REFRACTORY EMISSIVE COATINGS

L. N. Hjelm, Lt. USAF

Directorate of Materials and Processes, ASD

Introduction

The current interests in high temperature applications involving vehicle structures for long time or repeated use at high temperatures in air has spurred considerable activity in the field of refractory coatings. Radiation cooling as a thermal protection technique came to the forefront with the development of glide re-entry vehicle concepts. It is here that refractory coatings became not only interesting, but mandatory. The long service lives (30 minutes and up), and repeated use requirements on top of the high surface temperatures of 2500° - 4500°F, necessitated designing structure surfaces which are stable in air at these temperatures. Thus, for perhaps the first time, the feasibility of a vehicle design was dependent upon refractory protective coatings. These coatings can be conveniently categorized into two general areas by temperature requirements, namely those useful below 3000°F and those useful above 3000°F. The systems useful up to 3000°F are the coated molybdenum and columbium alloy systems and coated graphite. Those useful above 3000°F are generally the refractory oxides in various composite designs. Since radiation as a thermal protective system is dependent upon maintaining a very high surface temperature for efficient re-radiation of thermal energy, these designs are very dependent upon internal thermal insulation for payload protection.

However, these insulation systems are very dependent upon specific design trade-offs and cannot be considered here except in general terms. It should be noted, however, that in many of these refractory composites considerable insulation is provided by the composite itself which helps pay for its weight.

To illustrate the vehicle application discussed here, figure 1 illustrates a typical re-entry glider. The various critical areas of interests are the nose cap with maximum temperatures to over 4000°F, the leading edges with maximum temperatures to 3000°F, and the various skin areas with maximum temperatures below 3000°F. These are indicated in figure 2.

With these typical structural applications in mind, the various materials systems can be discussed.

Coatings for Refractory Metals

The attractive high temperature properties of the current refractory metal alloys of molybdenum and columbium have provided the designer with an additional 1000°F above the 2000°F limitation of the super alloys in the design of structural components. This allowed designers to use familiar sheet metal construction concepts in building re-entry vehicle components, rather than forcing them into the distasteful task of learning to design with the brittle, unpredictable ceramics available. It is well known that all the refractory metal alloys require coatings for protection from oxidation. This has greatly increased the difficulty in design and construction.

Nevertheless, the very encouraging results from coating development programs have provided several families of coatings with sufficient protection for current requirements. This now allows the use of Mo and Cb alloys for high temperature structural components.

These coatings can be described as "diffusion coatings". Several elements, such as Si, Cr, Al, Ti, etc, are deposited on the surface of the metal, and concurrently or subsequently heat treated to allow diffusion and to produce the intermetallic systems which are the coating. The two generally used deposition methods are cementation and slurry or dip coating. The cementation method, taking its name from its similarity to carbonizing, has been the most actively pursued technique especially for moly alloy. Several variations of this technique exist but the basic principles involved are essentially the same. In pack cementation, the part to be coated is packed in a retort with a powder consisting of the coating elements such as Si and Cr, an activator or carrier such as I_2 or a halide compound and an inert filler such as Al_2O_3. The retort is then closed, sealed, purged, and heated to 1900°F for several hours. During the heating period the halide vapors carry the coating elements to the metal surface and deposit them. At the high temperature of processing these elements then diffuse into the surface and form the intermetallic compounds which constitute the coating.

In the slurry and dip processes, the coating elements are deposited by coating the part with a slurry, or by dipping the part into a molten bath of the mixture. The part is then heat treated to allow diffusion to occur.

These coatings have not been a panacea for the problems of using refractory metals, due to characteristics such as their low temperature brittleness and the complication they add to the manufacturing operations. Nevertheless, the availability of these coatings has allowed the development, manufacture, and successful testing of many types of high temperature structures for glide re-entry vehicles. The following illustrations show the current high temperature structural applications of coated refractory metals.

Figure 3 typifies the "hot structure" concept where the refractory metal acts as a non load carrying high temperature skin operating at over 2500°F and the true structure a superalloy is kept to some reasonable temperature below 1800°F by insulation.

Figure 4 typifies the cooled structure concept with a coated refractory metal skin operating at over 2500°F attached to a well insulated, cooled Al structure operating at 200°F.

Figure 5 illustrates a complex, coated structure which skin panels could operate at 2500°F.

The current capabilities of coatings for moly and Cb alloys provide very reasonable lives in air of many hours at 2700° - 2800°F for molybdenum and 2500° - 2600°F for Cb, with useful lives at 100° - 200°F high temperature.

Figure 6 typifies in generalities the reported lives of various systems. It also indicates that specific systems do indeed have very sharp maximum temperature capabilities, where protection ceases. Also, and more important, there are no systems available with useful lives much over 3000°F.

Graphite

The primary problem pertaining to the use of graphite in air at high temperatures is the same as that of the refractory metals namely oxidation. The coatings available for graphite are somewhat similar to those of the refractory metals. They are silicide coatings applied by a diffusion process.

Current uses for graphite in these applications are limited to temperatures below 3000°F because of the coating systems available. Because of this limitation, the attractive properties of the commercial graphites cannot be fully exploited. Moreover, the difficulties, involved with designing with a sensitive, brittle material often cannot be substantiated if use temperatures cannot be over 3000°F. Therefore, in the past graphite has been used mostly in composite structure where it acts as a transition material - useful at only slightly higher temperature than coated refractory metals but much easier to work with and perhaps lighter than the refractory oxide systems.

The recent activity in the pyrolytic deposition of graphite and graphite alloys have produced the only truly new class of engineering materials. The potential of these materials has been demonstrated in many short time applications. However, chemical compatibility and long time stability at high temperatures remains to be determined. More important, however, is the fact that design concepts have yet to be developed to provide mechanically reliable structural components of these brittle materials.

Sprayed Coatings

Certain applications in vehicles, such as the nose area and leading edges may require additional coatings to overcome the 3000°F limitation of current coatings for refractory metals and graphite. Here the objective is to provide a thermal insulating refractory oxide top coating capable of withstanding the higher temperatures. These could generally be flame or arc sprayed over an oxidation protective coating. The main problem is the usual poor match of thermal expansion between the coating and the substrate, resulting in susceptibility to thermal shock and consequent spalling of the top coat. Several techniques such as the gradated coating and the multi-layer coating have been developed to overcome this problem. These techniques modify the thermal expansion characteristics of the coating by varying its composition so that at any point it is able to withstand the reduced resultant thermal stress.

Figure 7 illustrates the concept of gradated coatings where the composition of the coating is varied from the substrate to the surface to remove the critical interface problems.

Reinforced Ceramics

The use of solid ceramics in structural components of advanced vehicles has been limited again by a lack of understanding of design techniques for brittle materials. Although the oxide ceramics offer the only materials stable at high temperatures in air, their extreme shock sensitivity and tendency to crack catastrophically have precluded their use as monolithic structural components. Many efforts to use oxide systems as insulating, radiating structural protective systems have resulted in the development of several types of metal reinforced ceramic systems. Super alloys, coated, and uncoated refractory metals, and noble metals have been used in a great many configurations as the reinforcement for various oxide systems. These concepts are typified in the following illustrations: figures 8, 9, and 10.

The bulk of reinforced ceramics concepts are dependent upon chemical bonding techniques for the oxide systems. This is true because of the high sintering or hot pressing temperatures generally required for refractory oxides. A chemical bonding is necessary for two reasons: first, the temperatures involved in sintering Al_2O_3 and ZrO_2 systems would melt all but the refractory metals and preclude the use of superalloys. Second, with a metal backing the thermal stresses set up upon cooling from the sintering temperature would fail the composite. Also, chemical bonding allows the fabrication of complex and large components since many application techniques such as spraying, trowling, casting etc., may be used. Chemical bonding generally involves mixing the powdered oxide with an acid such as phosphoric acid, forming the desired shape, and curing the system at a temperature anywhere from room temperature to 1000°F. This developes a hard, strong body which retains its strength and does not shrink when heated to high temperatures, if done properly.

The oxide systems used are generally based upon Al_2O_3 systems for use up to 3500°F, and ZrO_2 systems for use up to 4500°F. In many systems these oxides are alloyed with other metal oxides such as Cr_2O_3 and/or rare earth oxides to increase the emittance of the system. Oxides such as ThO_2 and HfO_2 are used for very high temperature systems. Also, many oxides are used in these ceramics alloys to control and adjust the thermal expansion characteristics.

These systems are being proposed for many applications and are being evaluated for vehicle applications such as skin panels, leading edges, and nose caps. The following illustrations show some of these concepts: figures 11, 12, and 13.

