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THE TRAVELLING SOLVENT METHOD OF CRYSTAL GROWTH

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I. INTRODUCTION

During this period work has been directed along the following avenues:

(1) Construction of an ultra high vacuum system containing facilities for electron beam heating of SiC and for vapor deposition of chromium upon clean silicon carbide surfaces.

(2) Investigations of the SiC-Cr, SiC-Si and SiC-Pt systems.

II. DISCUSSION

(a) The Silicon Carbide-Chromium System

Chromium has been successfully passed through silicon carbide by the Travelling Solvent Method of Crystal Growth (TSM). Fig. 1 is a photomicrograph of one specimen. The arrows indicate the position of the chromium layer prior to zone passing. As is readily seen complete regrowth occurred and no interface is discernable.

Previous reports prepared under this contract have discussed the difficulties encountered with this system; in particular, wetting has always been difficult to accomplish in reproducible fashion. If interfacial dissolution is taken as a criterion of wetting, the existence of difficulties in this area is rather surprising since it is well known that silicon carbide dissolves, in appreciable quantities, in molten chromium. Confirmation of solubility was obtained at TLI in an experiment where silicon carbide was introduced into molten chromium in an arc furnace. Dissolution was observed to occur readily. In view of this data, the probability arises that some physical barrier (an oxide film or adsorbed gas layer for example), preventing wetting, exists at the SiC-Cr interface and that in the particular specimen configuration and conditions used for TSM, the molten metal is unable to penetrate the barrier.

Silicon carbide is only obtainable in reasonable quantities in pieces of irregular shapes and sizes; cutting and grinding operations are, therefore, necessary prior to final specimen assembly. The usual technique involves polishing with diamond powder and etching in molten sodium hydroxide at 700°C as finishing operations. Careful observation of specimen surfaces strongly indicates the existence of an oxide film (specular surface colorations) of appreciable thickness following etching, a process usually assumed to "clean" surfaces. In addition, the process is not readily controllable since various colorations result even though care is exercised in controlling the etching parameters such as temperature and time.

An alternative surface preparation procedure has been devised which attempts to eliminate the apparently inherent variables discussed above, and to produce really clean silicon carbide surfaces on which to

place chromium. The technique involves subjecting samples to vacuum approaching 10^{-10} mm Hg and heating by electron bombardment to 1300°C - 1400°C . This process removes adsorbed gas films and also apparently strips off surface oxide layers. The immediate visible result is that of greatly enhanced reflectivity. (Such techniques are used frequently for producing ultra-clean metal surfaces to facilitate measurement of such parameters as thermionic work function.) Subsequent to electron bombardment, a thin film of chromium is evaporated onto the cleaned surfaces, in the same apparatus, using a heated tungsten filament. The apparatus is shown schematically in Fig. 2. In the high vacuum environment, it is not necessary to heat the chromium to its melting point in order to evaporate a sufficient quantity for surface coating purposes. Evaporation in a high vacuum chamber should greatly assist in purifying, with respect to gas content, the chromium metal. The possibility that impurities in the chromium play a part during wetting has been discussed in a previous Quarterly Report.

First attempts at preparing clean silicon carbide surfaces with chromium deposits upon them were very encouraging. The deposits were quite smooth and apparently adherent to the substrate since, immediately following deposition, the samples were reheated to 1300°C after which no evidence of peeling or blistering was observed.

Two pairs of specimens prepared by the new technique were assembled into sandwiches, containing thin slices of chromium metal. The sandwiches were placed upon a graphite block which was heated by r. f., cooling from the upper surfaces of each sandwich being by radiation. Argon was used as a protective atmosphere during the duration of the experiment. Prior to the zone passing attempt, a small quantity of the vapor-deposited chromium was removed, by scratching with a steel point, from a limited area of one silicon carbide slice. The specimen was left in the atmosphere for twenty minutes before sandwich assembly.

