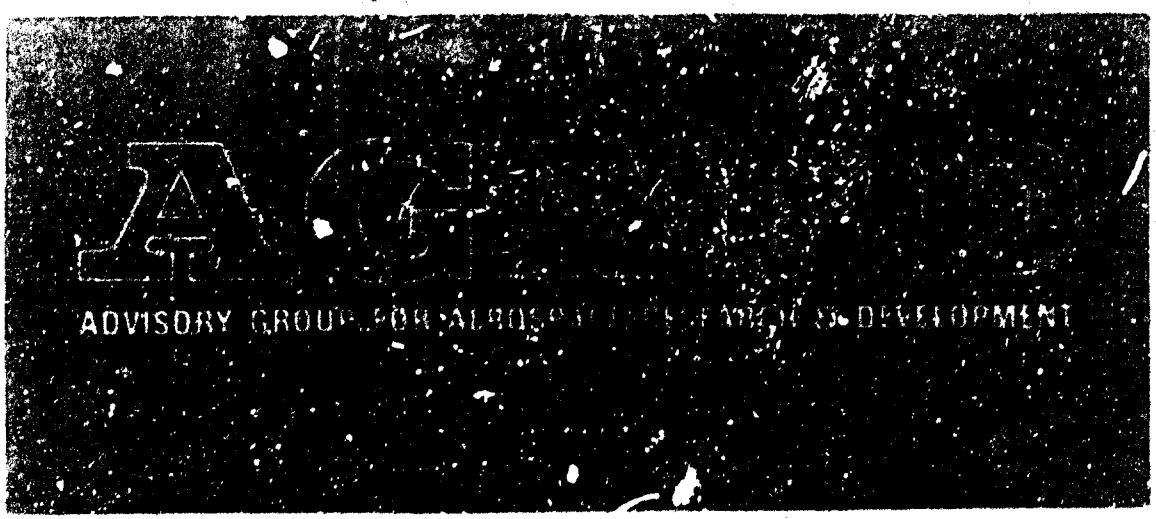


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Technical Evaluation Report on
AGARD Propulsion and Energetics Panel's
34th Meeting (8th Colloquium)

ON

Reactions between
Gases and Solids

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TECHNICAL EVALUATION REPORT
on the
AGARD PROPULSION AND ENERGETICS PANEL
34TH MEETING (8TH COLLOQUIUM)
on
"REACTIONS BETWEEN GASES AND SOLIDS"

by

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on behalf of the Propulsion and Energetics Panel

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I. INTRODUCTION

The 34th Meeting of the Propulsion and Energetics Panel on Reactions between Gases and Solids was an interdisciplinary colloquium held at the Aerospace Research Laboratories of OAR at Wright-Patterson AFB, Dayton, Ohio, 13 - 16 October 1969. The program committee chairman was Colonel Paul G. Atkinson, Jr., USAF.

The objective was to bring together experts in the diverse fields of corrosion, combustion, ablation, and erosion. Each of these fields is usually studied and practiced as a separate engineering specialty. Direct communication between specialists crossing interdisciplinary boundaries was intended to stimulate new insights in dealing with the many practical problems which involve some aspect of gas-solid reactions.

The colloquium subject was selected by the Panel. The agenda was structured to cover the fundamentals of kinetics and surface phase reactions, with surveys of the individual fields, current advances in these fields by various NATO laboratories, and a round-table discussion to consider the commonality of the various gas-solid reactions. The round-table discussion was chaired by Prof. S. S. Penner, University of California, San Diego. The other participants were Prof. Dr. Ing. K. Hauffe, University of Gottingen; Prof. I. Glassman, Princeton University; Prof. R. Monti, University of Naples; and Prof. D. E. Rosner, Yale University. Additional comments were offered by Dr. R. F. McAlevy III, Stevens Institute of Technology; Mr. J. Clark, AF Flight Dynamics Laboratory; and by Dr. P. Hancock, University of Glasgow.

As the round-table had been organized to include participation by scientists active in the various fields, the pertinent discussions contributing to an evaluation of the meeting are reproduced in Section III. For the convenience of the reader, the evaluation is summarized in Section II.

II. SUMMARY

1. From Professor Hauffe's and Mr. James Clark AFFDL Comments:

The objective of the metallurgist is to inhibit corrosion and increase the lifetime of metallic structures under conditions supporting oxidation at low and at high temperature. Our present knowledge of low- and high-temperature oxidation is well developed insofar as conventional techniques of metallurgy are concerned. To achieve further progress in inhibiting corrosion, we must employ new methods and approaches borrowed from solid-state physics. For example, the use of auxiliary electric fields to influence the migration of ions and electrons does influence oxidation rates. Some experimental data from the AF Flight Dynamics Laboratory support this contention. The application of a plus or minus 45-volt electrical potential to a type 347 stainless-steel insulated symmetrical airfoil reduced the corrosion rate by more than 60% when subjected to a gas flow of 1900°F.