The Role of Emissivity

These systems offer promise for long time use primarily because of their stability at high temperatures in air. The oxide systems of greatest interest are good insulators —— to keep internal temperatures as low as possible. Since these are vehicle applications, minimum weight is always the major objective, therefore, the system must provide the maximum thermal protection for a given weight. With a given designed set of conditions, the actual surface temperature is a strong function of its emittance as illustrated in figure 14. There are then, two requirements for high emittance. First these systems are used close to their maximum temperature or melting points; a lower E than desired could cause the material to melt at the maximum expected condition. Second, with a given environment and composite, a lower E than expected, with the higher surface temperature, would allow more heat to be transmitted through the protective system thus upsetting the internal heat balance and overheating the payload.

Figure 15 shows a typical time-temperature trajectory. It can be seen from this, how the usefulness of a system is dependent upon a high, stable, known emittance.

Future Prospects

1. Coatings for refractory metals and graphite must be developed with useful lives to at least 4000°F. If W and/or Ta alloys are to be used in structures they must be used at very high temperatures to offset their very high density. Also, as the characteristics of current coatings become better understood, compositions will be developed or modified to provide high emittance long lives, and high reliability.

2. Oxide ceramic systems will be developed for use at higher temperatures through the use of ThO_2, HfO_2, etc. systems. Emittance control techniques will be developed which

will provide a high stable emittance through alloying with systems such as the rare earth oxides. Finally chemically bonding techniques will provide a wide range of ceramic systems for use with new reinforcement materials and techniques. The object here will be low conductivity, long lives, and controllable properties.

3. Current developments in the pyrolytic deposition of materials are providing an entire family of radically new and different materials. In addition to the popular pyro-graphite with its extremely anisotropic properties, there are alloys of pyro-graphite with elements such as Boron which offer a wide range of properties. Also other compounds such as BN being produced this way appear to offer radically different characteristics than the more common forms. Many of these materials may offer sufficient oxidation resistance for consideration in these applications. However, these are still brittle materials subject to catastrophic mechanical failure, so that considerable development must be done in design concepts and material characterization before confidence will be placed on their use.

4. Oxidation resistant materials are being developed which will be useful structural and protective materials without the use of coatings. These will allow simpler, more reliable designs to be used because of their self protection. A few very promising systems are currently being developed, and several are available. Ceramic bodies are being developed which like SiC and $MoSi_2$ are self protective and may be useful over 3500°F in air. There are interesting developments in cermet-like materials that may behave like metals and yet be oxidation resistant to 3000°F.

5. Emittance control will be provided by a better understanding of surfaces and surface effects, by composition variabilities built into the composite systems, and perhaps as important, through the use of more realistic, more accurate emittance measuring equipment.

BIBLIOGRAPHY

1. "Development and Evaluation of Insulating Type Ceramic Coatings", WADC Technical Report No. 59-102, E. W. Blocker, C.A. Hauch, S. Sklarew, and A. V. Levy (November 1959)

2. "Development of a Cementation Coating Process for High Temperature Protection of Molybdenum", ASD Technical Report No. 61-241, P.J. Chao, B. S. Payne and D. K. Priest (June 1961)

3. "Summary of Second High-Temperature Inorganic Refractory Coatings Working Group Meeting", WADC Technical Report No. 59-415, D. Roller (June 1959)

4. "Private Communication", J. R. Myers, Dyna-Soar Engineering Office, ASD (June 1961)

5. "Development of Reinforced Ceramic Materials Systems", W. Sterry, L. Stejskal, and J. Gunderson, Boeing Airplane Co., WADD Technical Rpt. No. 60-491 (May 1960)

6. "Structural Materials Research for Manned Lift Re-Entry Vehicles at Materials Central, WADD", D. H. Cartolano, A. Olevitch, J. R. Myers, presented at American Institute of Chemical Engineers Conference, Washington, D. C. (Dec. 1960)

7. "Leading Edge Segment Development Program", G. C. Irons, Marquardt Summary Report on Project No. 502 (March 1959)

8. "Refractory Metals Structural Development Program", Quarterly Progress Reports on Contract AF 33(616)-6578, McDonnell Aircraft Corp., (Sep 59-Oct 60)

9. "High Temperature Coatings for Aero-Space Applications", WADC Technical Memorandum No. WCLT TM 59-104, J. R. Myers (Nov. 1959)

10. "High Temperature Composite Structure", Quarterly Progress Reports on Contract No. AF 33(616)-7497, The Martin Company (Oct. 1960 - Apr 1961)

TYPICAL GLIDER

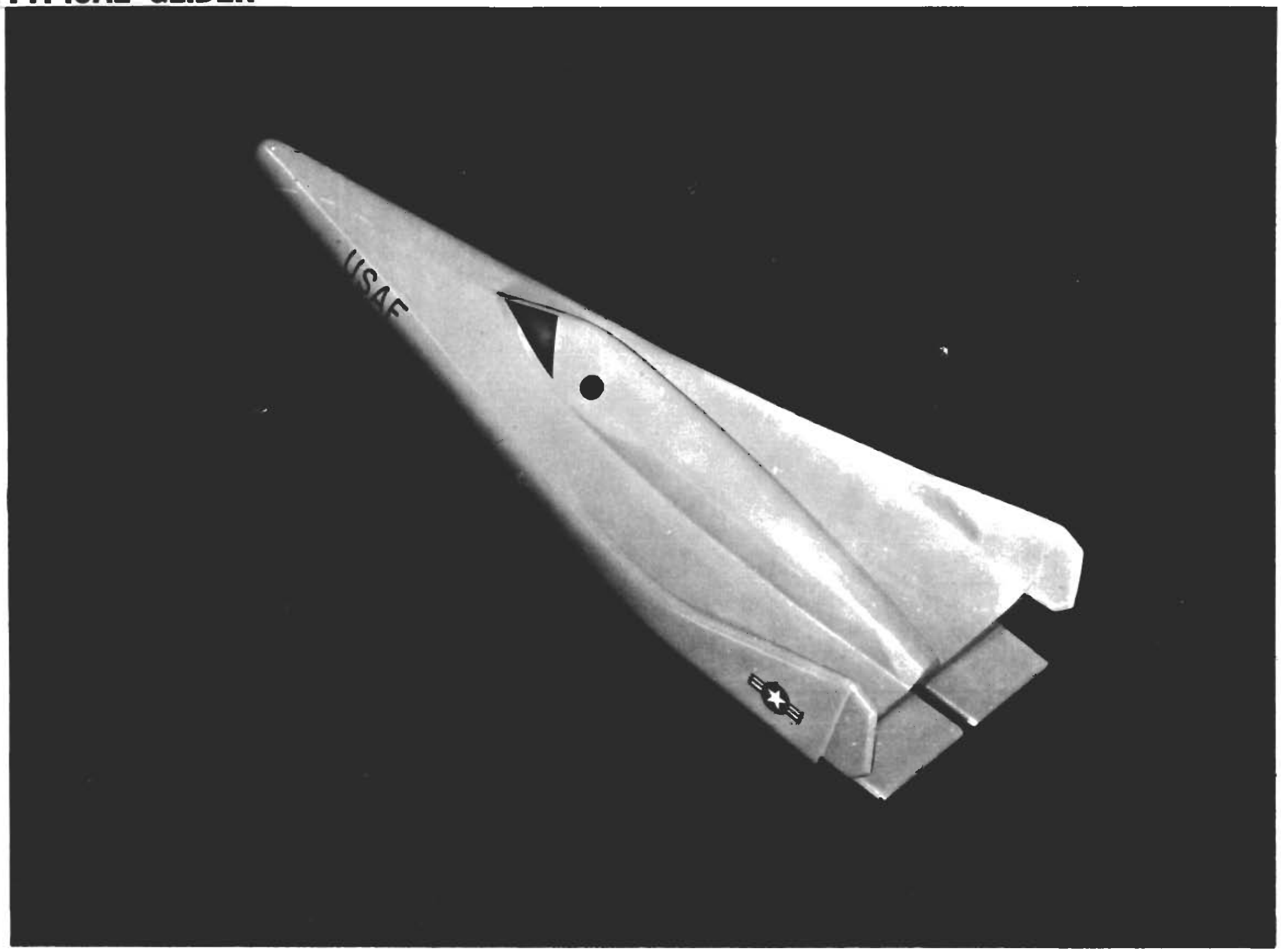

Figure 1.

ESTIMATED SURFACE TEMPERATURES OF A GLIDER DURING REENTRY FROM 26,000 fps.