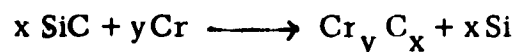
After flushing the apparatus for ten minutes with argon, the graphite block was heated to 1870°C (optical pyrometer reading) and held at this temperature for 1 hour, 40 minutes. The temperature gradient across the sandwiches was of the order of 100°C . Fig. 1, discussed in the

opening paragraph of this report, demonstrates that complete zone passing took place during the experiment and that regrowth, from chromium solution, of silicon carbide onto a silicon carbide substrate is possible by TSM. That the original internal surface of the substrate is not discernible, emphasizes the excellent manner in which crystallization has occurred using this novel approach to crystal growth.

Fig. 3 is a photomicrograph of a section through the sandwich containing the partially removed chromium deposit. The void present corresponds to the region where the deposited chromium was removed, and demonstrates that wetting did not occur over that area. Over the remainder of the specimen, where the deposited film was complete, regrowth occurred.

The new surface preparation procedure described above may, at first sight, appear somewhat extreme. We suggest, however, that the results obtained using the first specimens prepared in this way, and particularly the findings illustrated by Fig. 3, fully justify the effort involved, and demonstrate the significance of good wetting in TSM. Using these techniques, P-N junction fabrication in silicon carbide will be attempted.

A detailed consideration of the SiC-Cr system suggests that crystal growth and possible P-N junction fabrication may require, for optimum conditions, rather more control than was previously believed. For example, published thermodynamic data show that the reaction



is thermodynamically feasible. If the above reaction does, in fact, take place, it appears to proceed slowly since no experimental observation of chromium carbide formation has been made during our work on this system. It appears, therefore, that the kinetics of the reaction are determining, so that the absolute value of temperature (of sandwiches) may also require control in addition to the temperature gradient which provides the driving force for zone movement.

Accurate temperature control of sandwiches during zone passing is not readily accomplished with either r. f. heating or with the radiation heating apparatus utilizing a directly-heated graphite strip (previously described in Quarterly Report #3.) A simple electron beam device has been constructed to facilitate the desired control and flexibility. This

is shown schematically in Fig. 4. The length of "A" (Fig. 4) may be readily varied in order to change the temperature gradient across the specimen. A 4,000 V, 25 ma power pack capable of delivering up to 100 watts with continuous power control is sufficient to produce the necessary specimen temperature; 1900°C in the case of the chromium silicon carbide system.

(b) The Silicon Carbide-Silicon System

The potential value of silicon as a solvent for silicon carbide in TSM has been discussed in a previous Quarterly Report. In contrast to the case of chromium discussed above, no serious wetting problem has so far been encountered. Figure 5 shows a typical sandwich prepared simply by melting a small quantity of silicon between two silicon carbide slices, using r. f. heating. As can be seen from the micrograph, the junctions are extremely planar, and wetting appears quite complete. Molten salt-etching of the silicon carbide samples prior to sandwich assembly was observed to produce somewhat inferior results and has accordingly been discontinued.

No evidence of zone movement has been obtained in the silicon-silicon-carbide system to date. The problem appears to be one of temperature gradient. Specimens placed upon a small graphite block in contact with a water cooled heat sink and heated from above using r. f. heating showed no measurable (optical pyrometer) temperature gradient. Replacing the graphite with a small tungsten rod improved the gradient conditions. When the films of gallium were placed at the specimen-tungsten interface and at the tungsten-base plate interface, the measured gradient across the specimen (typically 3 mm thick) increased to 160°C. However, no zone movement was observed after two hours at temperature. Placing the specimen in direct contact with the water-cooled base plate resulted in excessive heat losses, and the specimen temperature could not be raised to the melting point of silicon.

