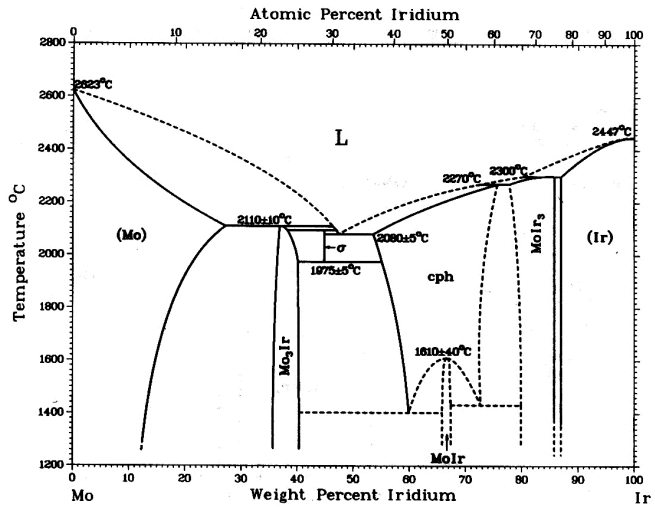
Recommendations of Future Research

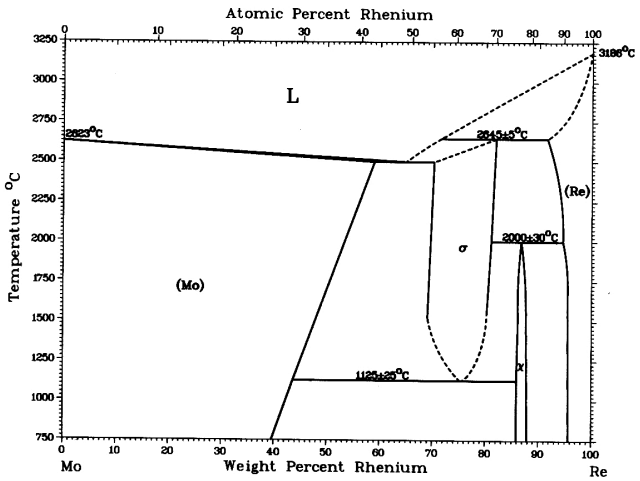
The formation of crystals on the orifice and skirt of the quartz melter is the main reason for failure and subsequent shutdown of quartz melters. Considering the findings above, two potential approaches for extending the quartz melter lifetime can be considered. The first is to eliminate or reduce the rate of crystal formation. The second is to control the location and or direction of crystal growth. Alternative design changes that could potentially eliminate / minimize or direct crystal growth away from the orifice and need to be evaluated and tested.

Iridium and rhenium coatings on molybdenum offer potential for reducing or eliminating crystal growth in quartz melting furnaces due to lower oxide partial pressures. Yet due to diffusion, the coating thickness likely needs to be about 1mm thick in order to provide benefit for 1 year of service. This thickness is at the high end of the range of coatings deposited by CVD and electro deposition. It is a thickness frequently deposited by plasma spraying. In any future testing coating thickness should be considered as a variable. Future testing could be used to validate diffusion simulations and provide better thermodynamic data and information on intermetallic precipitation at the metal-metal interface. The surface composition as a function of time could be calculated using thermal diffusion software. It would also be useful to characterize both diffusion couples by electron microprobe to assure proper phase identification and to determine the concentration gradients in the solid solution phases. This information could then be used to verify the reliability of the diffusion model. To predict the effect of the glass melter on chemical activity as a function of time and diffusion, e.g. formation of volatile Mo-O_X species from the intermetallic phases requires data not available.

Published binary phase diagrams are available for W-Ir, Re-W, and Mo-Re.



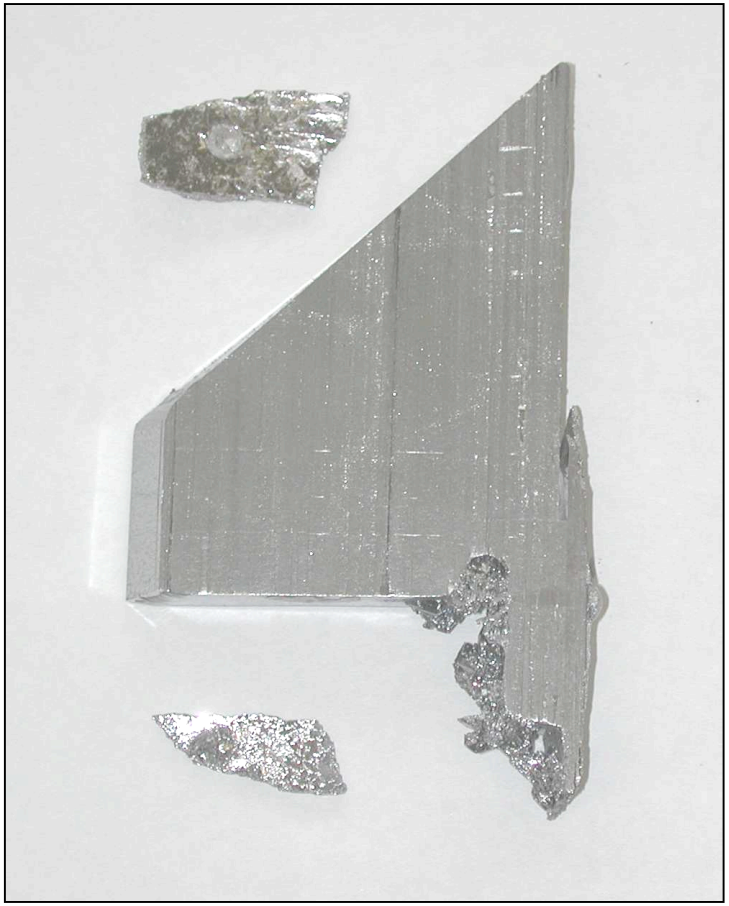




- **However, computational thermodynamic data for these systems are not established yet.**
- **Therefore, simulations considered only solid solution end members and ignoring the formation of intermetallics.**