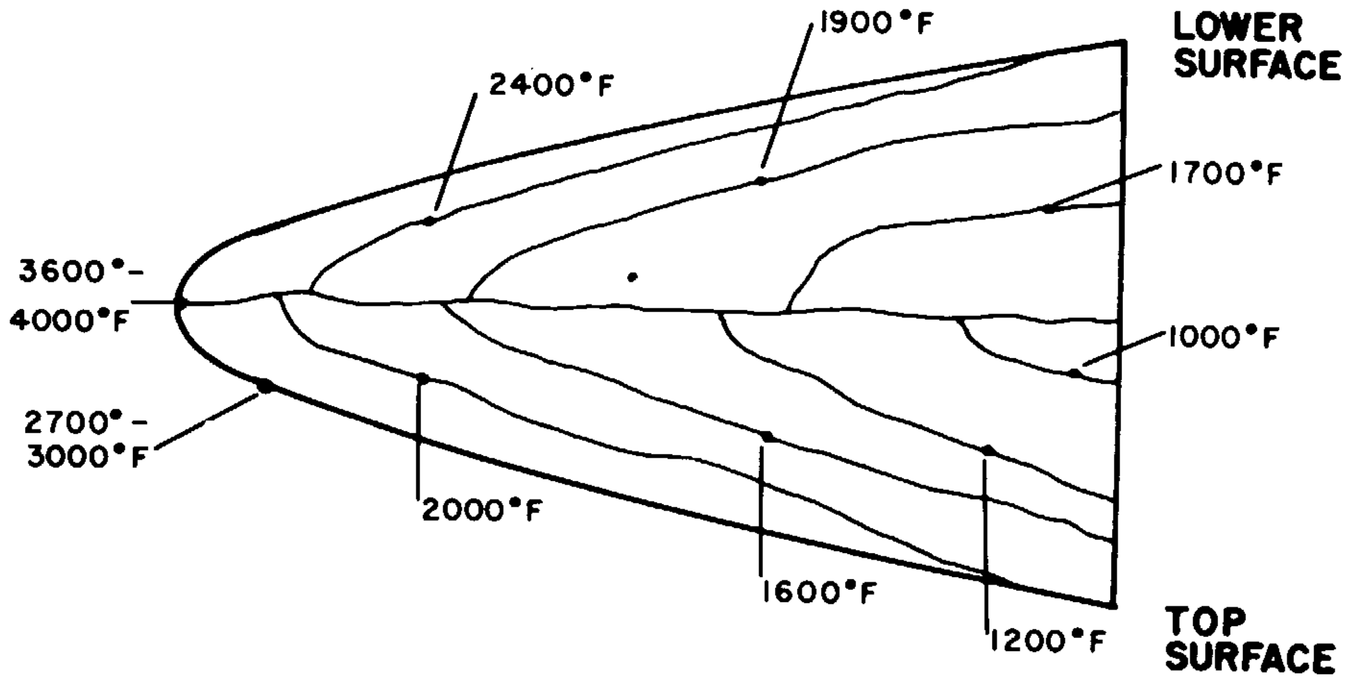

Figure 2.

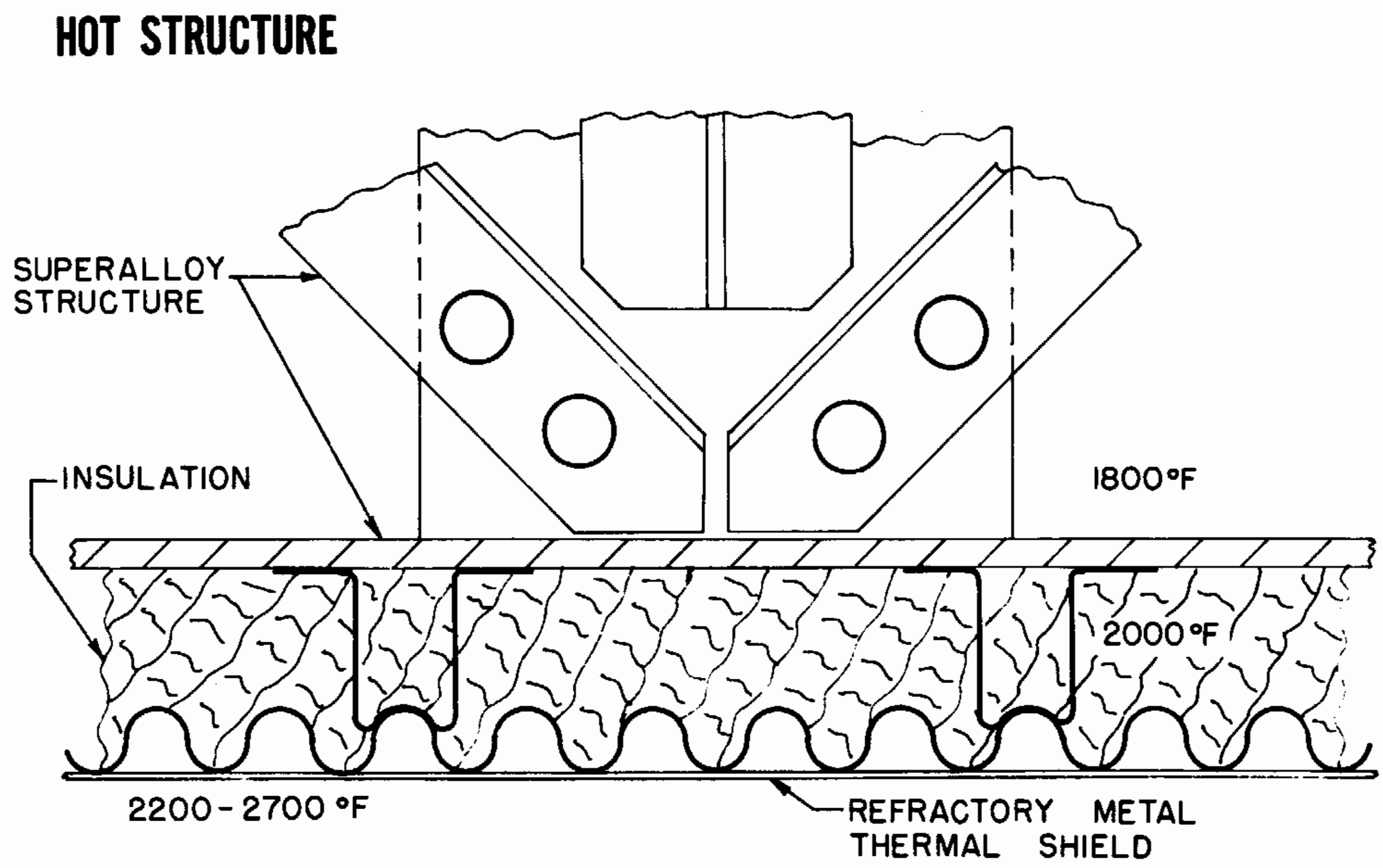
HOT STRUCTURE
SUPERALLOY STRUCTURE
INSULATION
1800°F
2000°F
2200-2700 °F
REFRACTORY METAL THERMAL SHIELD

Figure 3.

INSULATED & COOLED STRUCTURE

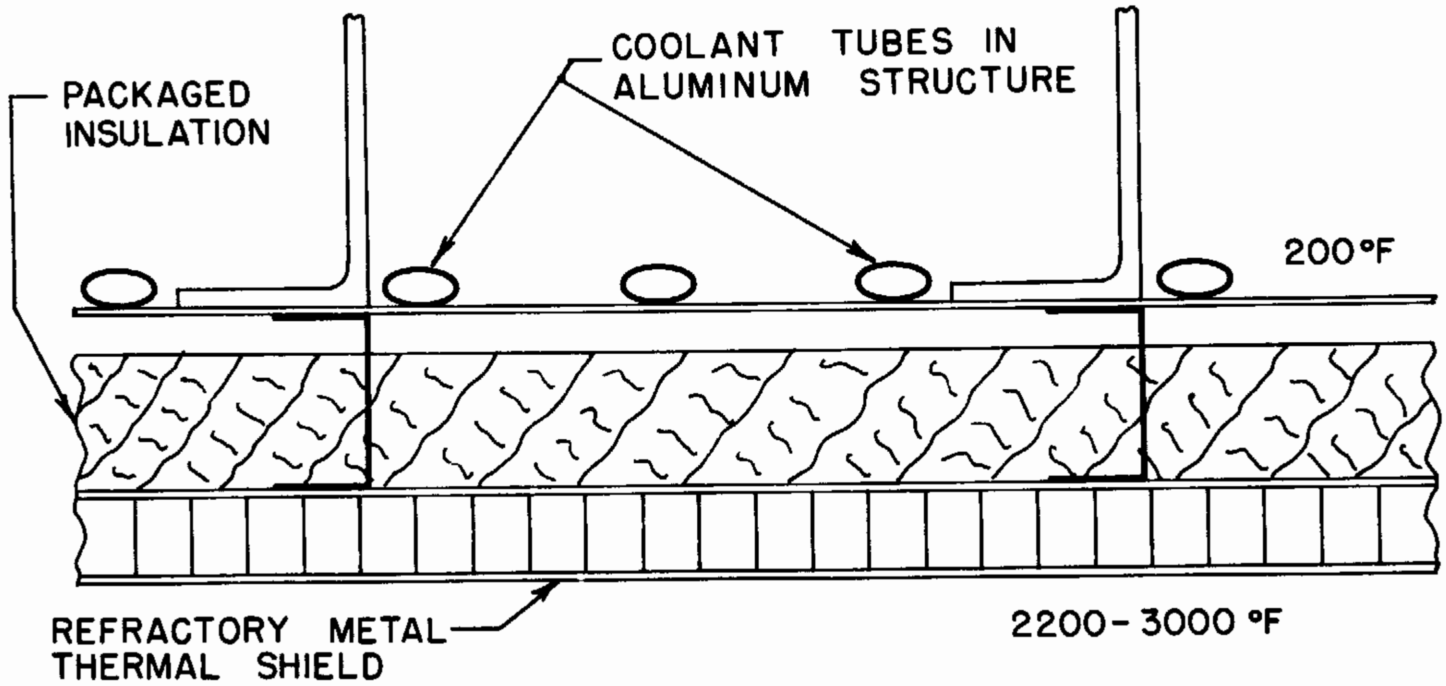

Figure 4.