Further knowledge of surface chemistry and ceramics could lead to achieving a compact, coherent oxide layer which adheres to the metal itself and inhibits further oxidation of the metal. We can also learn from those studying the combustion of metals. Understanding the initial formation of reaction product layers is clearly important.

2. From Professor Glasman's and Professor McAlevy's Comments:

The interest in gas-solid reactions in combustion relates to promotion of ignition and oxidation of metals in order to obtain rapid and complete release of the heat of combustion in the chamber to obtain high-temperature cycles and high efficiency. Both are necessary for high performance propulsion devices. In solid propellants, which are highly loaded with aluminum, for example, the protective oxide coating is detrimental to combustion. The aluminum particles do not ignite spontaneously. Rather, they melt first, tend to agglomerate, and do not burn to completion in the combustion chamber. Similar problems exist with beryllium in rockets and with boron in oxygen or air.

Approaching the problem from a chemical point of view might well be productive. Introduction of a chlorine or fluorine atom may yield a more volatile oxide coating or else induce catalytic effects leading to better ignition, more rapid combustion and higher efficiency. Perhaps we could produce an "oxide" coating artificially by using chlorine instead of oxygen, this oxide coating would have a lower transition temperature and would be easier to ignite in practical propulsion systems.

3. From Professor Monti's Comments:

The general problem of heat and mass transfer is involved in combustion, oxidation, erosion and ablation processes. In the latter two, the experimenters are quite concerned with simulating the thermofluid-dynamic environment, whereas in studying combustion and oxidation this is not always the case. Additional efforts should be made to simulate the real conditions of heat and mass transfer (cooling and flow) in which combustion and oxidation occur in order to obtain realistic experimental data and better evaluation with consequent better understanding of the process.

In erosion, which occurs, for example, in rocket nozzles when solid particles are entrained in the gas flow, the importance of simple mechanical impingement is recognized. Two other effects which would be of interest for study are the heating effect caused by this impingement and the additional effect of impingement of particles on surfaces subject to mechanical stress. Better understanding of erosion phenomena would have immediate application to rocket nozzles and reentry vehicles.

4. From Professor Rosner's and Professor Penner's Comments:

In many investigations of gas-solid reactions, particularly those of an applied nature, we are faced with many complexities in the geometry, and physical and chemical processes which are occurring simultaneously. In the past, it has frequently been necessary to lump many of these processes into a few gross parameters to measure and analyze. A great deal of detail has thus been buried in a few parameters. Quantitative description of important phenomena is thereby lost or controlling phenomena remain unrecognized. However, progress is being made. The authors of several of the papers presented this week have shown what can be done with digital computation on systems which are both geometrically and chemically complex. But problems remain. One is that the requisite input data (on chemical kinetics, for example) are usually not available. In many cases, the available data were attained under conditions in which observed rates were influenced by physical phenomena. Sometimes, the basic input data we need involved novel environments such as irradiated atmospheres (nuclear environment), dissociated atmospheres (reentry regime), and ingested complex salts (in gas turbines). To obtain the necessary input kinetic data, we have to go to great pains to extract or eliminate the effect of physical phenomena. It is also necessary to simulate important aspects of the novel environments for which we need basic data. The detailed surface structure must be known for the solid which is undergoing a reaction with a gas. With more of these basic input data available and the use of digital computers, we should be able to obtain a much more complete description of complicated processes in combustion and ablation.

Better understanding is especially required in weapon-system applications. The most challenging task involves identification of controlling phenomena. Here we must draw on all relevant disciplines. That, in essence, is the challenge of effective engineering and applied science. Are there relatively simple processes with dominant influence? What is the principal driving mechanism? We may judge the success of our views by the correct prediction of gross observables. When these predictions are in error, we must reexamine the fundamental inputs.

5. From Professor Hancock's Comments:

Metallurgists have worked for some years in high-temperature corrosion seeking a protective oxide film for turbine blades which will resist disintegration by chloride ions in a salt air environment. Because of structural limitations, the work was carried to about 1000°C or to temperatures up to about two-thirds of the melting temperature for blade material. The problem in boron and aluminum as rocket propellants is the inverse. Here we must find a means of breaking down the oxide layer (perhaps with a chloride ion to enhance oxidation). This need has reopened the field for the metallurgists, and there was some optimism expressed that the effective utilization of boron in rocket engines may be accomplished with better knowledge of gas-surface interaction phenomena.

III. ROUND-TABLE DISCUSSION

Professor S. S. Penner: As I indicated this morning, one of the principal purposes of this discussion is to help the responsible panel members prepare an appropriate evaluation of the meeting. The session originally had the title of "Something on the Commonality of Fundamentals", and as I suggested this morning we might expand that to discuss new problem areas, interface or commonality problems, and applications.

