CeramPhysics, Inc.

921 Eastwind Drive, Suite #110, Westerville, Ohio 43081
 Telephone (614) 882-2231 FAX (614) 882-1437

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QUARTERLY REPORT

Dept. of Energy Contract No. DE-FG01-88CE15401

A Miniature Inexpensive, Oxygen Sensing Element

Quarterly Review

R.W. Arenz

AWA

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J. Aellen - DOE

Calvin Lee - DOE

W.N. Lawless - CPI

C.F. Clark - CPI

✓ OSTI - DOE

R. Tostevin - GBC

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OXYGEN SENSOR 9th QUARTERLY REPORT

7/1/90 - 09/31/90

Overview:

We have made good progress in formulating our procedures for assembly of prototype sensor parts to alleviate problems of oxidation/reduction of components and possibly deleterious interactions of component materials. We have been working exclusively with the simplest form of prototype, i.e. without an incorporated heater. This has been to save assembly time and materials and to simplify the system of the components while we have dealt with overriding, "non-heater" assembly issues. It is anticipated future inclusion of the heater will introduce some new problems to be overcome, but we do not think these will be overwhelming.

Though we have made good progress in many ways, finished prototypes are not exhibiting expected theoretical response to oxygen partial pressure. We have not had success at maintaining perfect hermetic sealing of sensor components, and the simplest hypothesis explaining the deviation of observed response from theoretical is that the tiny leaks which have been present in our prototypes are allowing significant mixing of sample and reference gases, thus reducing sensor response.

Our emphasis in the remaining months of this program will be to produce several hermetic sealed devices; either through persistence in trials using the present sealing glass and methods, through some variation of component surface preparation or glass use, or through some simple re-design of sealing method. Resultant devices will be tested as completely as time and resources allow.

Task I: Choice of sensor ceramics, development of sealing technique and design of heating element.

We are now fabricating our own type K thermocouples for our sensors using a wire bonder to spot weld 0.010" dia. chromel and alumel wire together. This has proved to be a very economical move and is working quite well for us.

Further development of sealing technique and heating element design is now most appropriately discussed under Task II.

Task II: Preliminary fabrications

This past quarter we have used first "scrap" parts and then "final" parts from Glass Beads Materials, Inc. to fabricate a number of "heaterless" sensor assemblies. These assembly trials have revealed some of the behaviors and interactions of the various sealing, electroding, ceramic and metal components going into the sensor, and have given us answers as to how assembly may be carried out so that "bad" behaviors and interactions are avoided. We are not putting heaters in these assemblies because we wished to solve the initial problems of sealing, materials compatibilities, etc. before adding another time-consuming layer of complication to the problem (issues of final heater construction, allowable power densities, and so on).

Last quarter we voiced a concern that the sealing glass(es) used appeared to migrate across/interact with the platinum electroding on the sensor disk component, and that this interaction might affect sensor operation. We have found, contrary to our earlier thought, the OS-3 joint between the "disk" and "collar" portions of the assembly does NOT act as a good barrier against glass intrusion onto the inner electrode if the inner sensor electrode extends to the disk edge. We now routinely "pull back" the electroding several millimeters from the sensor disk edge on both

disk sides to prevent any contact with the sealing glass. We have stopped the visible glass/ electroding interaction with this "pull back".

We also noted last quarter we had seen strong evidence of diffusion of the A3058 silver paste over large distances on or perhaps through the OS-3 ceramic. We have confirmed our observation during this quarter: while exploring a possible lead attachment method, we fired an A3058 track on some OS-3 disks prior to the disk to collar joining step. Though the A3058 paste had been completely fired onto the disk, a gray stain originating at the A3058 paste track crept through the OS-3 parts during the disk to collar joint firing. To prevent this silver migration and other problems, we have subsequently broken our assembly/ firing steps into several parts, so that one assembly/ firing step is completed before proceeding to another, and so that the peak firing temperature used for each step diminishes with each step.

Because of the temperature sequencing of firing steps, we now perform the outer electrode lead attachment as the last step, after the OS-3 to SS446 (glass) sealing step, and we use a "low - firing temperature" (~600°C) silver paste, A4594. Before, we had used the A3058 which fires at a high temperature (~850°C), and we made the lead attachment in the same step with the sealing. Using the latter procedure we had occasionally seen a blackening of the electrode similar to the seal glass/ electrode interaction noted above, thus implying an interaction of the A3058 with the electroding. (Oddly, we have not seen this interaction between the A3058 and the inner electrode). We have found no interaction problems with the A4594, and this paste gives us very excellent lead attachments.

We now include a constant small air flow into the firing ovens as a precaution to prevent any unwanted reduction of the OS-3 material and to aid the burn out of organics in the glass and

electroding ink pastes. We further use a 500°C hold step when we fire pastes to make certain organics are completely burned out before proceeding in the firing curve.