While no really accurate constitutional diagram of the silicon-carbide system exists as far as we are aware, it is known that silicon carbide is soluble in liquid silicon and the solubility increases with temperature. The available data, however, indicate that the slope of the liquidus

is very steep, e. g. , one tentative diagram shows solubility increasing to 10 at % from the melting point of silicon to about 2300°C. From such data, we conclude that in order to provide a driving force of sufficient magnitude for zone movement, the gradient across the specimens must be relatively large, i. e. , of the order of 250 - 300°C. A similar state of affairs existed in the cases of gallium arsenide and gallium phosphide during work within this laboratory, and in these instances zone passing occurred quite readily when sufficiently large temperature gradients were obtained. At present, active experimentation is in progress aimed at optimizing the thermal conditions for the silicon carbide-silicon system.

(c) The Silicon Carbide-Platinum System

During the course of the last month, initial studies have been made on the use of platinum as a solvent for silicon carbide in TSM. The selection of platinum as a possible solvent resulted from a chance observation of a solid state reaction occurring between a piece of silicon carbide and a platinum-platinum rhodium thermocouple during an experiment.

The resistance heating temperature gradient apparatus (previously described) has been used for studying the platinum-silicon carbide system. Sandwiches may be prepared quite readily, and wetting does not appear to be a problem. A number of difficulties involving loss of platinum, apparently resulting from too high temperatures and subsequent evaporation, have been encountered. In the particular apparatus used, limiting the specimen temperature to a maximum of about 1860°C has solved the evaporation problem.

Fig. 6 is a photomicrograph of a typical sandwich containing platinum between silicon carbide slices. The "reaction zones" between platinum and silicon carbide are clearly visible along each interface. The particular sandwich was prepared by raising the temperature to 1860°C (optical pyrometer reading), holding for ten minutes, and cooling. In a similar fashion to the silicon-silicon carbide system, the junctions appear flat and wetting quite complete. Fig. 7 shows the structure of the reaction zone (junction between platinum and the reaction zone is shown also) between silicon carbide and platinum for a sandwich heated to 1860°C with

an excess of platinum present. No attempt was made to move the zone in this case, the specimen being subjected to essentially isothermal conditions. The structure observed is eutectiferous and on a very fine scale. Of course, the exact morphology of such a structure is strongly dependent upon the cooling conditions. However, from this experiment we conclude that an eutectic exists in the platinum-silicon carbide system, and that the solubility of silicon carbide in platinum at about 1860°C is of the order of 40 vol %.

Figure 8 shows the appearance of a silicon carbide surface after heating in contact with a small quantity of liquid platinum for a period of only 5 minutes. At the end of the heating cycle the sandwich was split open; Fig. 8 shows the appearance of one of the silicon carbide surfaces immediately beneath the position of the molten platinum drop.

Minor modifications to the strip heating apparatus resulted in superior temperature gradient conditions, and some evidence of zone movement has been obtained in the first zone passing attempt made, although localized cracking of the silicon carbide used in this experiment tended to complicate the interpretation of the results. Of particular interest, however, was the observation that movement only occurred over that region of the sample exposed to the direct radiation from the graphite strip heater. The specimen used was larger in surface area than the hole in a small radiation shield placed between specimen and heater, and movement only apparently took place over a region of comparable dimensions to the area of the radiation shield hole. This observation, we feel, is of great significance emphasizing, as it does, the fundamental importance of sufficiently large temperature gradients to provide the driving force for zone movement in TSM.

III. CONCLUSIONS

Solution of the wetting problem, by means of stringent surface preparation, has resulted in successful zone passing and crystalline regrowth using chromium as solvent for SiC. Experimental findings confirm our thesis that good surface wetting is a basic requirement for crystal growth by TSM.

The provision of a suitably large temperature gradient for the silicon-silicon carbide system now appears to be the only barrier to a successful zone passing in this case.

The most encouraging results obtained from the limited study so far afforded to the platinum-silicon carbide system strongly indicates that further effort on this system is justified.