Let me usurp my prerogative for a couple of moments and make some observations for the meeting before letting our distinguished colleagues, who really know what they are talking about, tell us what is going on. The success of any technical meeting is always judged by the quality of the papers. I believe that is axiomatic. When looked at from this point of view, I am certain that we have had an outstanding meeting here. I have read all of the papers and heard many of them, and they are all very good. I think from another point of view the meeting is also successful. When you have speakers from very different disciplines get together and listen to each other, and you find that, after two or three days, in a very subtle way, ideas from Field A are being taken for granted in Field C, then you know that we have made some progress. It would be very easy to demonstrate, I think, the validity of this observation. Yesterday, for the first time, I learned about Dr. Hancock's intriguing work on the mechanical properties of materials at high temperature (15)* and perhaps I was not the only one who did not know of this work before coming to the meeting. And yet today it was perfectly clear that one of our distinguished colleagues here spoke as though he had been aware of this work for at least ten years. Now that is the kind of progress, the kind of success, that we really want to achieve. I believe the converse is true also, that the people working in fundamental disciplines find that their work has additional areas of relevance to the ones that they knew about. And again, this conclusion is easy to demonstrate by noting that people were delighted to find that the upper limit of the temperature range that they thought they should be working in was really not the upper limit that was of interest to other people. So in this very subtle way, I think the planners of this meeting, especially Colonel Atkinson, have been successful. It appears that there are complementary disciplines that people working in this general area of metal-gas interactions, ought to know, that they are getting to know, and are beginning to appreciate. I think that was McAlevy's famous comment this morning, that they are beginning to appreciate what they have been missing. If we accomplish just that at a meeting of this sort, I think we have some real progress to report.

I would now like to go to the more formal presentations, noting, however, that the distinguished people here are not proposing to preempt the evaluation. I suggest that each man here speak for somewhere between five and ten minutes. After that, any man in the audience who has something wise to say, and I am excluding all or part of a prepared lecture when I say something wise, please raise his hand and comment on where we are.

Professor Hauffe will make some observations on the relations between the entire meeting and physical phenomena in low temperature oxidation.

Professor Hauffe: It is a very hard job for me to summarize but, I believe that the low temperature oxidation and also the high temperature oxidation depend on the composition and the structure of the material. Our present knowledge is very well developed and I believe we have just arrived at the so-called limit. Now if we wish to be more successful, we should invite quite other peoples, let me say from semiconductor research, as we have to develop completely new methods. I remember for instance that we can employ a so-called auxiliary electric field to influence the migrations of the ions and electrons on the one side. On the other side, we have to cooperate with the ceramicists who are interested in fundamental research to find the right approach to get a better adhesion of the various growing oxide scales. The main trouble is that we have not succeeded in the development of corrosion resistant metals like Zirconium alloys which are so important for the atomic reactor industries. If we could employ this material for higher temperatures then we would not have to work with the enriched material. We could employ the classical metallurgy to increase the oxidation resistance of titanium and alloys. All these questions are closely connected with the question of how we can proceed in the formation of a coherent and compact oxide layer without any splitting off and breaking off. But this is a problem where we can no longer employ the methods which we have employed to date.

Professor Penner: Do you want to make some comments on the interplay between your area of activity and some of the adjacent fields you heard about here? This is, the detailed knowledge that you have that is not yet used. For example, in any of the models, let's talk about metal ignition. In an appreciative way, yes, in a quantitative way, that is not there.

Dr. Hauffe: I believe that the cooperation of people from the solid states curricula with those who are engaged with the ignition of metal vapors, would make some progress in this field and I believe that the lecture on this subject was very impressive, very instructive and very stimulating. I am going home with many ideas about what we should do further. I believe that the understanding of the initial formation of reaction product layers is very important.

Professor Penner: Thank you very much, Professor Hauffe. I might make a comment that about six weeks ago I saw an extraordinary demonstration of the interface between metals and explosions, in this case. We had a picnic on a Siberian peninsula and among the demonstrations there was a demonstration of explosive welding; of explosive cladding, of two metallic substances that are essentially incompatible.

* Numbers in parentheses refer to papers listed at the end of this report.

I don't want to pretend that I really understand the physics that is involved in making this kind of bond. That is an impressive example again of where different disciplines produce something unusually useful.

Professor Hauffe: If I may make a comment. For instance, it is of interest that space vehicles do not use titanium alloys although titanium alloys have many useful mechanical properties. The reason is very simple. If we employ titanium alloys for instance for a container of liquid oxygen and you shoot a bullet through it, then you've got an explosion and this is very dangerous. On the other hand this is also stimulating. When you have a compact material, thick compact material, and you have in this material the oxygen reactant and you now give them initial ignition - suddenly the reaction is going very, very fast.

Professor Penner: Well, I'm glad you closed with that remark because that leads very naturally to our next commentator who will now explain that phenomenon and others.

Professor Glasman: You know, I do have an explanation for that one. That's another area of work and I think there are some other results in regard to flames and liquid fuels that could perhaps shed some light on that problem. But I think, Sol, you asked me first to comment on solid propellant effects. I think that was the major point, and how.....