STRUCTURAL COMPONENT

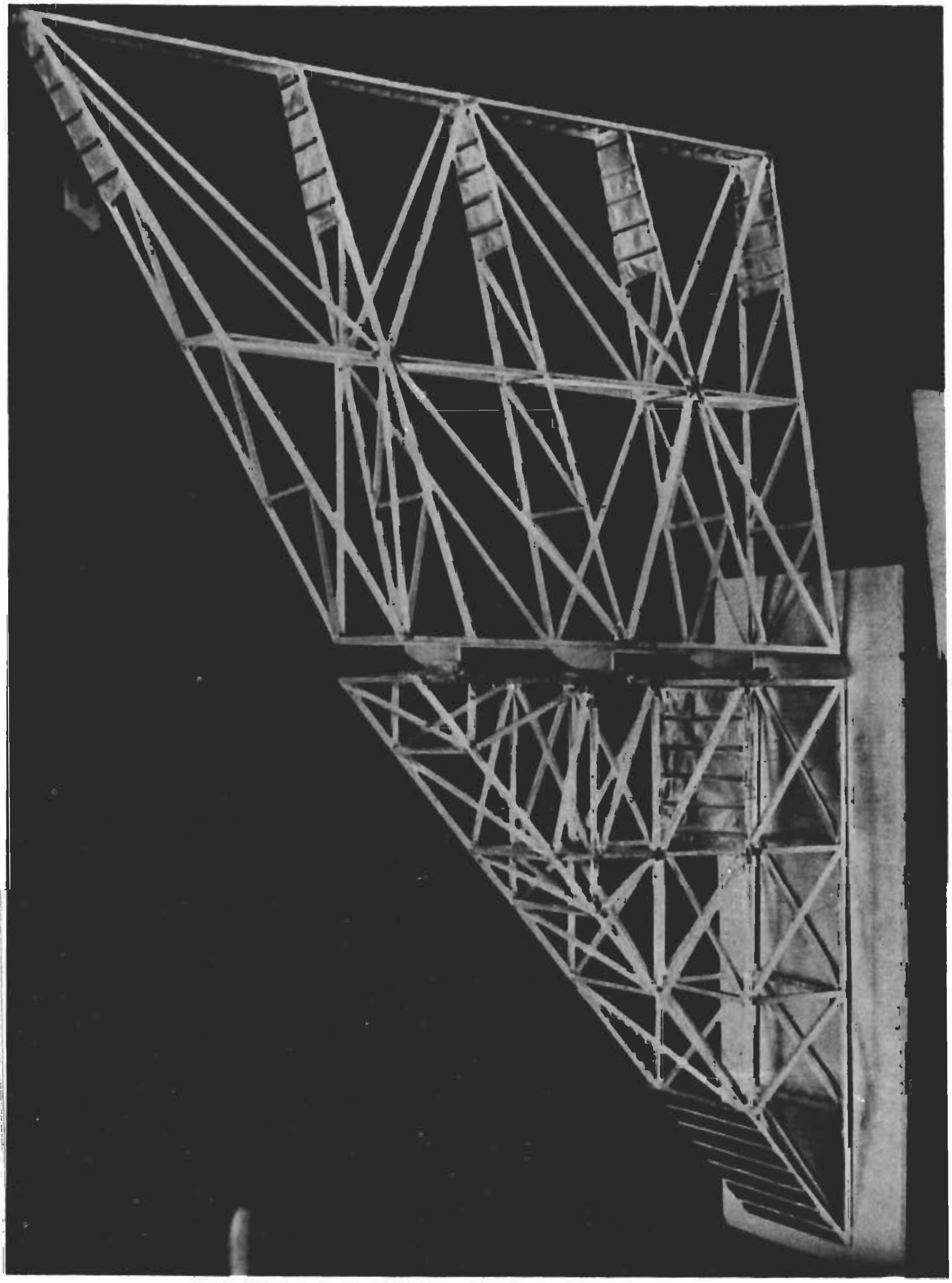

Figure 5.

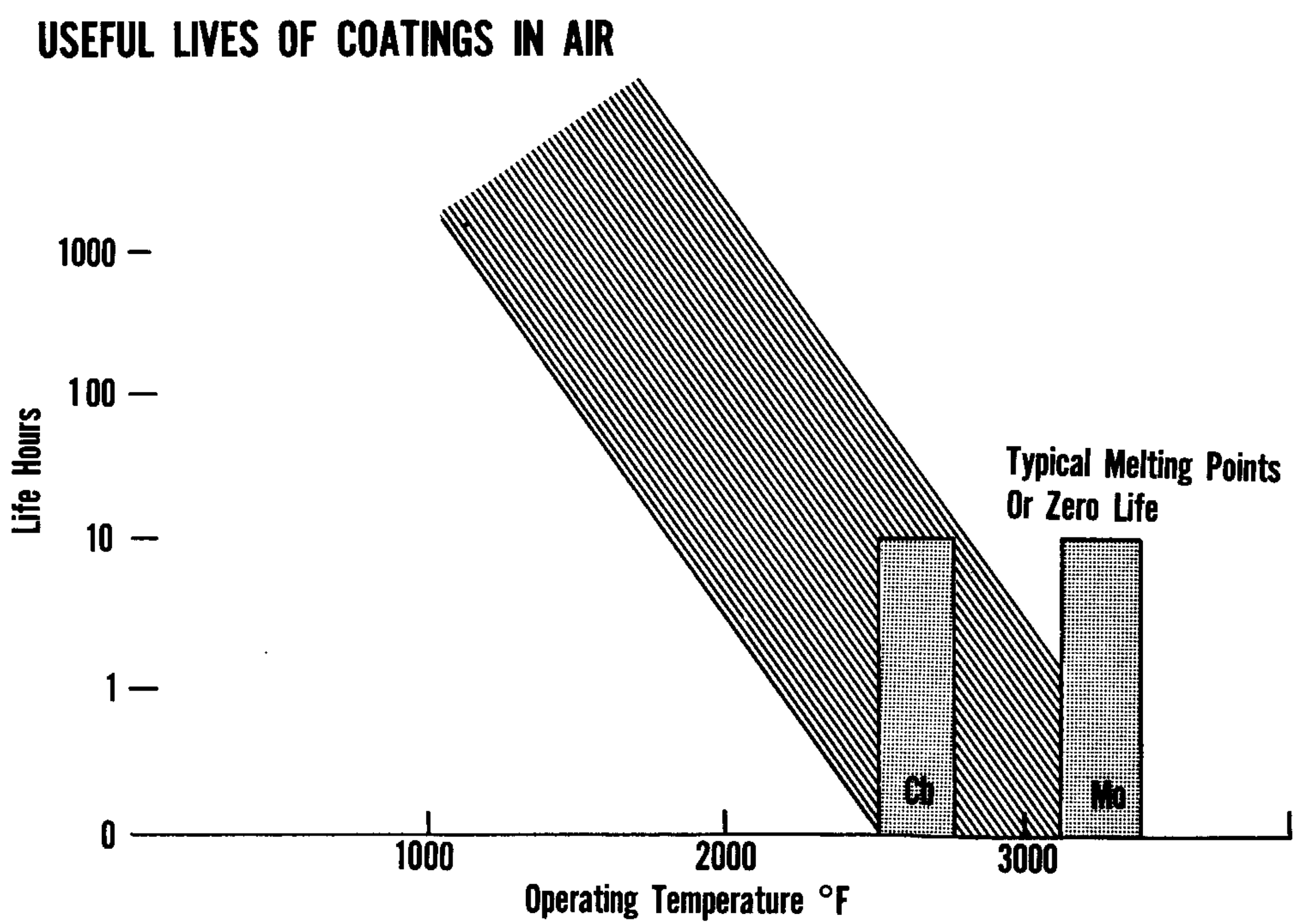
USEFUL LIVES OF COATINGS IN AIR
Life Hours
1000
100
10
1
0
1000
2000
3000
Operating Temperature °F
Typical Melting Points
Or Zero Life
Cb
Mo

Figure 6.