Fig. 1

OSRAM ‘02 Samples Locations



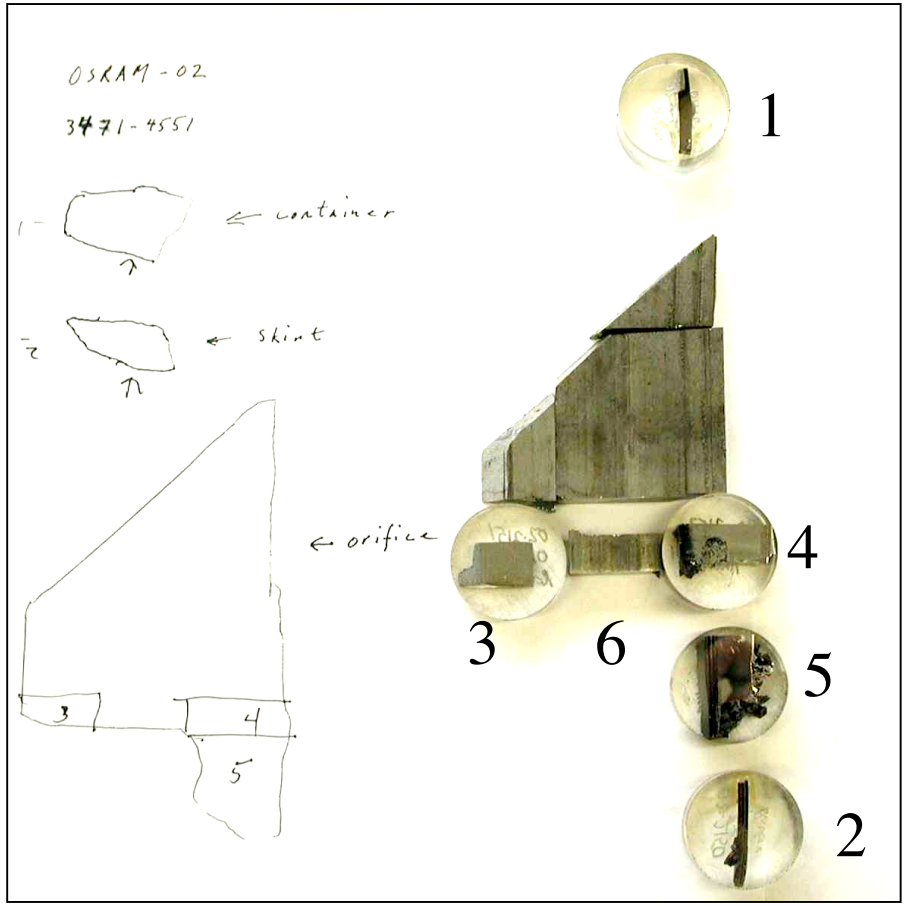


Fig. 2

OSRAM '02 Orifice Sample 5 - EDS Spectra

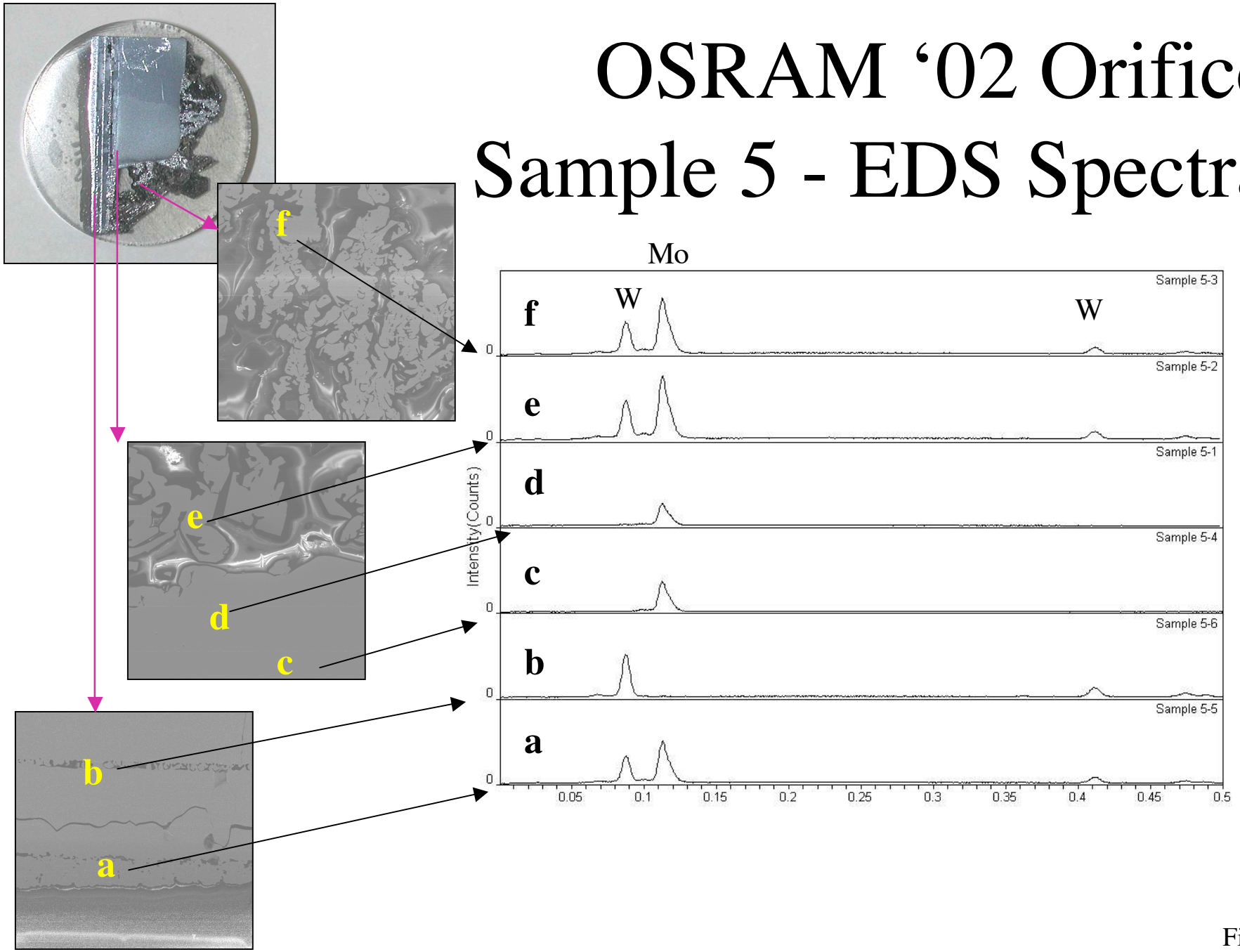


Fig. 3

OSRAM '02 Orifice Sample 4 - EDS Spectra