Professor Penner: Combustion processes and solid propellants, in general.

Professor Glasman: Well, I think the way I would like to approach that problem, is simply to say that there are fundamentally three major problems, I think, which exist in the propulsion area today with respect to metals. There are probably more, but three come to mind. These questions really arose in the question period after my presentation. (19) But to reiterate, I would like to mention them again. One, is the ability to burn aluminum well. I think one of the major problems today in highly loaded aluminized propellants, whether you want it for the direct solid propellant or the solid propellant in which you afterburn the metals, using certain polymers, is that the aluminum will agglomerate on the surface. It is my feeling that the agglomeration is caused, in part, by the fact that these particles do not ignite instantaneously, and melt and then agglomerate. I again feel that if we could do something about this protective oxide coating which is detrimental to us, but is important to the metallurgists, then perhaps we could effect this problem as well. I still think there is work to be done on how one would alleviate the problem of the high, to use my own terms, transition temperature of aluminum.

The second major problem, I think, is one that very many people disagree with me on, and that is, a greater understanding of the ignition characteristics of beryllium. I am still very strong for beryllium as a propellant and I think more studies are necessary in this area. The third, and most controversial area, I believe, is that which has to do with boron. I do think if one could burn boron in oxygen, particularly in systems which will later use air, that the advantages are enormous, as much as my statements about beryllium in a pure rocket system. The question I would like to pose to my colleagues who are more interested in oxidation processes has to do with what we could do to make boron burn, and I'll say this in quotes, "in the vapor phase". That is, to burn rapidly. The question arises, "How does one remove the oxide coating which forms on the surface very rapidly?" In fact, if I may generalize on all three of the metals, I notice a hole in the work that has been carried out by the metallurgists, and probably rightfully so. They still have a lot to do, and I say this hole is as follows: they have concerned themselves with the oxidation processes and the mechanical properties of the metal. As Dr. Hauffe said, they are interested in the solid state phenomena. But I suggest that perhaps a chemical approach may be wise. As I watched the various data put on the board during the past two days, I saw only certain compounds. I mean I saw metals, mostly in oxygen, some in water vapor, and some in CO₂. What would happen if I put a small impurity of a halogen in the system? I think a colleague here referred to that in his question to me. "What would happen if I added a chlorine atom or a fluorine atom or any other atom?" Would that alter the characteristics of the oxide coat? Is there a possibility of adding another atom which would provide a volatile oxide, in the case of boron? If so, tremendous strides could be made in the propulsion field. It doesn't seem incomprehensible to think of this as a possibility. Perhaps what I'm urging is that you change your chemical composition a little - - move away and try what we would call a catalyst which will make boron burn more rapidly or to make aluminum ignite more quickly before it agglomerates. All these things cut down very appreciably on the efficiency. So, if I have any message, if I learned anything, I wish to encourage more work in this area because as I said in my presentation I think it is very important. Thank you.

Professor Penner: Thank you very much. I think we ought to proceed with the prepared comments. Our next discussor is very much out of context here because he has not yet been Chairman of the session that he is supposed to be chairman of. His topic has not yet been adequately reviewed at the meeting. Nevertheless, in anticipation of great things yet unheard, he is going to comment on one of the fundamental problems that relates to metal-gas interactions in a flow system, namely, the general problem of heat and mass transfer to and from solid surfaces.

Professor Monti: I was very kindly commended by Professor Penner to say something about this rather large and broad field. Of course, everything that has been said here is related to heat and mass transfer. No matter what problems were discussed, we had oxidation, ablation and we will have erosion, and they all deal with heat and mass transfer. We did not hear, and will not hear about the rather simple, if I may say so, processes like transpiration cooling or film cooling or family fusion processes, where the main heat transfer is not the heat released by a chemical reaction. But at the same time, as I said, all the papers will be concerned with heat and mass transfer. Now, it seems to me that one can separate the fields of ablation and erosion from the field of oxidation as far as the line of attack is concerned. The ablation and erosion people seem to be quite concerned and they try to simulate the

the thermo-hydrodynamic environment in which a solid material is burnt. In contrast, oxidation by definition is more basic. It seems to me that they are not so much concerned with simulating the real conditions. I think an area to investigate is simply oxidation under a real simulated environment to have a better evaluation of materials. As someone else will say something on ablation, I will make just a few remarks on the subject of erosion, which will be held tomorrow. I think that an interesting suggestion that will be made by one of the next speakers is about the erosion in two phase flow, mainly, in a rocket nozzle. Now, when you have particles in flow and you try to bend their trajectories you have quite an important erosion phenomena not so much due to the mechanical effect but due to what is called heating impingement. Heating impingement in two phase flow with different parameters seems to be quite an interesting area to explore. At the same time another important effort in two phase flow is the growing size of the particles, like oxide particles in a rocket exhaust. Another field which seems to me not to have been considered here is the erosion phenomena under mechanical stresses which would be a great interest. Of course, now, this subject of erosion as we treat it here is mainly concerned with aerospace applications and this leads to your second question. With rocket trajectories there is an immediate application in aerospace for all these studies which you shall be hearing at this meeting.