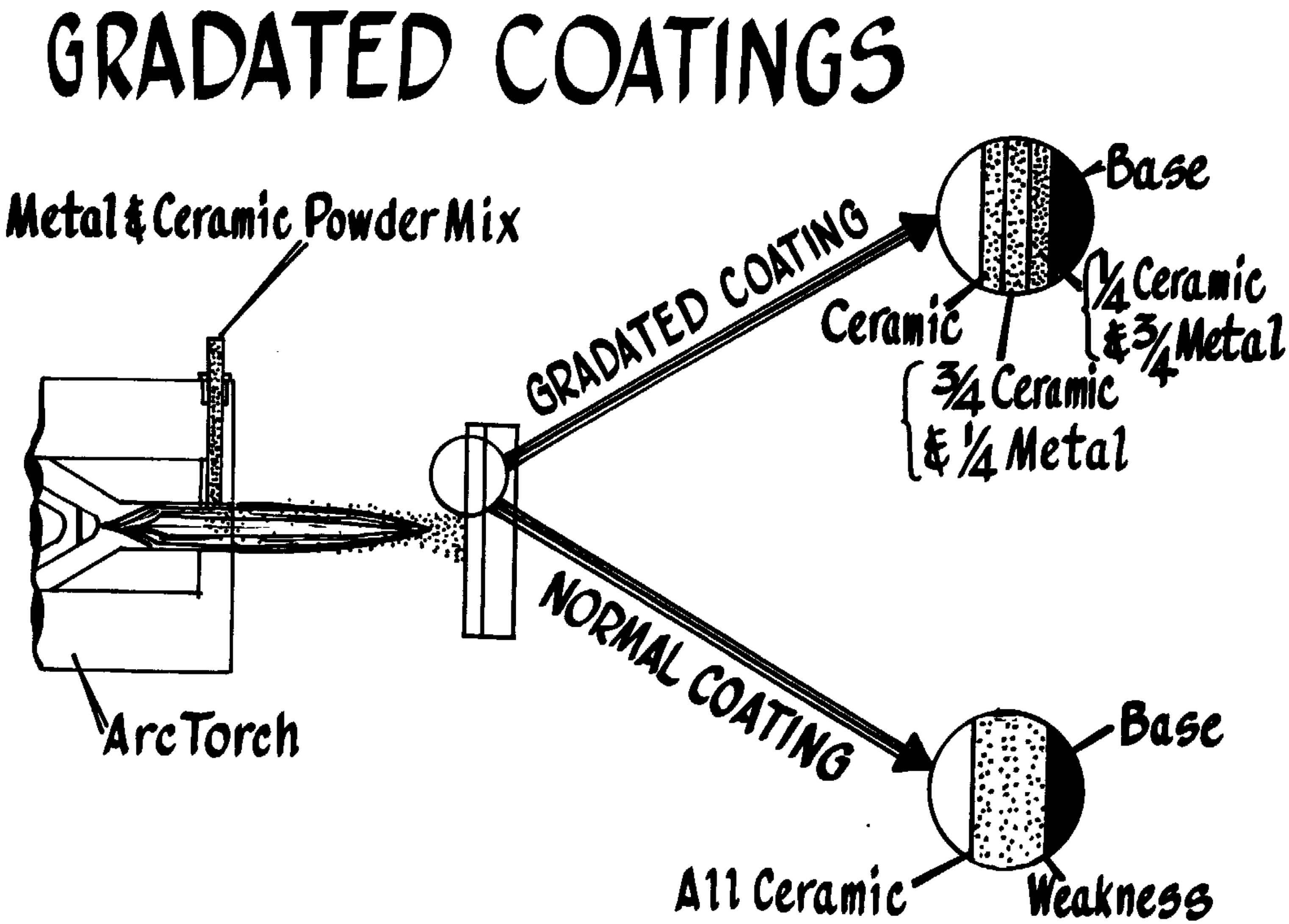
GRADATED COATINGS
Metal & Ceramic Powder Mix
Arc Torch
GRADATED COATING
NORMAL COATING
Base
Ceramic
1/4 Ceramic & 3/4 Metal
3/4 Ceramic & 1/4 Metal
Base
All Ceramic
Weakness

Figure 7.

CERAMIC FILLED HONEYCOMB

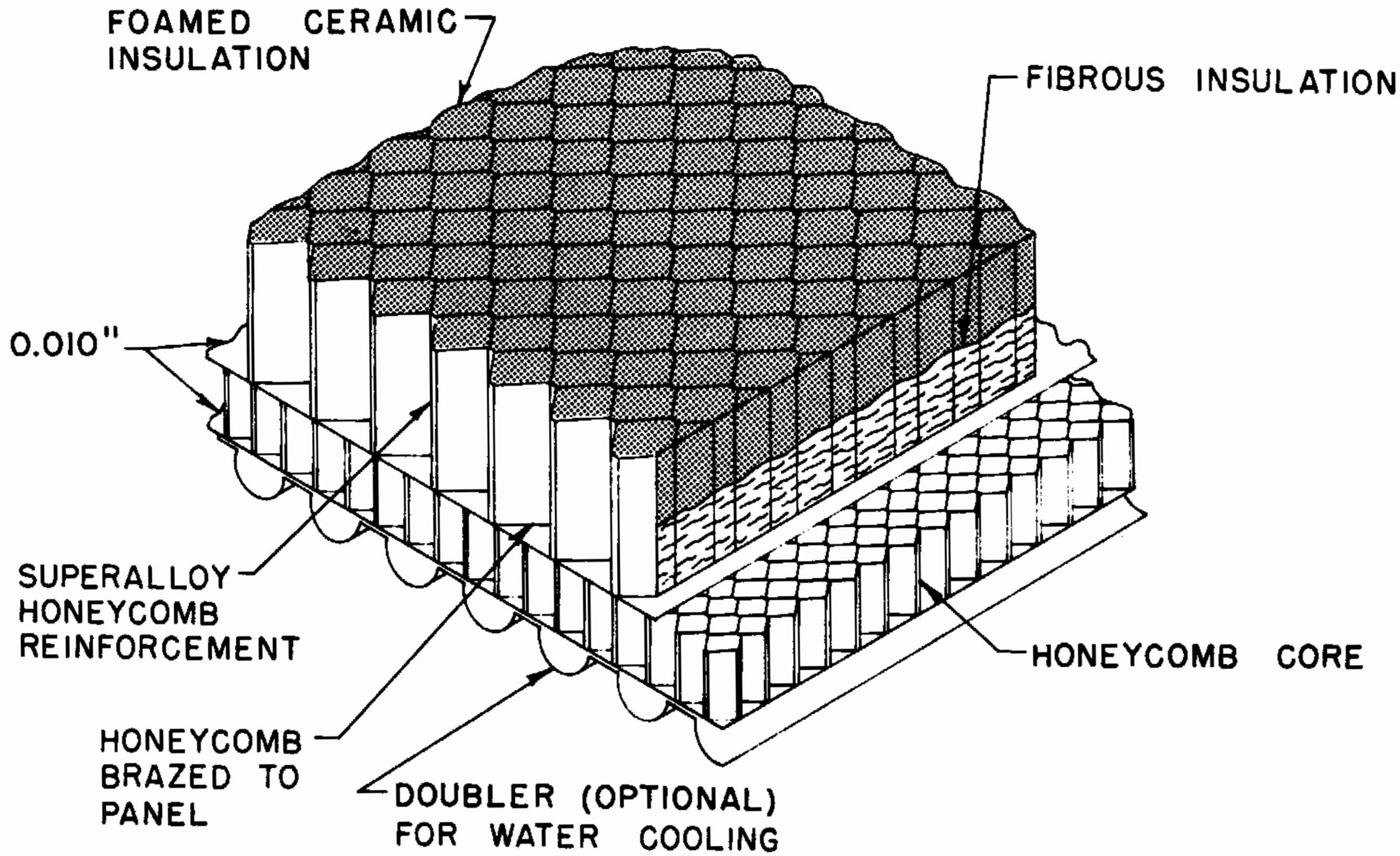

Figure 8.