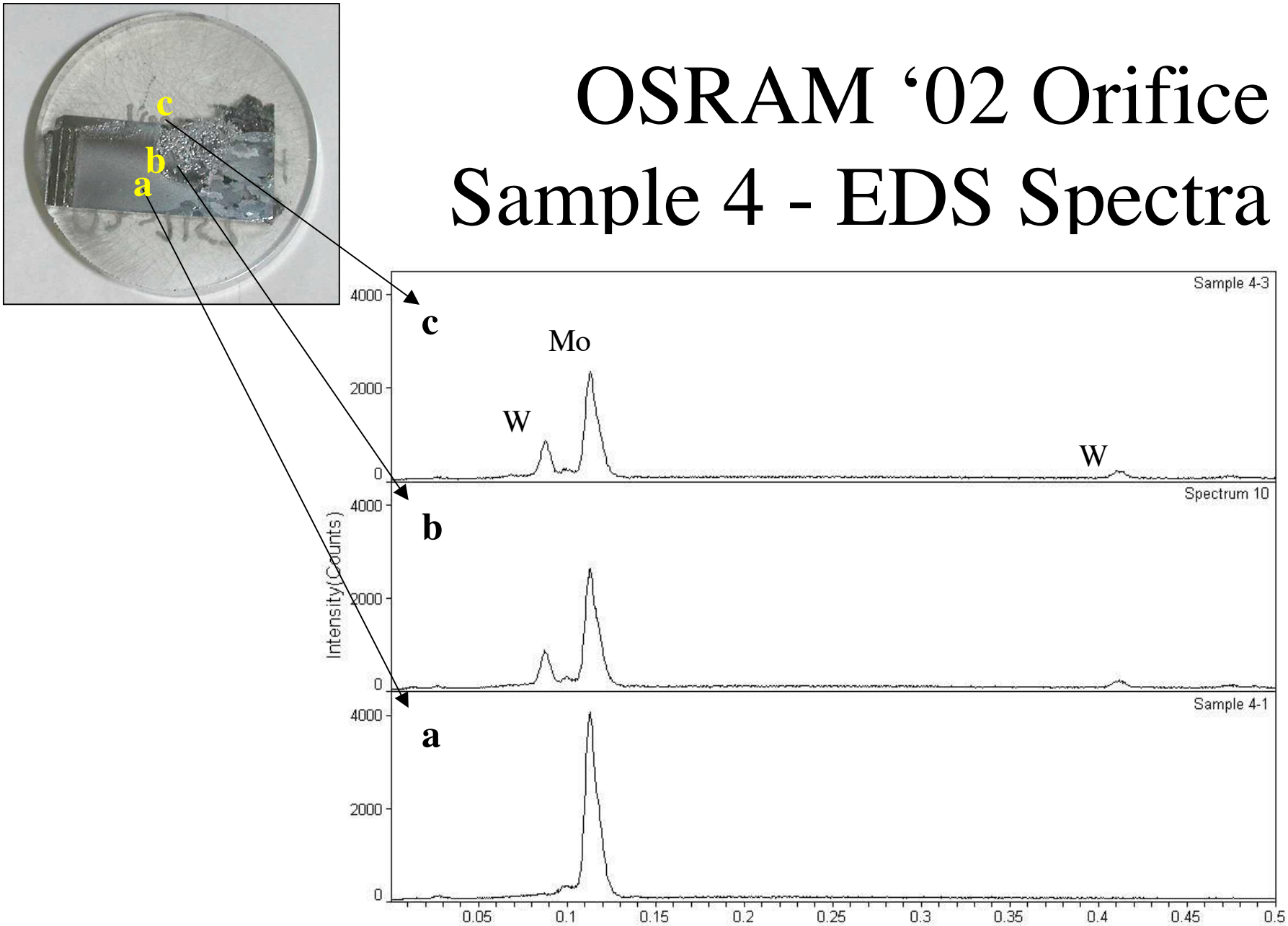


Fig. 4

OSRAM '02 Skirt
Sample 2 - EDS Spectra

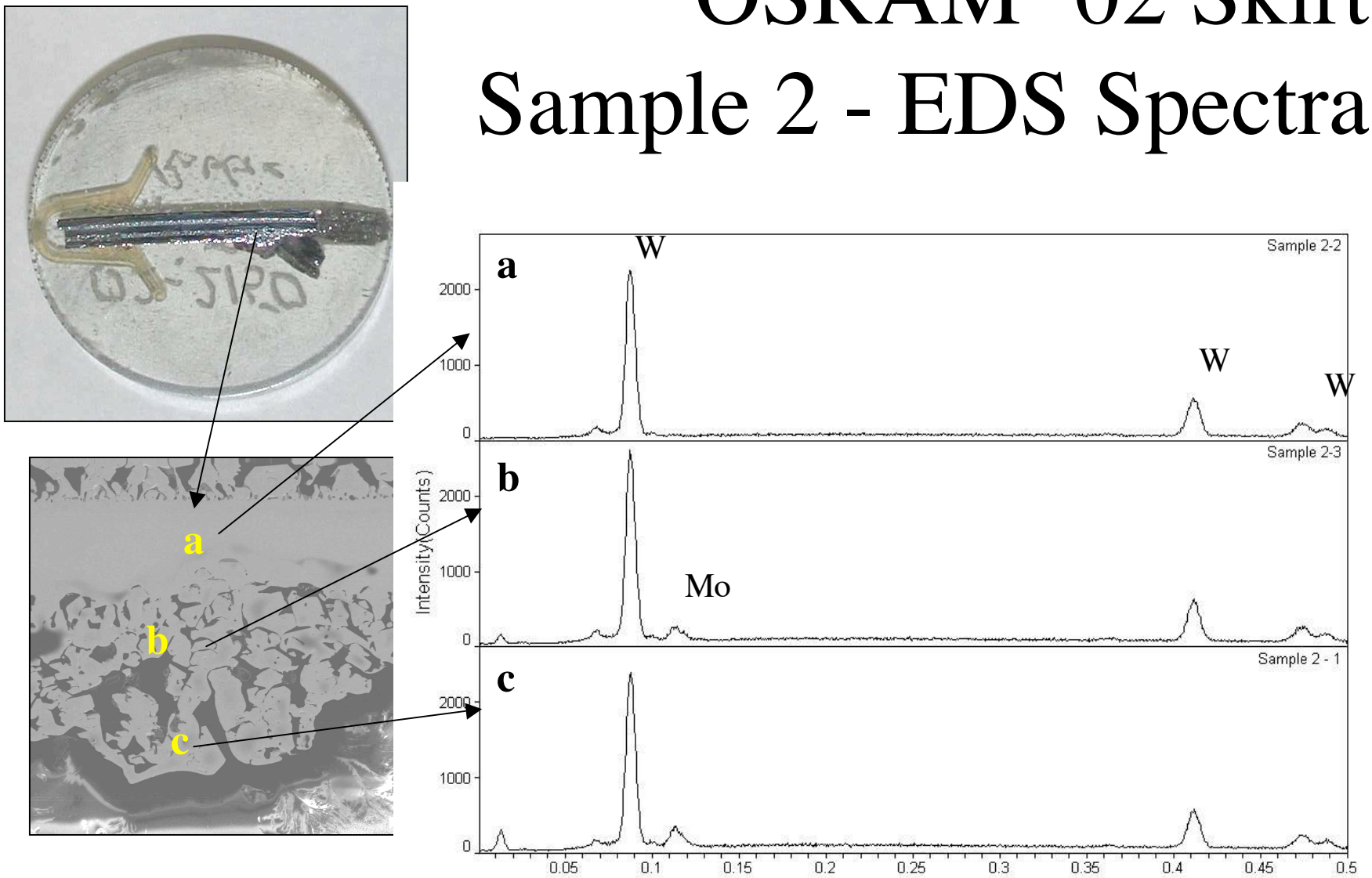


Fig. 5

OSRAM ‘02 skirt was sampled at 3 locations starting near the orifice