Professor Penner: Thank you very much, Dr. Monti. The three principal topics that I posed, I would like to remind the audience and the one remaining speaker, are new fundamental problems that seem to have been suggested by the discussions here, interface problems, and applications. I believe each one of the speakers has commented to some extent on these three subjects. I would like to turn now to Professor Rosner who is going to discuss ablation processes and catalysts and whatever else the others here on the table have not commented on. After that I would like to return to the audience for a general discussion. Professor Rosner.

Professor Rosner: One theme which keeps reappearing, particularly in the applied papers of Heath (28), Guerini (3), and Barrere (20) is how inadequate many of the simple thermochemical bounds we have been used to using are, and how impatient one is becoming with previous lumped parameter analyses. A great deal of detail has been buried in a few parameters in a rather ingenious way, but many important phenomena are thereby lost and unpredicted. It's clear that once experiments on complicated systems have established what phenomena are involved in the overall process, that a lot can be done with computers if the requisite input information is available; that is, input information on the thermodynamics, transport phenomena, and the kinetics. I think the papers of Gibson (21), Baronti (25), and Guerini (3) give some insight as to what can be done with digital computation on fairly complex systems, both geometrically complex and chemically complex. However, the important condition is that the requisite input data be available and more often than not, of course, it is not available. Then the question is, why and what can be done about it. I'll concentrate my remarks now on unknown kinetic phenomena, particularly gas-solid kinetic phenomena. There are usually two reasons that available data is inadequate, at least in my own view. One is that much of the available information was attained under conditions where physical phenomena have intervened in determining the rates of reaction so that rather than being able to extract fairly general and elementary kinetic information one has the ambiguous situation of not knowing to what extent the observed rates were influenced by physical phenomena such as gas phase diffusion. The second reason that requisite information is frequently not available is that the environments we are interested in are quite novel in many respects. For example, we have heard papers on corrosion in irradiated atmospheres or in dissociated atmospheres, and in gas turbines that have ingested complex salts. Now to obtain data, one must go to non-classical techniques. It seems to me, you cannot just reach to the nearest shelf and pick off a furnace, pick up a microbalance, and start doing some experiments. One has to go to great pains to eliminate physical phenomena, particularly for rapid interfacial processes. I think at this conference we have heard or will hear such papers, by Lewis (29), by Grabke (8) on the uptake of gases by metals, and my own work. I have also gone to great pains to be able to extract and eliminate physical phenomena in studying the kinetics of gas-solid reactions. The second feature in these non-classical experiments has to do with the environment that is being studied. Now, it's not really essential that "complete simulation" be achieved, but at least the right kinetic processes should be studied. We have heard, for example in Hutcheon's paper (16), that you could be led far astray by examining data on the thermal CO₂ reaction of porous graphite if one wanted to predict the behavior of graphite in a reactor pile. Similarly, if one is interested in designing leading edges for reentry vehicles and the vehicles are traveling so fast that fully dissociated or partially dissociated air is being encountered, one might be led far astray by looking at the oxidation kinetics of diatomic gases when in fact, an appreciable fraction of the impinging species would be atomic. Indeed one could optimize one's materials based on stable species reactions and find that the material chosen is not at all optimum in a dissociated gas. I've recently been struck by how rapidly a fairly stable material such as silicon carbide is attacked by atomic nitrogen in my own work. We've also heard a number of instances in which gas mixture phenomena come into play. This has been alluded to by panel members here. How a small amount of methane can severely poison the oxidation of graphite. How small amounts of oxygen and sulfur can poison the uptake of nitrogen by iron. We have also heard about silicon carbide and water vapor oxygen mixtures. There are many situations where one cannot really anticipate the complications that do exist in the large effects that can be produced by small amounts of species. The fact of life is that we are always dealing with environments with more than one chemical species involved. Another point that keeps coming up that interests me is what is the real nature of the surface under conditions of reaction? This came up again in the discussion on the oxidation of silicon carbide (10). Is the surface really covered by some kind of a continuous film of silica? Is it a porous film? Under what conditions would this film not be present? This again relates to the boron question. When would a boron oxide film really be there? Would it be there under all conditions? If one added a different mixture of gases, halides to the gas, would the film be there? Can one effect the sublimation kinetics of the film? It seems to me there is a great deal of work necessary on the sublimation kinetics of vitreous and crystalline films under conditions of impinging gas species rather than vacuum sublimation. I think some of the papers we have heard indicate methods of studying the questions of what the nature of the surface is. Frequently, one must quench these specimens and do post-mortem type investigations using electron microscopy, or some kind of spectroscopy. One interesting paper indicated what can be learned

about simple crystalline materials under conditions of adsorption using electron diffraction (4) . All these experimental studies are needed; experimental studies in which physical phenomena are eliminated judiciously, experimental studies in which a relevant environment is produced, and perhaps in which detailed studies of the nature of the surface under reacting conditions can be examined. These will all ultimately lead to a much more complete description of complicated processes of combustion and ablation. I think this is important, as it will also lead to enlightened empiricism in making estimates for future systems. We will be able to make much more educated guesses even where all the dots have not been put on the i's, just by having available more detailed kinetic information - the kind I've mentioned.