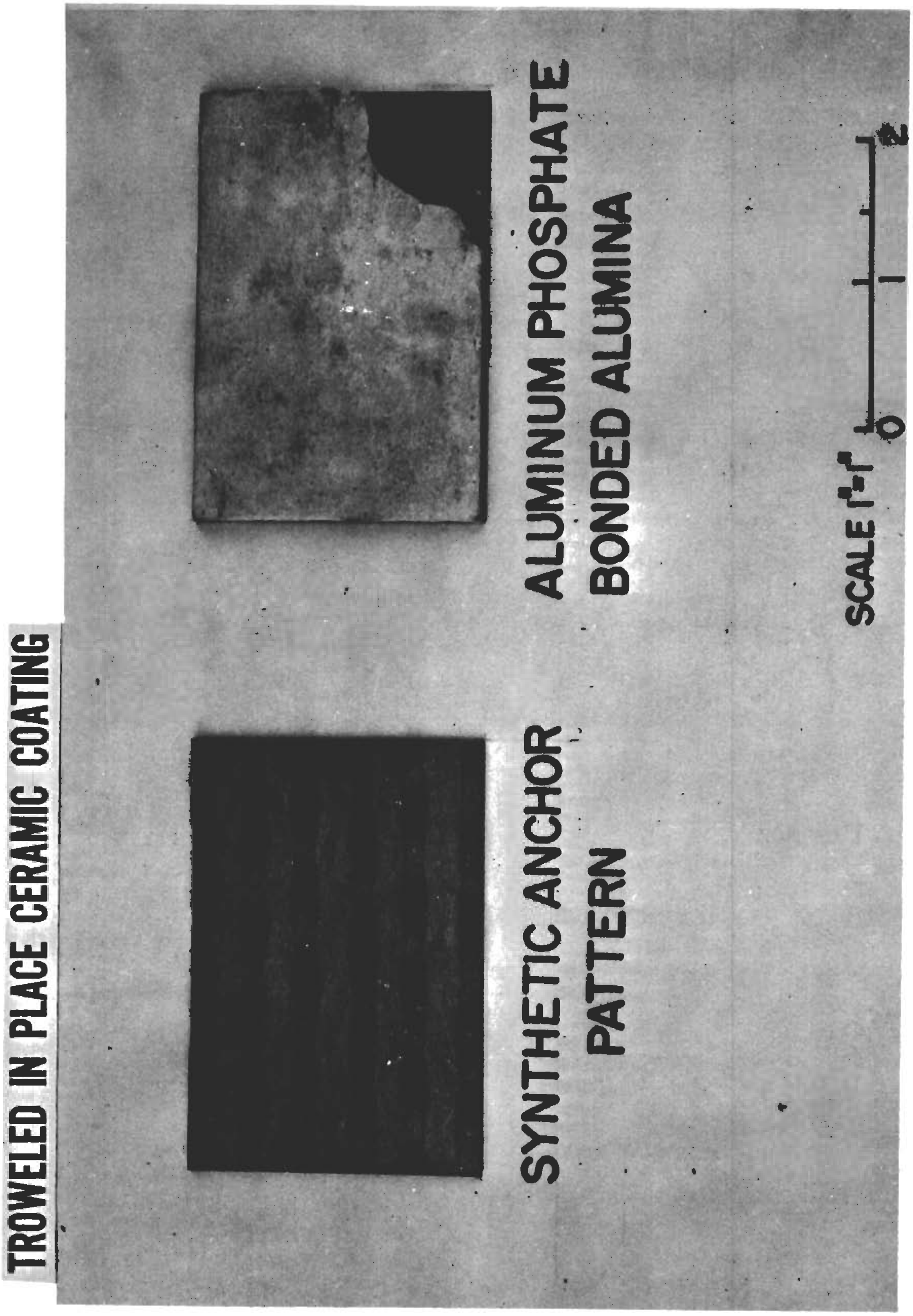
TROWELED IN PLACE CERAMIC COATING
SYNTHETIC ANCHOR PATTERN
ALUMINUM PHOSPHATE BONDED ALUMINA
SCALE 1"=1"
0
1
2

Figure 9.

METAL- CERAMIC COMPOSITES

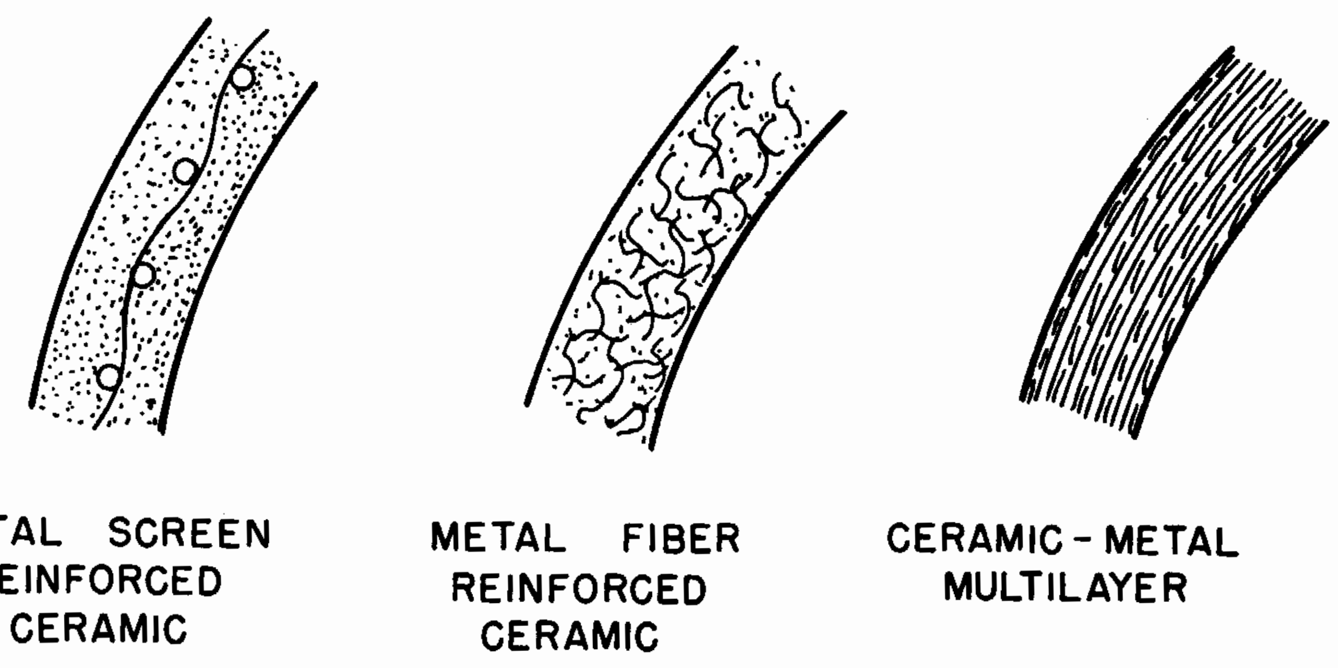

Figure 10.

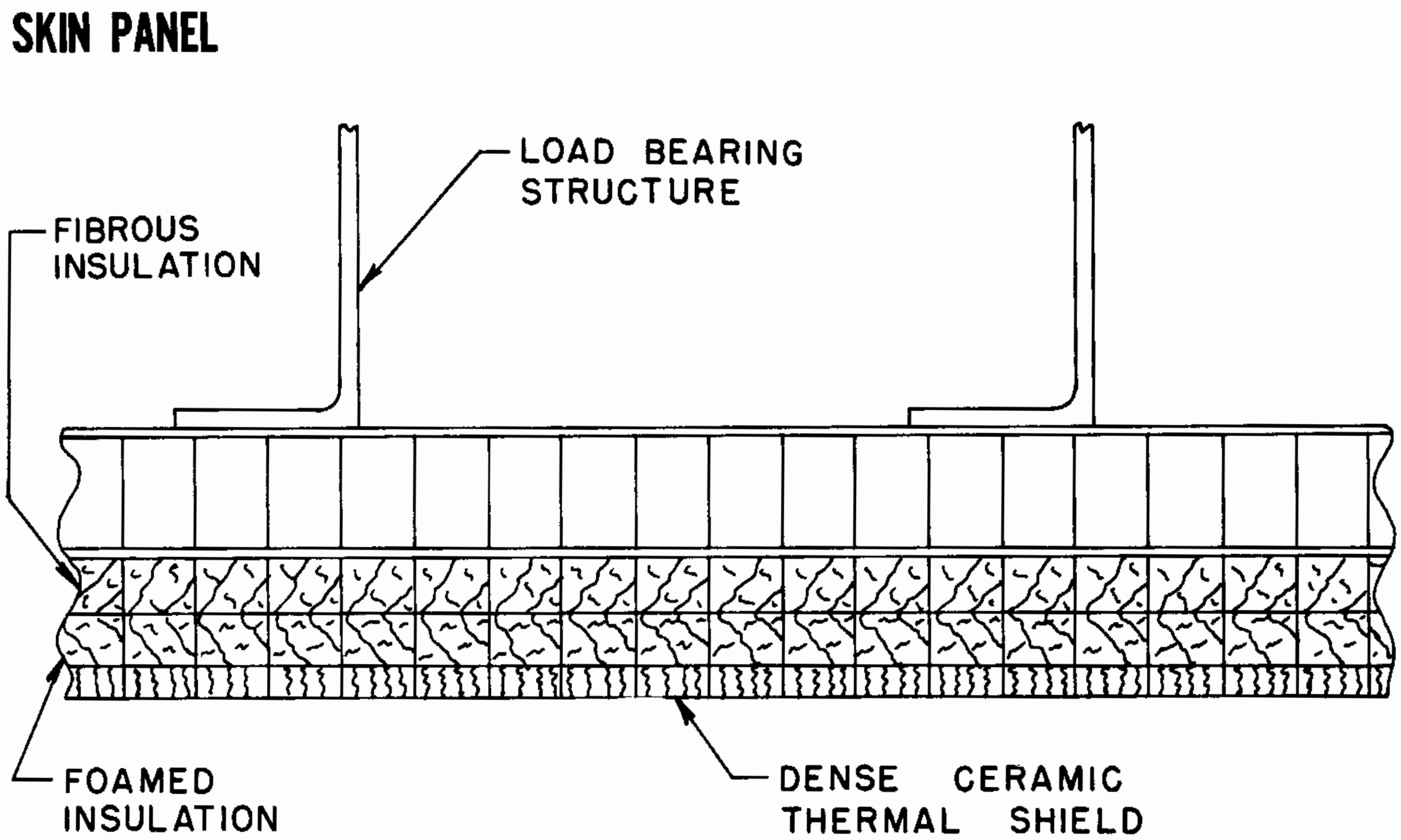
SKIN PANEL
LOAD BEARING STRUCTURE
FIBROUS INSULATION
FOAMED INSULATION
DENSE CERAMIC THERMAL SHIELD