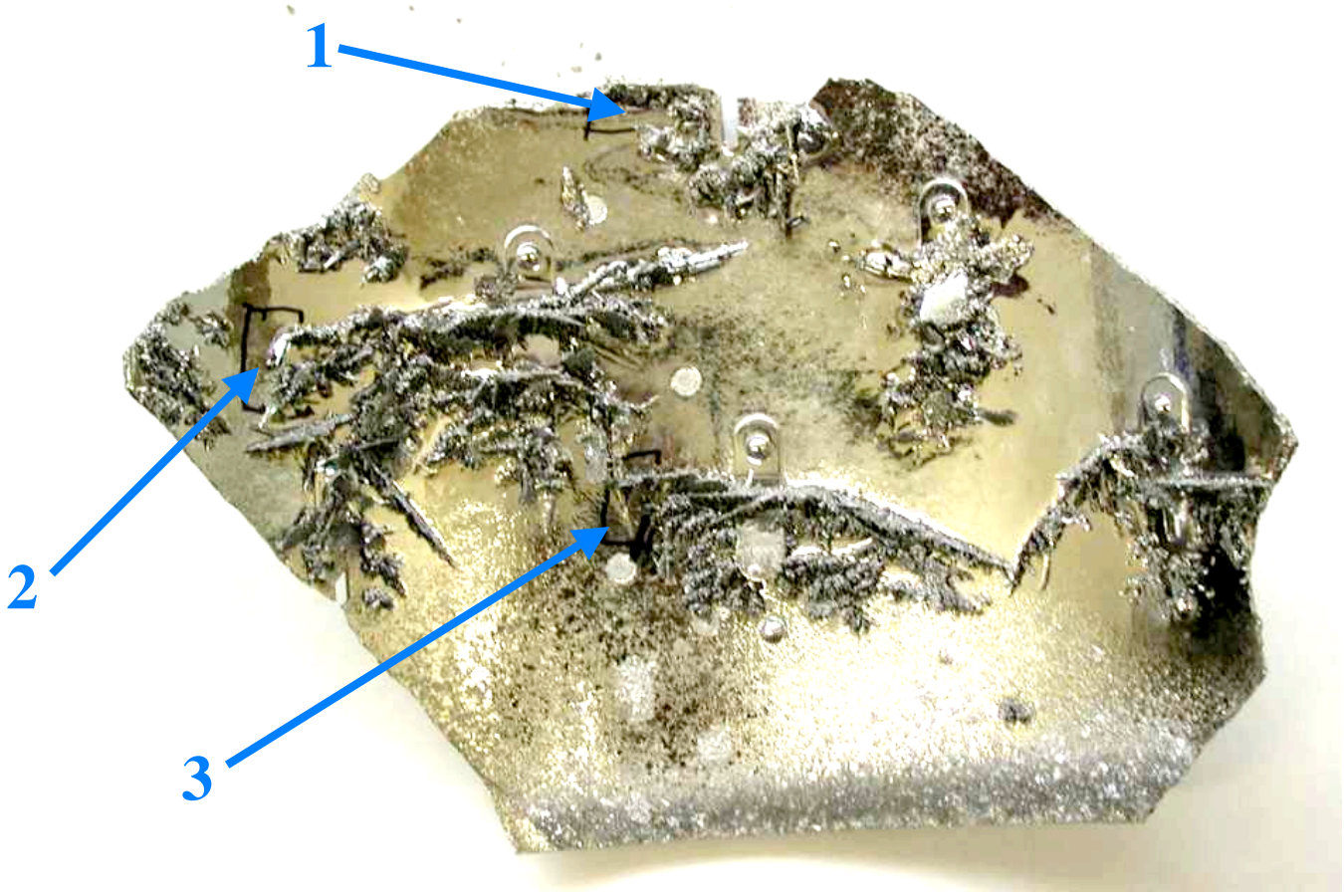
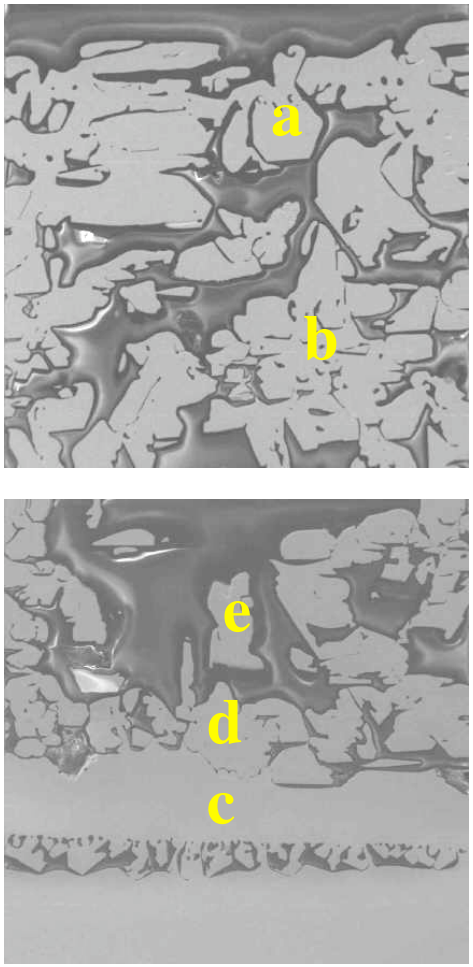


Fig. 6

OSRAM '02 W skirt sample #1 located near the orifice



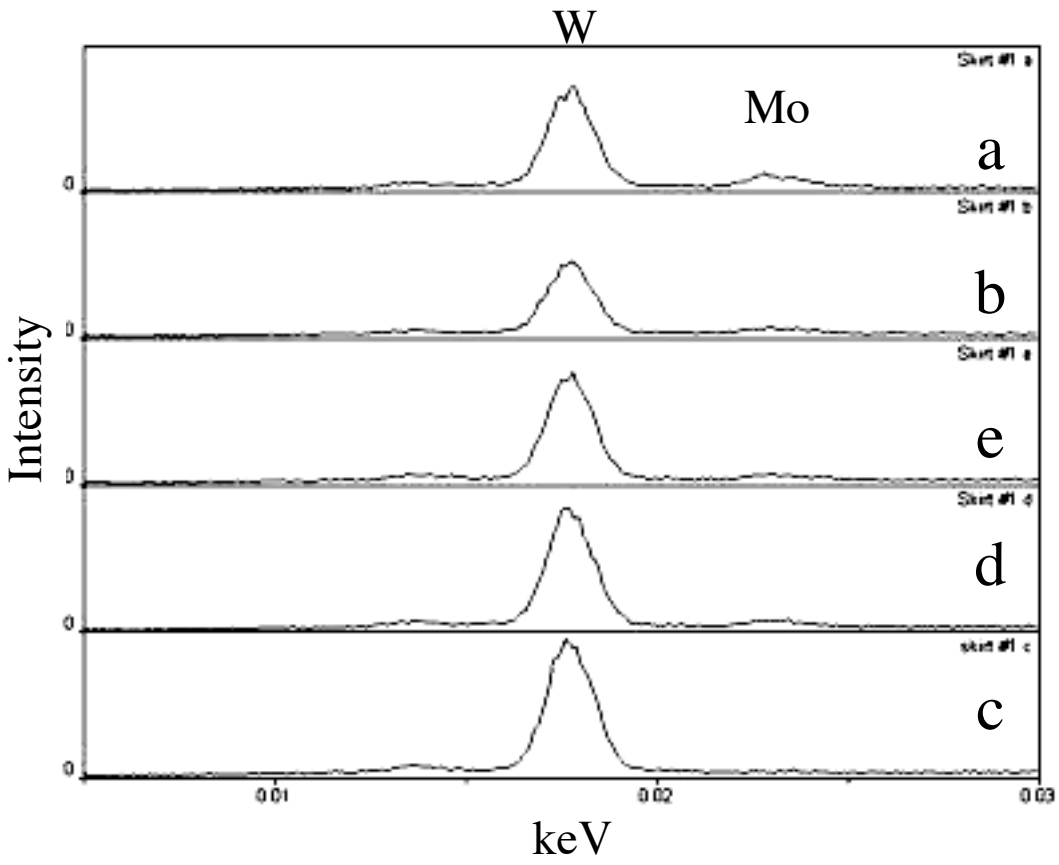
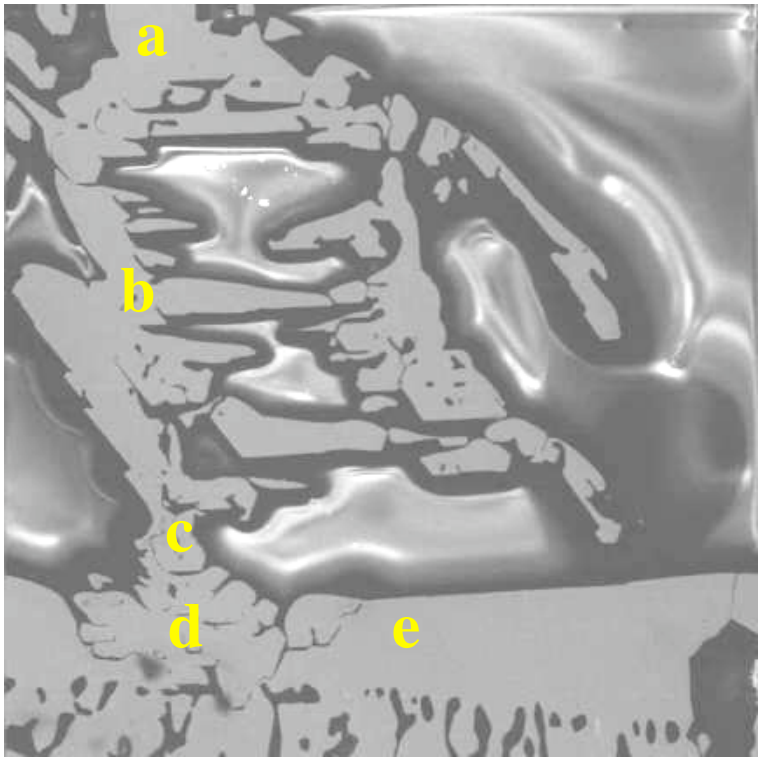