**Fig. 1 - Section Through Regrown SiC Sample
mag. x 80, unetched**

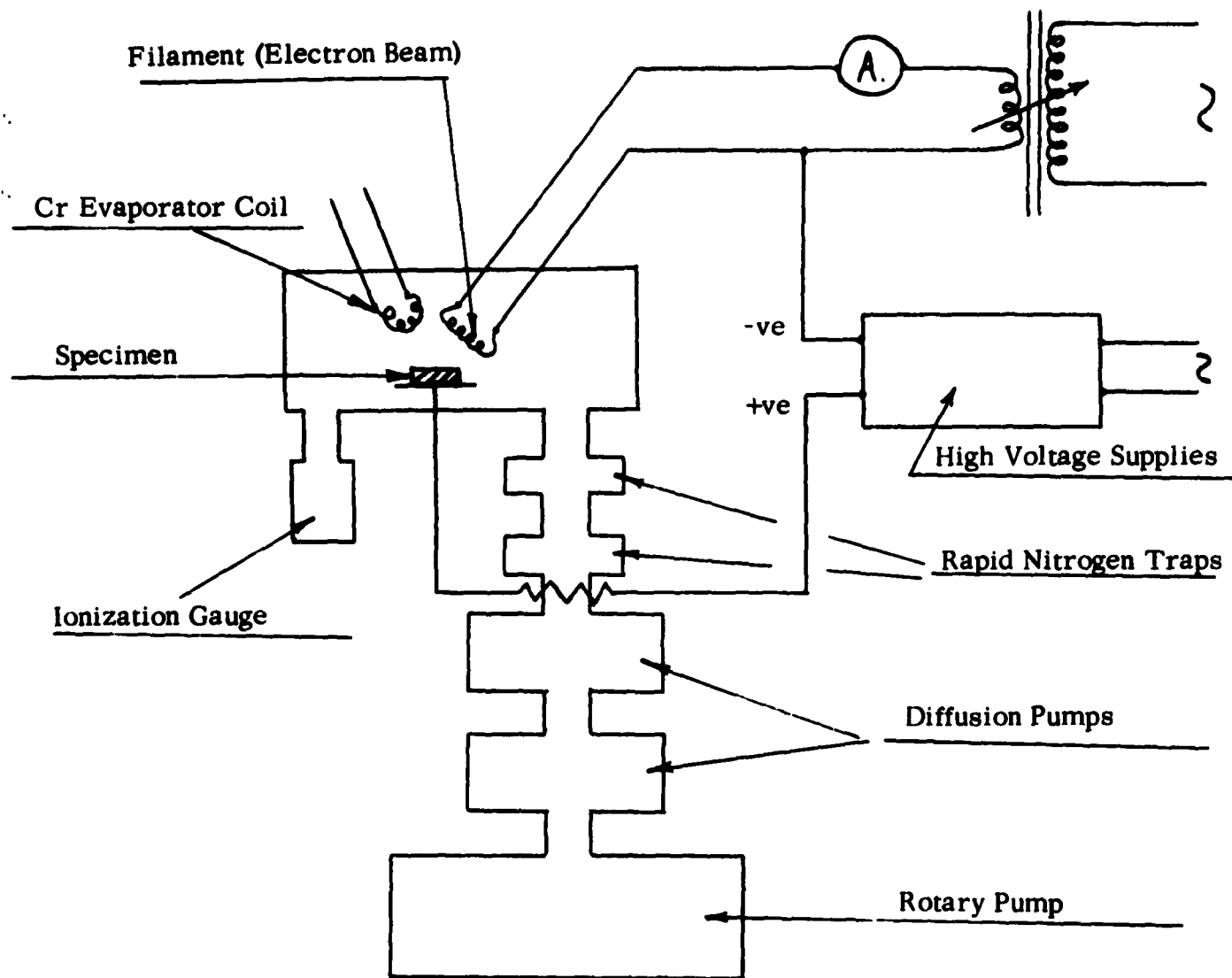
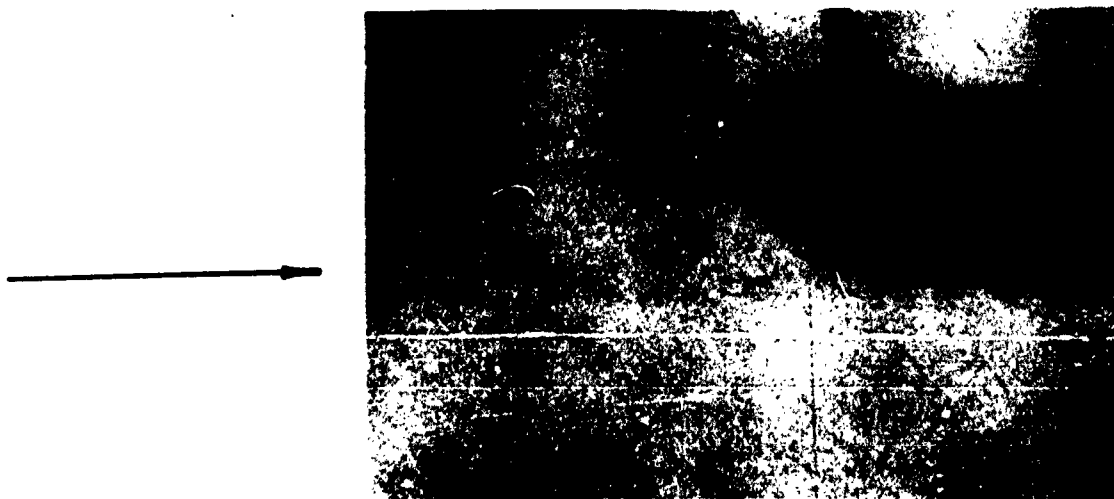