Figure 11.

METAL REINFORCEMENT FOR LEADING EDGE

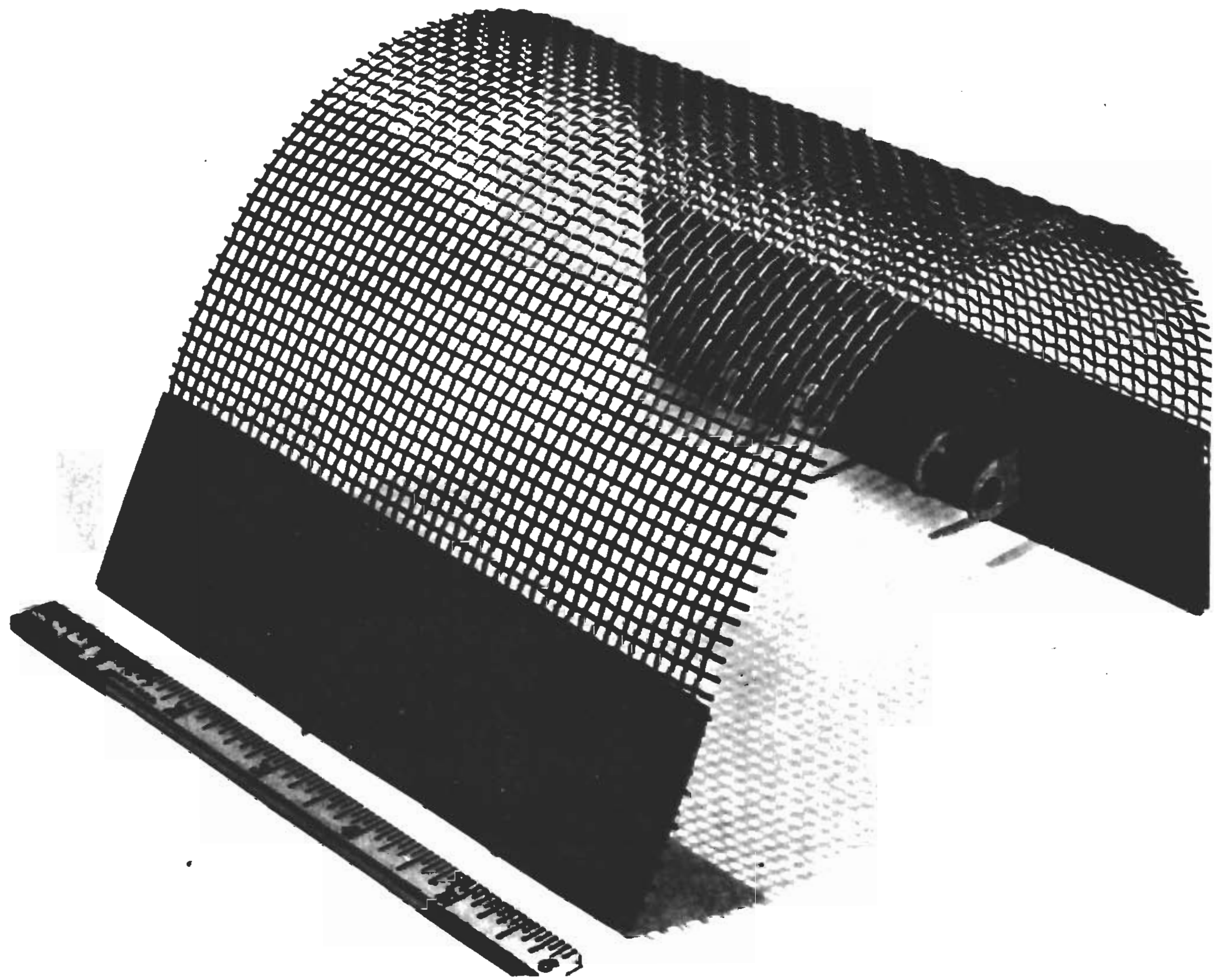

Figure 12.

REINFORCED CERAMIC LEADING EDGE

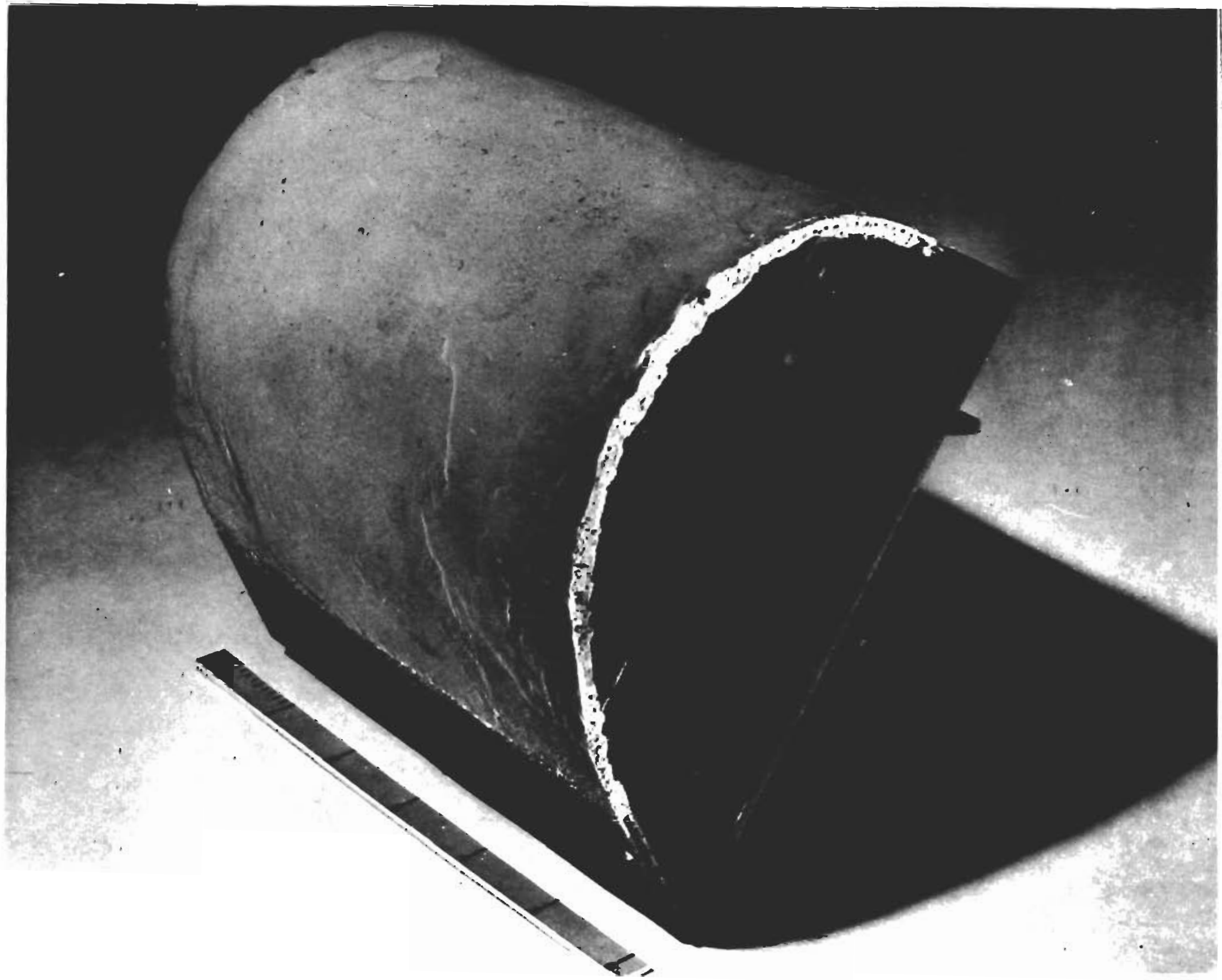

Figure 13.