Fig. 7

OSRAM ‘02 W skirt sample #2 located half way down the skirt



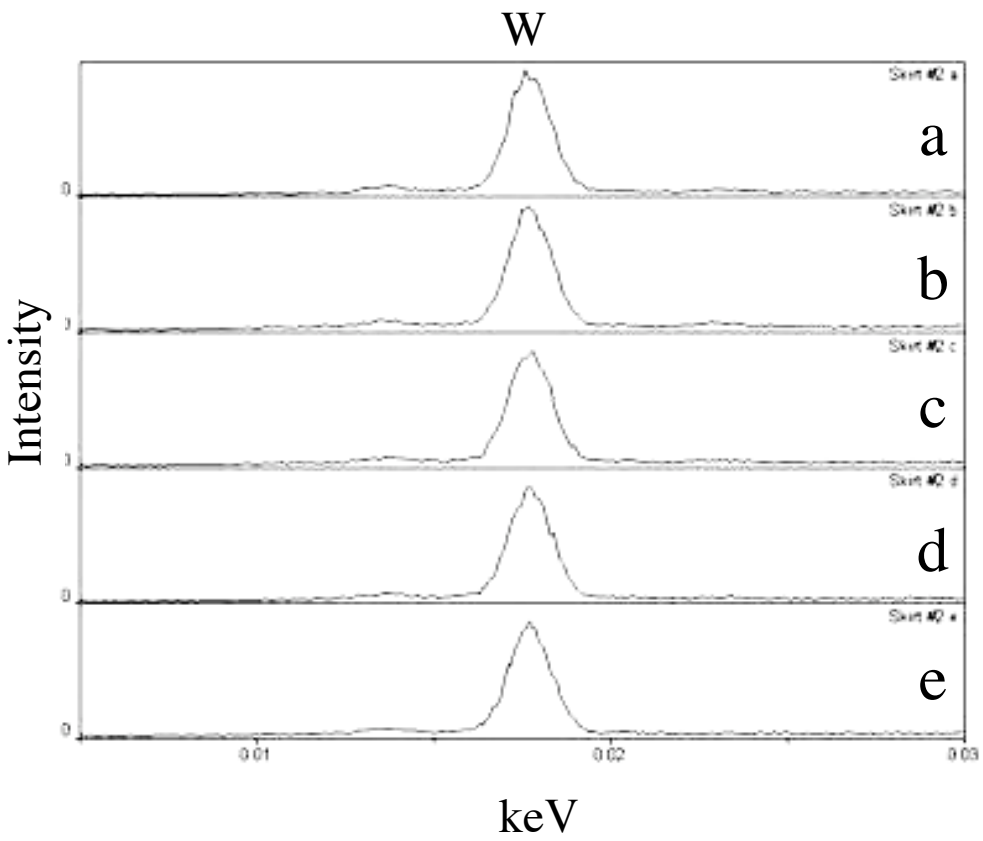
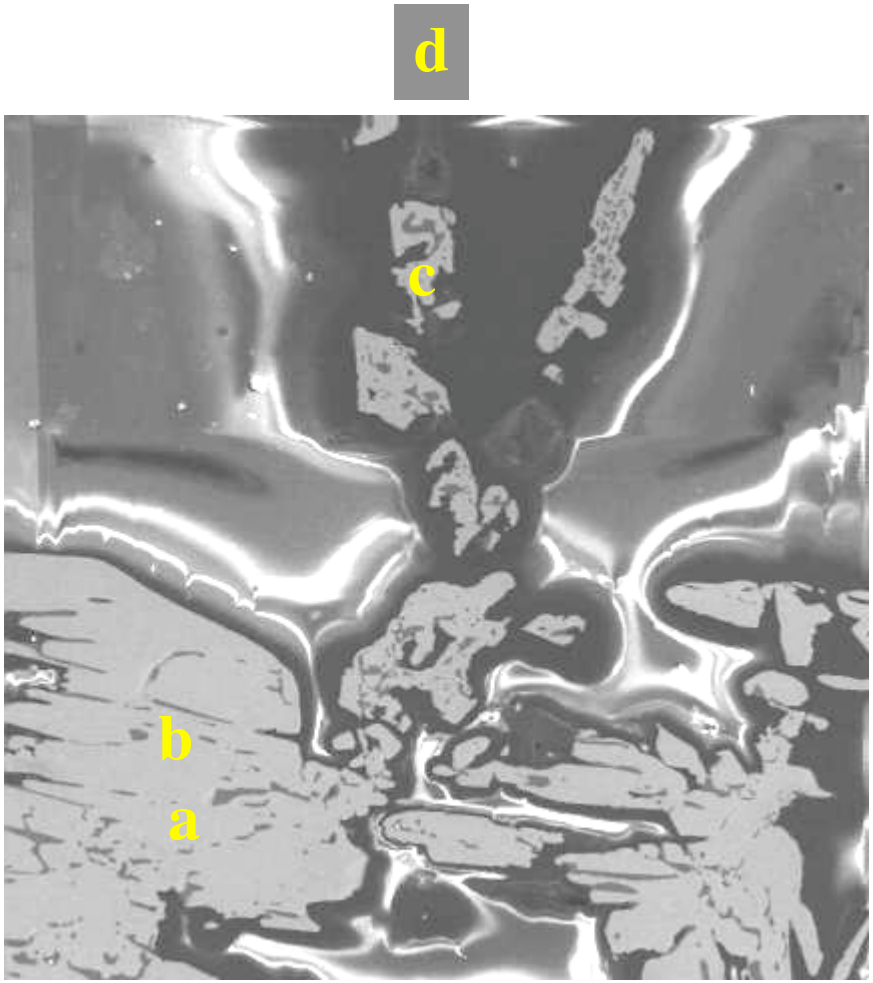