Fig. 2 - Schematic of Vacuum System with Electron-Beam Heating and Chromium Evaporation Facilities



**Fig. 3 - Section Through Regrown SiC Sandwich Showing
Region where Vapor-Deposited Cr was Removed
mag. x 80, unetched**

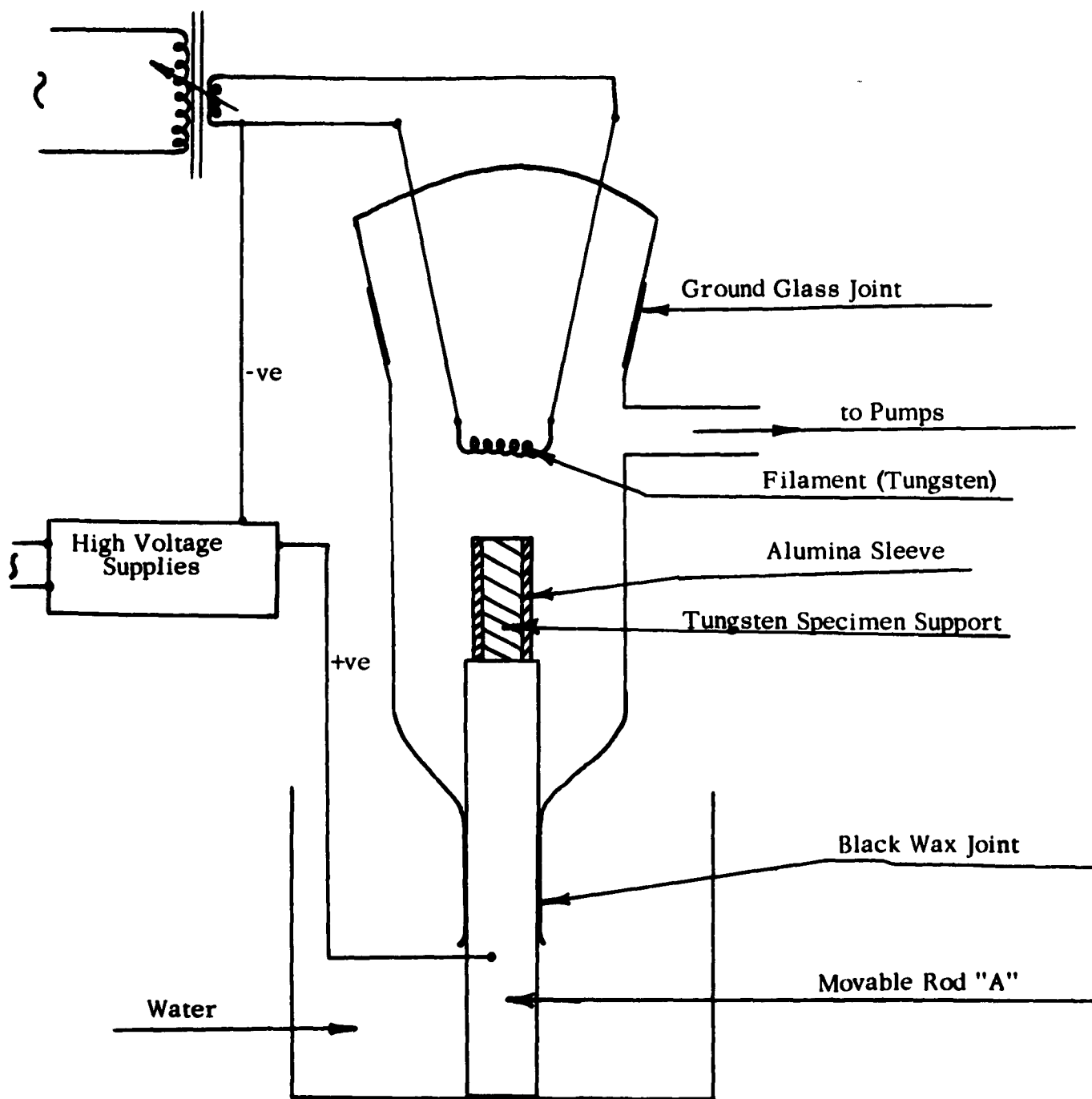


Fig. 4 - Experimental Electron Beam Heating Apparatus

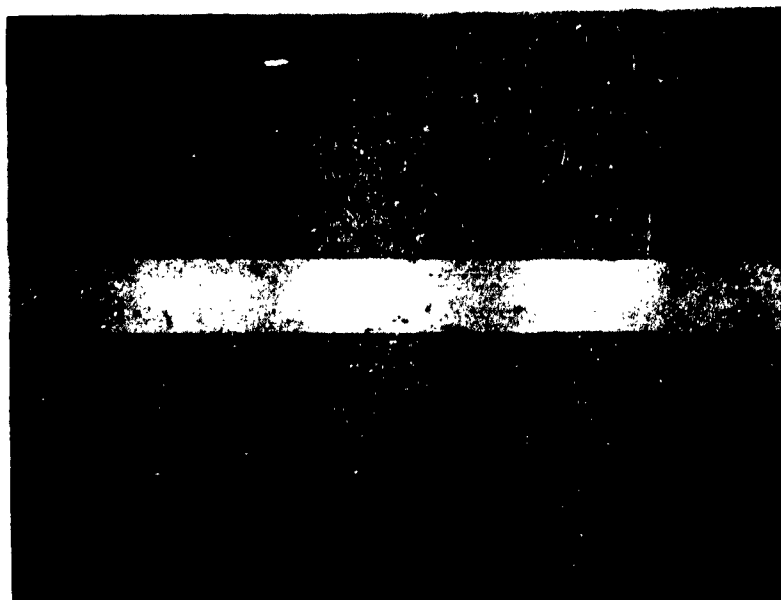


Fig. 5 - Section Through SiC-Si-SiC Sandwich
mag. x 150, unetched



Fig. 6 - Section Through SiC-Pt-SiC Sandwich
mag. x 1000, unetched



Fig. 7 - SiC-Pt System. Structure of Reaction Zone
mag. x 1500, unetched. Edge of Pt Layer at
left hand side



Fig. 8 - SiC Surface after Contact with Molten Pt
mag. x 250, unetched

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Rpt No. AFCRL-62-971. THE
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no. 6, 15 Dec. 1962, 14p., illus.,
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