Professor Penner: Thank you very much, Professor Rosner. I think those are very valid comments. They probably have validity outside of this specific area that you discussed, namely, the kinetic area, and, in general, when we talk about applications, the man who has to do the grand synthesis has the challenging job of trying to figure out what is important and throwing away everything else. That can be very trying and a very difficult job, and in doing this job well he must draw on all disciplines. He really has to know much more than the man who studies a simple, or relatively constrained basic program. That's the challenge of applied science, in essence. It is very, very comforting and at the same time very disconcerting to look at some of the results that were presented here and find the dichotomy between input and output. An excellent example of this is given in the very nice paper that Dr. Morgan presented this morning (21) . On the one hand radiant heat transfer is the dominant effect. On the other hand, it's greatly oversimplified. Thirdly, when there is swirl present, which shouldn't really affect the radiation except in a secondary way, the whole system doesn't work again. When you see data like these you know that you have a challenging problem in which the really controlling effect has not yet been quite identified adequately. Or, to take another example, the very beautiful work of Dr. Barrere (20) that shows the combustion velocity varying very rapidly with pressure, going through several maxima and minima. Well, what is all that about? Obviously, the first order cut there doesn't answer the question, and we have to look at much greater detail. And I think when you ask the question from this point of view, and I realize I'm doing little more than reiterating in slightly different language what Professor Rosner just said, you are impressed with the importance of getting the right physical concept from the right basic investigation, and that, in a sense, brings us back to the very purpose of this meeting, that when these details come out wrong, or when the big thing comes out wrong, the detailed input must be incorrect. Then we have to go back and redo our basic concepts, our basic research. I would now like to open up this brief evaluation session to all of my colleagues again and to the audience.

Professor McAlevy: I don't pretend to be a metallurgist. I don't know the difference between a eutectic and a struscan, but I thought, hearing the comments of Professor Glassman and others, there might be some merit in trying to artificially produce on the surface of metals that might be used in a practical application, layers, oxide layers that don't contain oxygen. I wonder, for example, if you could produce an oxide layer, using chlorine instead of oxygen, that might in Professor Glassman's jargon, have a lower transition temperature? I would imagine it would be more expensive because nature gives us the oxygen. You would have to preclude oxygen from access to the metal, but, under certain metallurgical conditions that might be produced, it might be possible to build up a layer that has a much lower transition temperature, but not based on oxygen. Professor Glassman showed (19) that for ignition of metal particles to take place it is necessary to break away the oxide layer clinging to the particle surface. This layer always contains oxygen in chemical combination with the metal. Would it be possible to prepare particles in a controlled way so that the layer contains, say, a halogen or some other substitute for oxygen? If so, the strength of these layers might be "weaker" than the normal oxygen-containing layer, and thus it might be easier to ignite such particles in practical propulsion situations. Is that a possibility?

Professor Penner: Professor Glassman will answer that question.

Professor Glassman: I discussed this particular point with Dr. Hancock. In the sense that you recall, we did it in the early days in dealing with inhibited red fuming nitric acid. We added HF to the acid to put a nickel fluoride coat on the nickel steel tank and this was very, very effective. The question arose, well, why not try to put a fluoride coat, say, on some of the steels or nickel steels to protect them? We were thinking of turbine blades. However, I am informed that these halides were quite volatile and when you get up to the temperature that we are concerned with that they would no longer be effective. That was a bit of information that I didn't know which I learned at this meeting. I think that in a way it answers in part his question.

Professor Penner: Further questions?

Mr. Chairman: My name is James Clark. I am employed by the U. S. Air Force and work in the Vehicle Equipment Division of the Flight Dynamics Laboratory here at Wright Field. I would like to report that this meeting of the Propulsion and Energetics Panel has provided us with the answer to a research problem which Flight Dynamics Laboratory has been seeking since 1963. Briefly stated, the problem was this: In 1962 and 1963, we conducted an in-house research program on the effect of impressed electric fields in the reduction of high temperature corrosion of Type 347 stainless steel. The objective of this research program was to explore new methods of reducing the high temperature corrosion of gas turbine component parts. A high temperature flow channel, simulating a small wind tunnel was constructed. The airflow over the test model was 1900° at 1050 ft/sec. The air was heated by a J-47 combustor mounted in the upstream part of the flow channel and burning JP-4 fuel. Two aerodynamic bodies made of Type 347 stainless steel were tested. The first body was a small symmetrical airfoil having the NACA 63-004 airfoil section. The other model was a flat plate 0.300-in. thick having a 0.15-in. radius leading and trailing edge. These models had a chord of 3.333-in. and a length of 2.900-in.