Fig. 8

OSRAM '02 W skirt sample #3 located away from the orifice



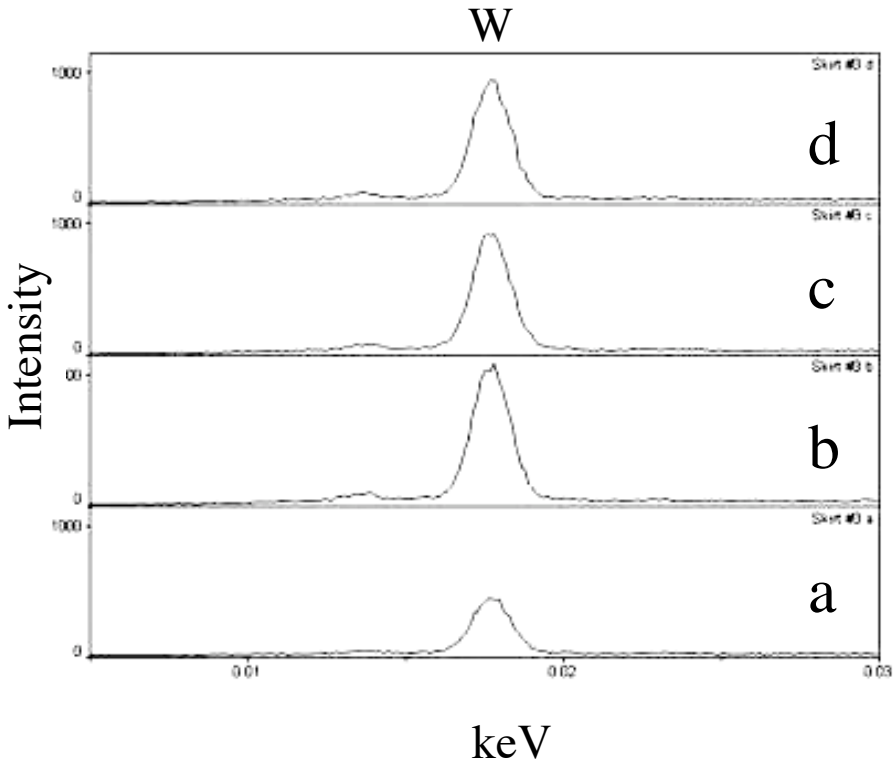


Fig. 9

Outer surface of crystals show some Mo deposition in skirt sample from near the orifice

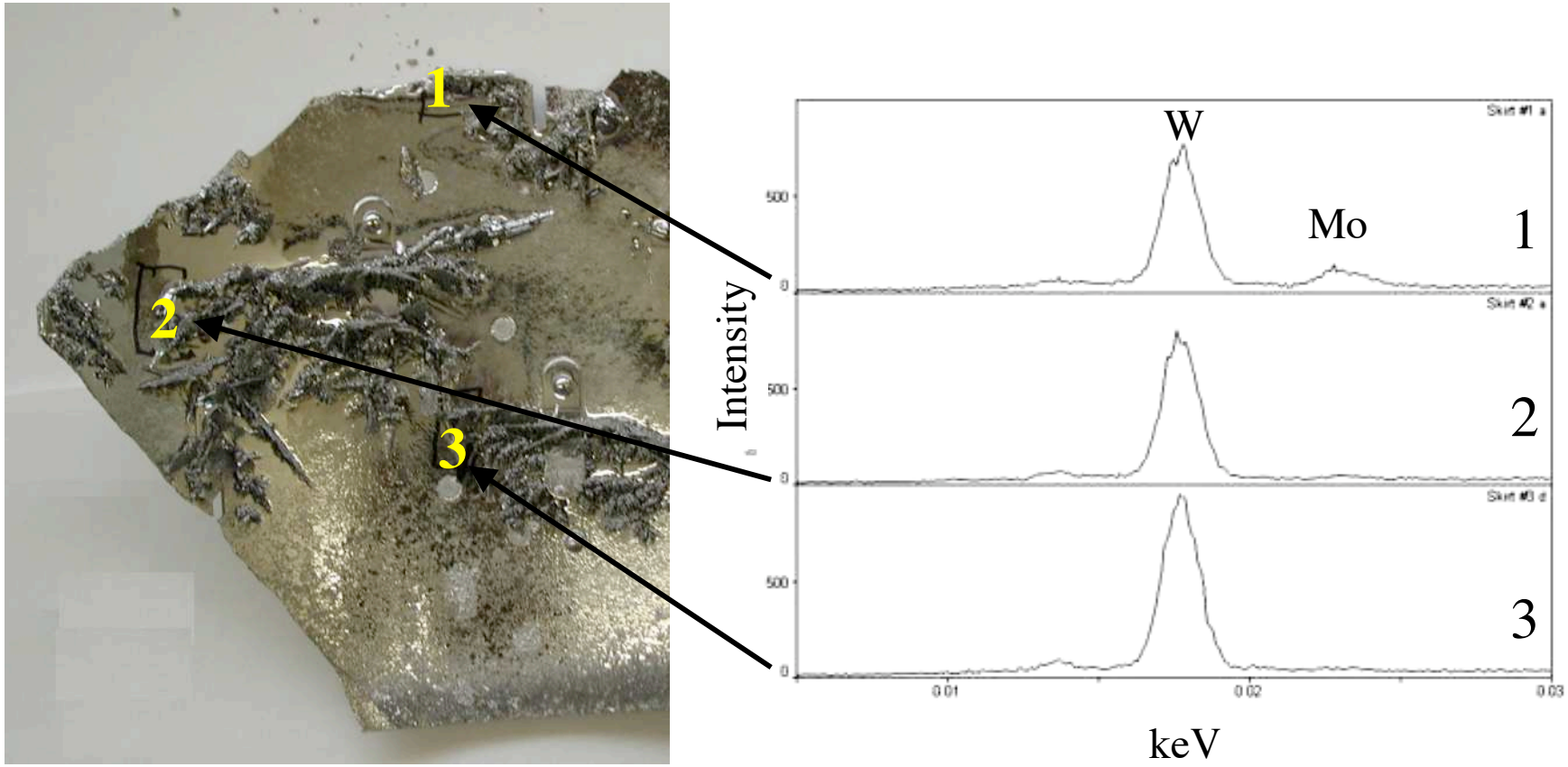
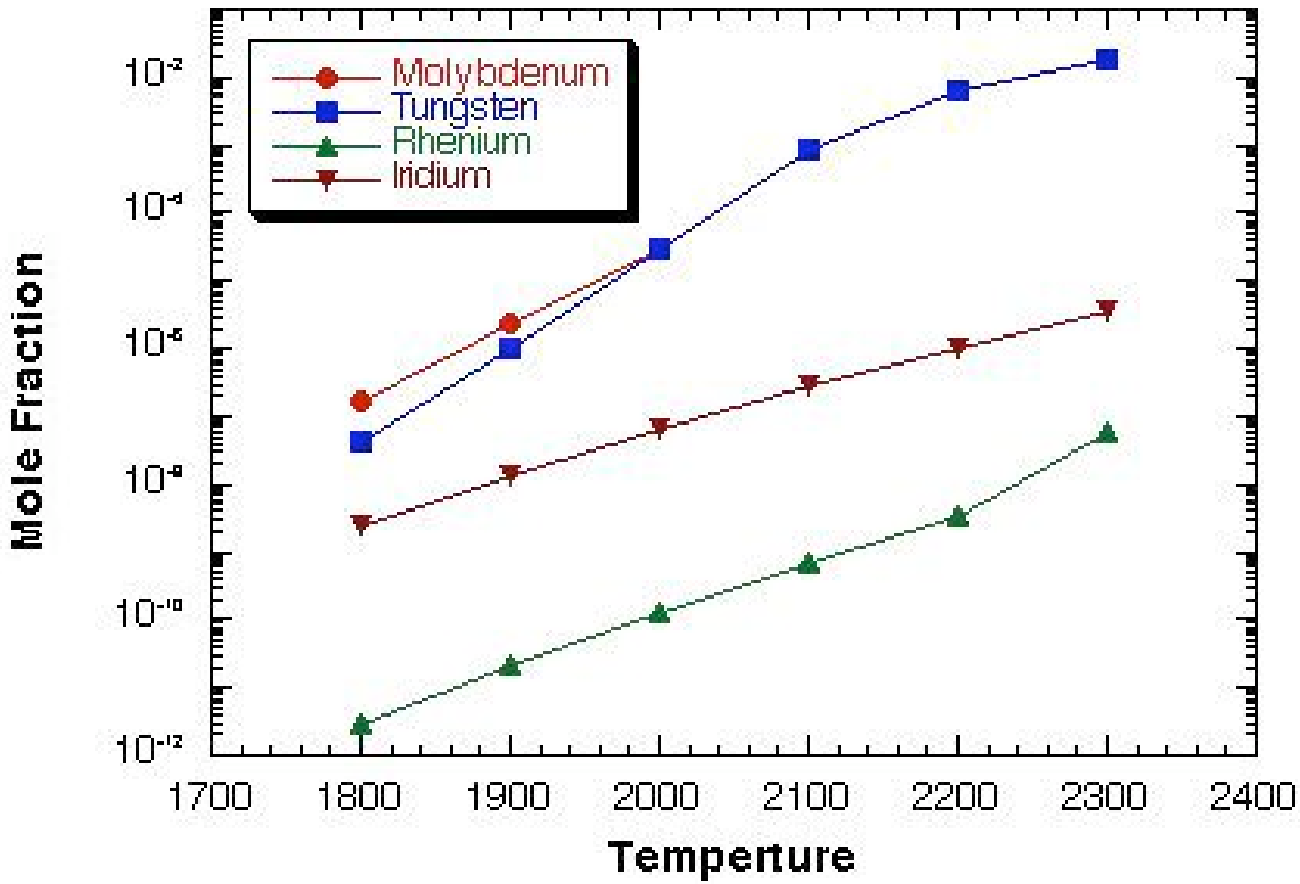