INFLUENCE OF EMITTANCE ON SURFACE TEMPERATURE

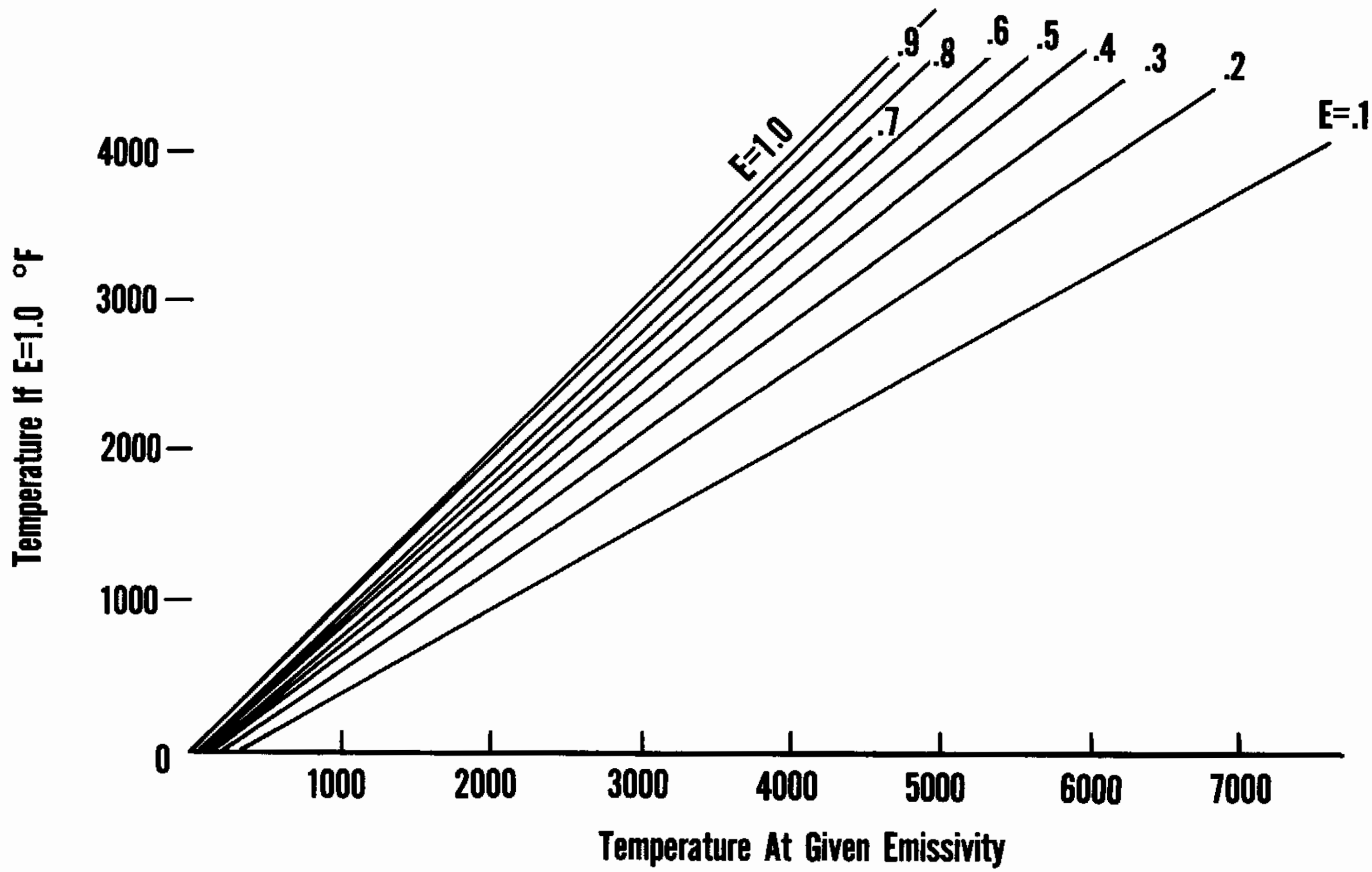

Figure 14.

THE EFFECT OF EMITTANCE ON VEHICLE PERFORMANCE

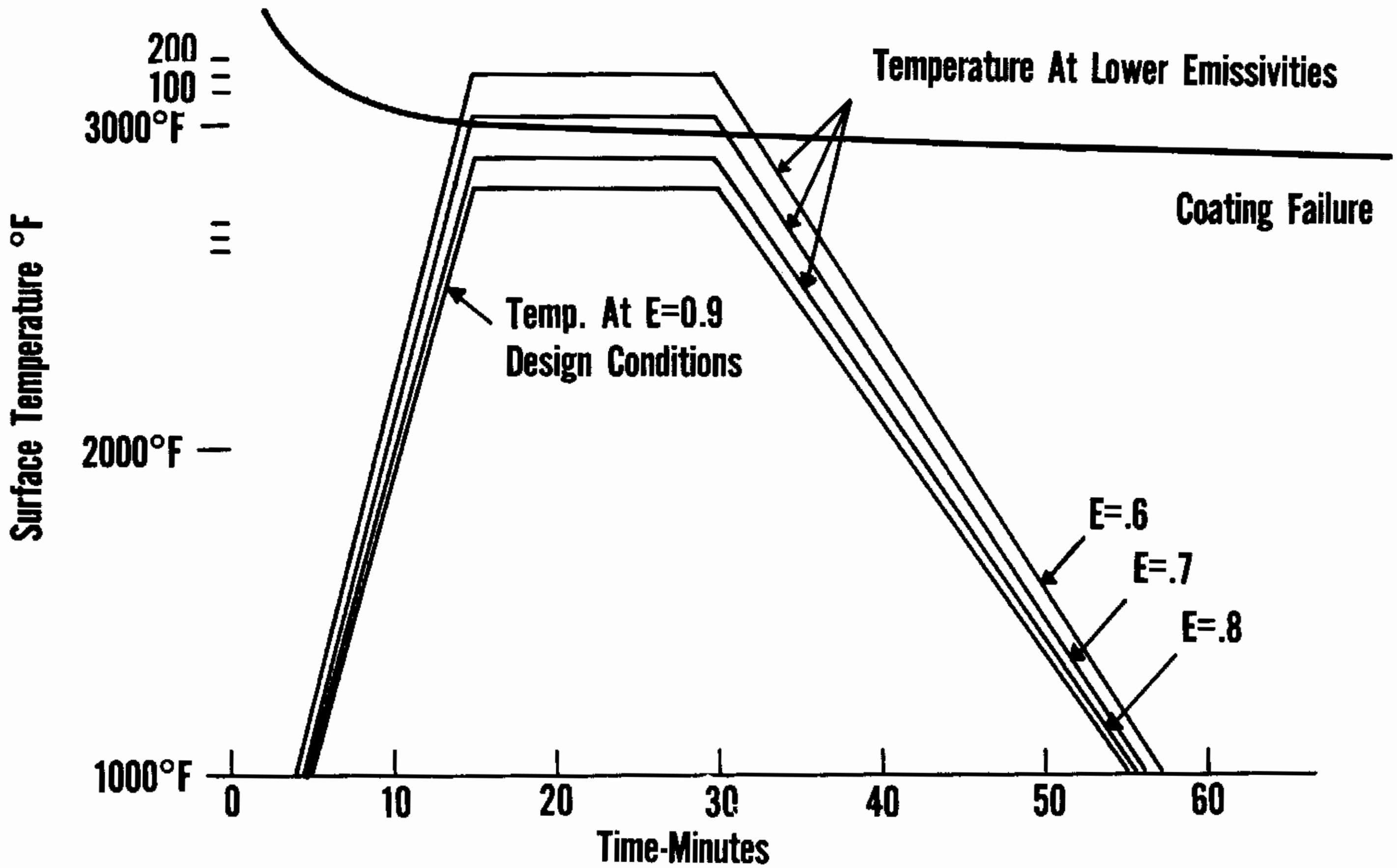

Figure 15.