These flow models were mounted between and supported by two fused quartz plates which formed the sides of the test section in this high temperature combustion gas flow channel. By supporting the test

models with the quartz plates, they could be electrically insulated from the metallic flow channel, thereby, permitting an electrical potential to be applied between the test model and the top and bottom of the flow channel. Tests with zero positive and negative potentials were applied to the models. The corrosion rate of the flat plate was greater than that of the Laminar flow type symmetrical airfoil. Also, the application of + 45 volts to the models relative to the metallic walls of the flow channel produced the following reduction in the high temperature corrosion of the test models:

PERCENT REDUCTION IN HIGH-TEMPERATURE CORROSION

<u>Model</u>	<u>+45 Volts to Model</u>	<u>- 45 Volts to Model</u>
Symmetrical Airfoil	61.8	69.2
Flat Plate	31.6	36.8

After the completion of these tests, there was considerable discussion as to the phenomena responsible for the reduction of this high-temperature corrosion since the current drawn from the battery was only a few milliamps. After listening to Dr. Karl Hauffe's paper on "Low-Temperature Reactions Between Solids and Gases" (18) and discussing this data with him in a private conference this morning, we are both of the opinion that this applied electrical potential changed the migration characteristics of either or both the electrons and ions through the semiconductor type crystal lattice of the oxide covering the test specimens.

The results of our discussion indicated that considerable benefits should be derived from a coordinated research program in this new field of high-temperature corrosion research.

I would like to thank you and others for the invitation to attend this panel meeting and discuss our research problems with Dr. Hauffe. You and others are to be commended on the excellent papers presented at this meeting and on the high technical level of the entire meeting.

Professor Penner: Professor Hauffe would like to make a comment.

Professor Hauffe: I believe this is a very important point. It is a completely new idea and yet is not so new, but the application is very stimulating. Your flame, nozzle and the whole material is an electro-chemical cell and then you employ an auxiliary electrical field and you are perhaps able to prevent the migration of ions and electrons through the layer and this is very important so long as we have the high temperature situation. When you go down with the temperature then unfortunately you can get into a very complex situation with breaking off and cracking effects and so on, but this is exactly what I mentioned before. We must cooperate and find with the ceramicists new ideas to achieve good adhesion effects.

Professor Penner: Thank you very much. Any further questions?

Professor Hancock: I would just like to make a very brief comment on some of the things that have been said by the panel. Particularly regarding the comment that has been going on about chloride ions. I think for many of us, working on high temperature corrosion we spend a good number of years and effort trying to stop chloride ions disintegrating oxide films. And now we get a message from the panel that really this is not what they want. That really they want to get an oxide film which is destroyed with chloride. Well, as a metallurgist, this sounds like the Promised Land. Do you really mean this?

Professor Penner: No, no, I think this isn't quite true. I think the message coming from the panel is they want you to do different things for different purposes. When they are talking about boron, and I want to disagree with Professor Glassman on this, the phenomenology is so rich that he doesn't think, and I do think, there must be a way of burning it efficiently. That's what we want you to do, find out what the additive ought to be to boron or to the gas to accomplish that, in that instance. But for the turbine blade that works in a sea environment, we want you to put a permanent coat on it so that it will never corrode at all.

Professor Hancock: Yes, but this is my point. The problem here at the lower temperatures, around a thousand degrees C, is to keep a coherent film. As I understand it, the problem in combustion is to make sure that this film is broken down. Now, it seems to me that in the oxidation work we've all stopped short of this because structurally, as I said this morning, you've begun to lose interest at about 2/3 of the melting point. And so one stops doing tests here, but it seems to me that you've really reopened this field in a negative sense. I repeat, it seems like a Promised Land to me.

Professor Penner: If you've got a new horizon because of this meeting, then we've been successful. I want to thank you for coming, and these four gentlemen for their excellent comments. Thank you again.

IV. CONCLUSION

There was general agreement that the interdisciplinary character of the conference had led to a fruitful exchange of views by giving new perspectives to the participants on areas of application of their work and on desirable directions for new studies.