Fig. 10

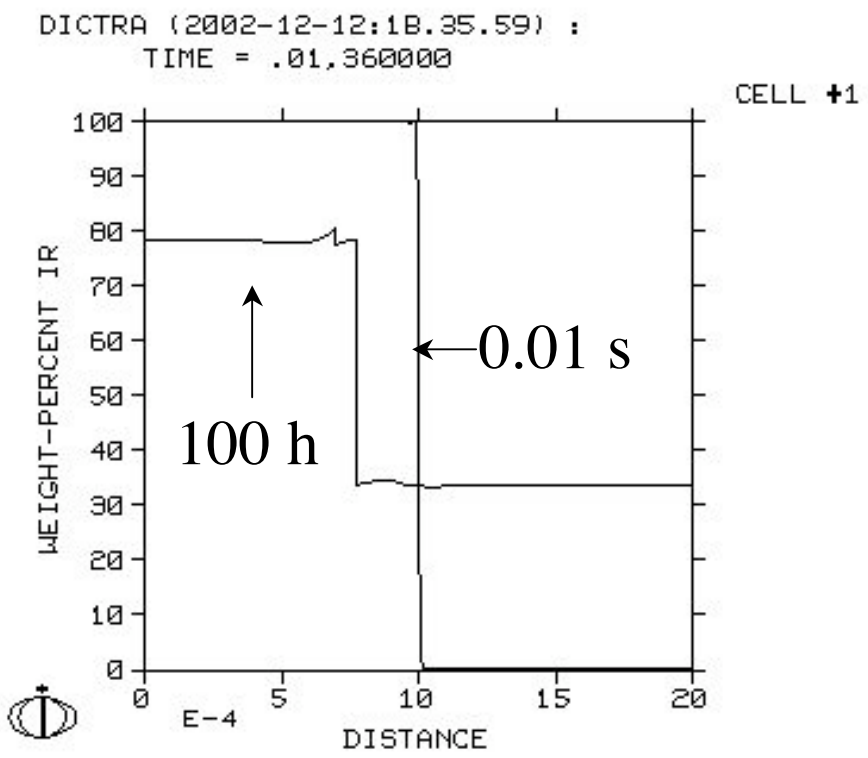
Re Appears to Have a Lower Mole Fraction Than Either Mo, W or Ir



The mole fraction of the metallic oxide species present in an idealized gas environment of a quartz melter were calculated for increasing temperatures.

Fig. 11

Diffusion controlled simulations for Ir(fcc)-W(bcc)



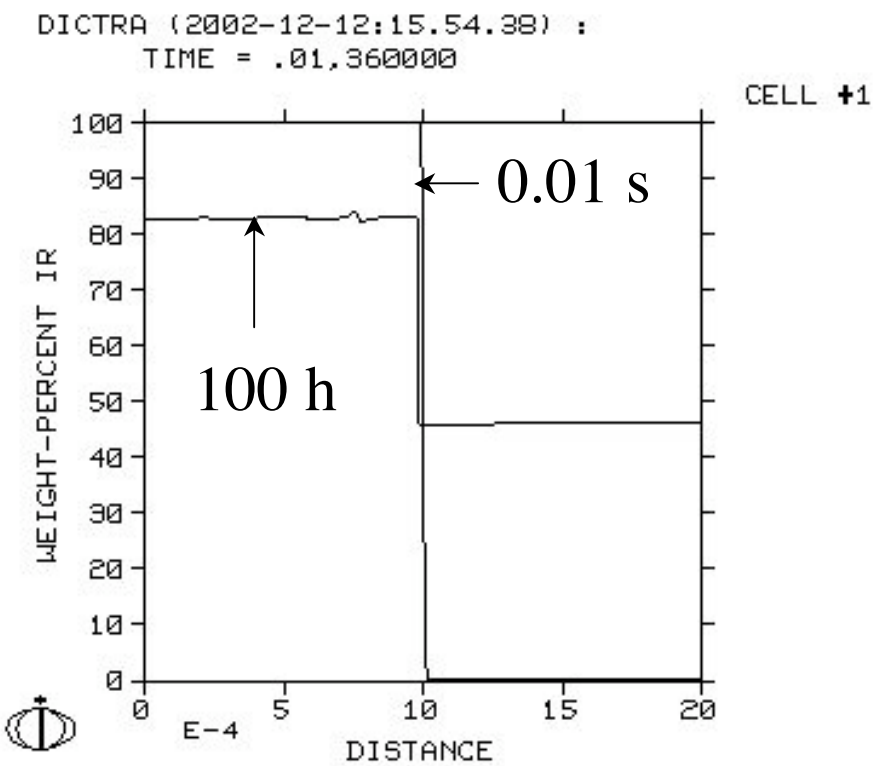
Ir	W

- **The simulations show cross diffusion & interface movement between these phases just after 100 hr at 2273 K.**

- **However, these calculations do not consider any intermetallic precipitation or σ phase.**

Fig. 12

Diffusion controlled simulations for Ir(fcc)-Mo(bcc)



Ir	Mo

- **The simulations show extensive cross diffusion but with limited interface movement between these phases just after 100 hr at 2273 K.**
- **However, these calculations do not consider any intermetallic precipitation.**

Fig. 13

Molybdenum – Iridium diffusion couple with likely phases.