We mentioned last quarter a "bubbling and blackening" of the seal glass was occasionally observed as we attempted to use isopropanol-based glass paste. (The isopropanol base affords a greater paste working time.) Over the course of a number of trials we have found "bubbling and blackening" to be the rule, not the exception, whenever isopropanol-based pastes are fired. We have attempted to find a reason and cure for this behavior, but there have been puzzling inconsistencies from test to test, and no "cure" derived from several working hypotheses has worked at all times. We have thus reverted to using methanol-based pastes.

Our glass supplier has suggested we use a new glass, V9, which is very near in composition to the V2B glass, yet which our supplier produces with greater regularity than V2B. (This allows our supplier to provide us with the small quantities we require much more easily.) We have used the V9 exclusively this quarter, and it seems to behave essentially the same as the V2B, except that V9 may be fired at a slightly lower peak temperature and has a slightly lower thermal expansion. We remain cautious, however, because a move to a lower expansion seal is a move in the wrong direction for our system of components, and the lower firing temperature may also be in the wrong direction. The lower firing temperature may indicate V9 is softer than V2B at any given temperature; we may find V9 to be too soft at our optimum sensor operating temperature when that temperature is determined.

Our "pull back" of the electroding, our changes in firing techniques, and our latest combination of materials now allows consistent assembly without electrode/seal glass interaction or the appearance of the silver drift "darkening" of the OS-3 material. We are regularly producing assemblies which look quite

nice as far as electroding and ceramic material integrity is concerned.

Seal integrity continues to be our (perceived) prime problem. We have now created a number of assemblies which appear good, but we rarely produce an assembly which is perfectly sealed. As the nature of the universe would have it, many of those assemblies which have passed preliminary room temperature leak check have ended up exhibiting other problems: e.g. a lead has broken irreparably, or seal glass has encroached on the electroding. Finally, we are experiencing development of tiny leaks and/or ceramic component fracture during thermal cycling of our assemblies.

We first discovered the utility of the V2B seal glass in a test which involved only the glass, a SS446 tube whose only surface preparation was to be wire brushed, and an OS-3 disk; the resultant assembly seemed completely leak tight and could be thermally cycled. The simplicity of the early success seems incongruous with the current failure rate. We are being led to explore other preparation/ seal materials possibilities.

We are in the midst of producing/evaluating several assemblies in which we have prepared the SS446 tube surface by nickel plating. Our first test using the bright nickel plate was quite encouraging: the seal seemed leak tight. Unfortunately, this was the device which developed the irreparable broken lead.

We have also obtained apparently leak tight seals in several test PIECES using mixtures of the V9 glass and a ceramic adhesive, S36; this mixture is fired, then overcoated with a thin layer of V9 and re-fired. The V9 overcoat on the one test SENSOR we have produced with a "mixture seal" interacted with the platinum electroding. We did test this prototype anyway, but obtained very strange results which might be attributable to the electrode/glass interaction. We will perform several more

assembly tests using "mixture seals".

The hairline fractures we have seen developing in the OS-3 components after several thermal cyclings may be an indication the V9 glass is not as well thermal expansion matched as needs be. We will be attempting a number of future assemblies using our remaining stock of V2B to see if cyclability improves.

Task III: Testing of prototypes and final fabrications:

We have continued to test "leak tight but imperfect" and "near leak tight" sensor assemblies in the gas-handling/analysis station we have described earlier. The "near leak tight" sensor assemblies continue to exhibit responses which are not commensurate with their predicted theoretical responses. The behavior seen has remained similar to that recorded in Figure 2 of last quarter's report. Since we have now tested devices which have not exhibited glass/electrode interaction problems as did the device of the Figure 2 data, we are now swayed to believe the reduction in output voltage we see (as compared to theoretical) is due to even the smallest of leaks allowing the interchange of gases between the reference and sample sides of the sensors. Consequently, we have focused our attention, as mentioned at the end of Task II above, to achieving true leak tight assemblies, to prove or disprove this hypothesis.

We still do not know with certainty how, or if, the visible interaction of our seal glass with our platinum electrodes affects the electronic behavior of the sensor. A recent result may be an indication, however. As mentioned above, we have tested a "S36/V9 mixture seal" sensor which appeared sealed at room temperature, but which exhibited glass/ electrode interaction/ discoloration. This "sensor" behaved quite peculiarly: all devices prior to this one have developed voltages which were of less than theoretical magnitude, but of proper

theoretical polarity. This recent device developed polarities which were completely REVERSED from theoretical, and this result was repeatable! This behavior cannot be explained by leaking between the sensor sample and reference sides; consequently we suggest it may be due to some complex interaction of the glass and electrode. It also may have been due to a Seebeck (thermocouple) effect, as the silver outer electrode lead wire contacted the SS446 tube; yet the simple addition of a constant voltage to our measured results only makes the inconsistencies with theory worse.

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