V. PAPERS PRESENTED

SESSION I. FUNDAMENTALS

	<u>Reference</u>
THE REACTION OF METALS AND ALLOYS WITH GASES AT ELEVATED TEMPERATURES by Robert A. Rapp	2
REACTIONS BETWEEN HIGH-TEMPERATURE-RESISTANT ALLOYS AND GASES by H. Pfeiffer	13
PARAMETRES THEORIQUES ET DETERMINATIONS EXPERIMENTALES DANS L'ETUDE DE MATERIAUX SOUMIS A L'ABLATION par E. Guerini et R. Joatton	3

SESSION II. SURFACE REACTIONS WITH GASES

CHEMISORPTION ON REFRACTORY METALS by T. W. Haas	4
TRANSFERT DE CHALEUR ET DE MATIERE AU DESSUS D'UNE SURFACE CATALYTIQUE DANS UN ECOULEMENT TURBULENT par M. Trinité et P. Valentin	5
A MODEL FOR THE INDEPENDENT REVERSIBLE POISONING OF POROUS CATALYSTS BY FEED STREAM IMPURITIES by F. Gioia, L. G. Gibilaro and G. Greco, Jr.	6
THERMIONIC EMISSION OF ELECTRONS IN THE PRESENCE OF ADSORBED GASES by F. M. Page and J. I. Wright	7

SESSION III. HIGH TEMPERATURE OXIDATION

OXIDATION STUDY OF ZIRCONIUM DIBORIDE WITH VARIOUS ADDITIVES by H. C. Graham and W. C. Tripp	9
OXIDATION OF SILICON AND SILICON CARBIDE IN GASEOUS ATMOSPHERES AT 1000-1300°C by J. E. Antill and J. B. Warburton	10
THE OXIDATION OF NIOBIUM IN THE TEMPERATURE RANGE 350°-600°C by J. S. Sheasby	11
THE OXIDATION OF NI-BASE SUPERALLOYS UNDER AIRCRAFT ENGINE CONDITIONS by C. S. Wukusick	12

SESSION IV. CORROSION PHENOMENA

LOW-TEMPERATURE REACTIONS BETWEEN SOLIDS AND GASES by K. Hauffe	18
MECHANICAL PROPERTIES OF SURFACE OXIDE FILMS AND THEIR EFFECT ON THE KINETICS OF OXIDE GROWTH by P. Hancock	15
REACTION BETWEEN SOLIDS AND GASES IN RADIATION FIELDS by J. M. Hutcheon	16
KINETICS OF PHASE BOUNDARY REACTIONS BETWEEN GASES AND METALS by H. J. Grabke	8

	<u>Reference</u>
<u>SESSION V. COMBUSTION REACTIONS OF GASES WITH SOLIDS</u>	
A REVIEW OF METAL IGNITION AND FLAME MODELS by I. Glassman, A. M. Mellor, H. F. Sullivan and N. M. Laurendeau	19
RESULTATS EXPERIMENTAUX RECENTS SUR LA COMBUSTION DE L'ALUMINUM ET D'AUTRES METAUX par M. Barrere	20
COMBUSTION OF SOLID PARTICLES IN A TURBULENT STREAM WITH RECIRCULATION by M. M. Gibson and B. B. Morgan	21
LA VITESSE LINEAIRE DE REGRESSION DU PERCHLORATE D'AMMONIUM DANS UN ECOULEMENT GAZEUX COMBUSTIBLE par C. Casci et L. De Luca	35
<u>SESSION VI. COMBUSTION REACTIONS OF GASES WITH SOLIDS (Cont'd)</u>	
PHENOMENES DE FUSION ET REACTIONS DE SURFACE DANS LA COMBUSTION DES LITHERGOLS par J. F. Lieberherr	23
SURFACE REACTIONS IN SOLID PROPELLANTS by H. Seizer	24
MIXING AND COMBUSTION OF SOLID PARTICLES IN TURBULENT STREAMS by P. O. Baronti and A. Ferri	25
DIFFUSION FLAMES OF MAGNESIUM VAPOUR AND OXYGEN AT LOW PRESSURES by B. E. L. Deckker and B. K. G. Rao	26
THERMODYNAMICS OF VAPORIZATION PROCESSES OF SOLIDS AT HIGH TEMPERATURES by G. De Maria	34
<u>SESSION VII. EROSION AND ABLATION</u>	
REPRESENTATION SCHEMATIQUE DES PROCESSUS D'ABLATION par J. J. Nicolas, S. Kohn et G. Taguet	33
SURVEY PAPER ON EROSION PRODUCED BY HIGH-SPEED TWO-PHASE FLOW IN SOLID PROPELLANT ROCKET MOTORS by R. J. Zeamer	27
A LABORATORY INVESTIGATION OF CARBON-GAS REACTIONS OF RELEVANCE TO ROCKET NOZZLE EROSION by J. C. Lewis, I. J. Floyd and F. C. Cowlard	29
THE ROLE OF CARBON-GAS REACTIONS IN THE EROSION OF ROCKET NOZZLES by G. A. Heath and R. W. Thackray	28
EXPLOSIVE ELECTRODE EROSION IN NANOSECOND HIGH DENSITY SPARKS by H. Fischer and K. Schonbach	30

Papers 1; 14; 17; 22; 31 and 32 were withdrawn.

Papers referenced by number above are published, with the same reference nos., in AGARD Conference Proceedings No. 32 - "Reactions between Gases and Solids".