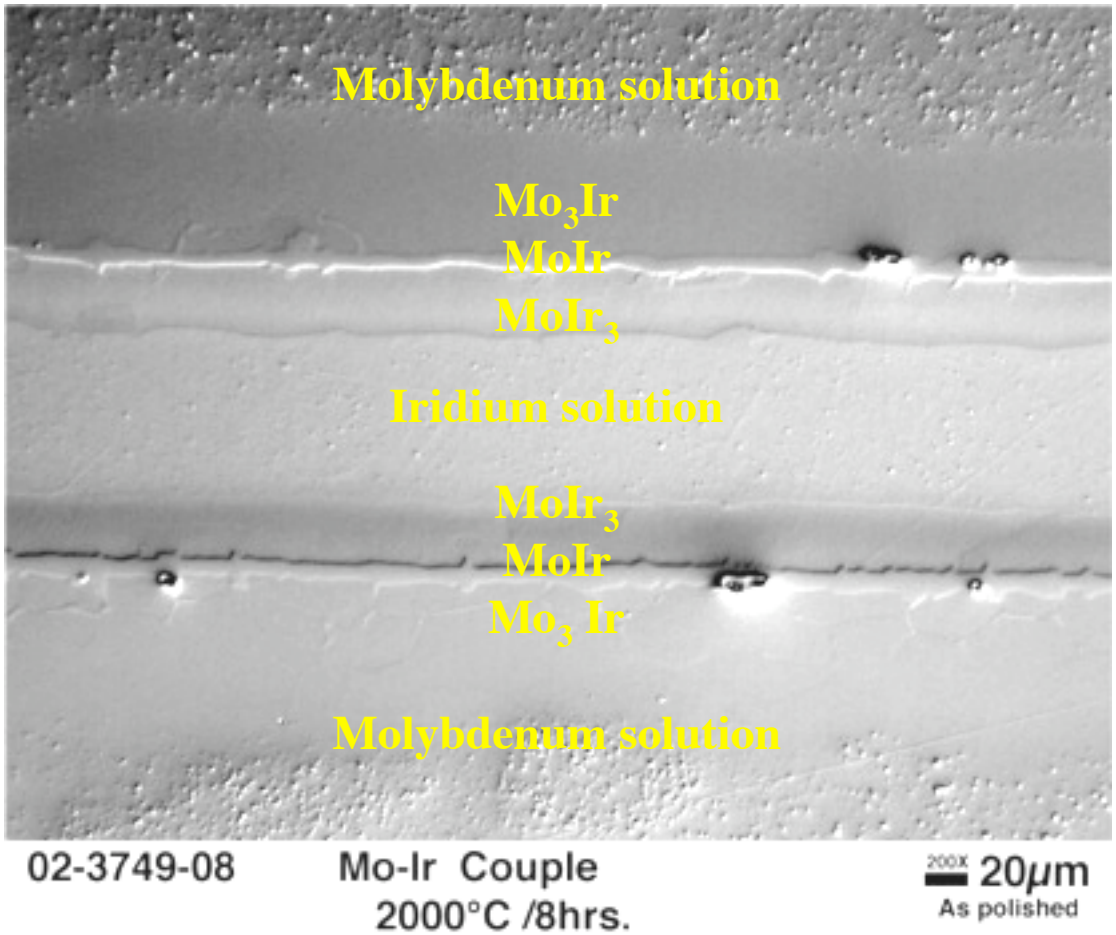
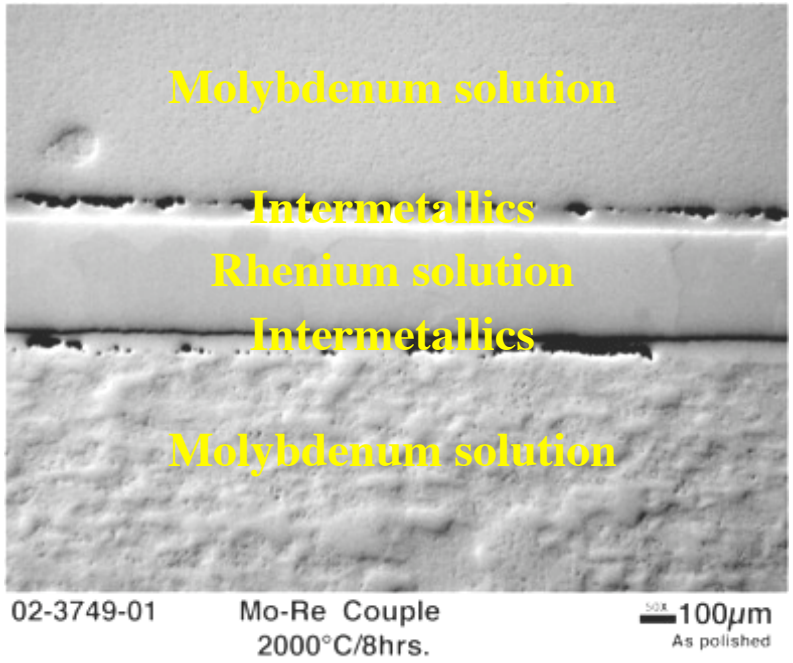


Fig. 14

Molybdenum –Rhenium diffusion couple with likely phases.



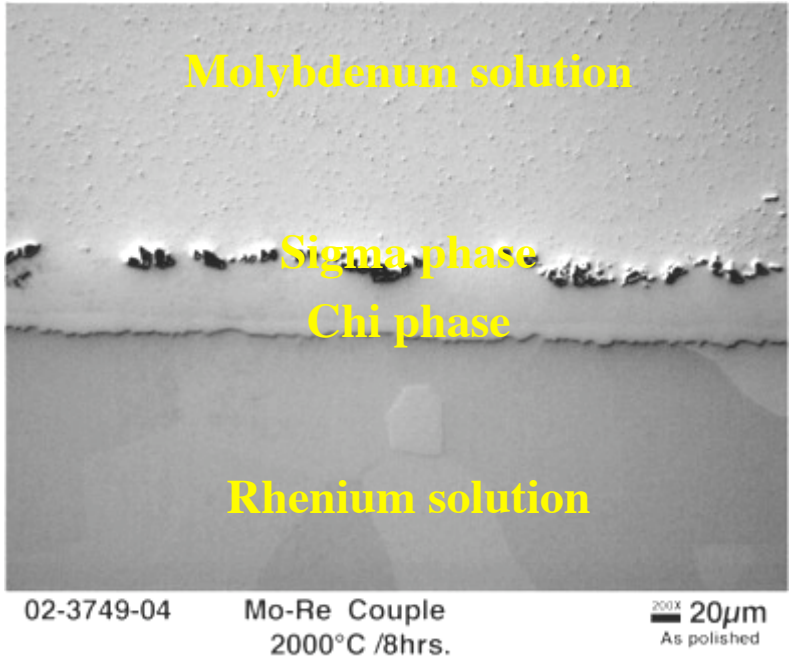


Fig. 15