

WADD TECHNICAL REPORT 60-825

contrails.iit.edu

W. G. L. L. L. L.

REFRACTORY COATINGS FOR TUNGSTEN

C. G. Goetzel

P. Landler

New York University

Research Division

MARCH 1961

PROPERTY OF
TECHNICAL INFORMATION CENTER
CHANCE VOUGHT CORPORATION

AUG 31 1961

WRIGHT AIR DEVELOPMENT DIVISION

49,024

contrail.iit.edu
NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.



Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.



This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C., for sale to the general public.



Copies of WADD Technical Reports and Technical Notes should not be returned to the Wright Air Development Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

WADD TECHNICAL REPORT 60-825

contracts.iit.edu

REFRACTORY COATINGS FOR TUNGSTEN,

C. G. Goetzel
P. Landler

New York University
Research Division

MARCH 1961

Materials Central
Contract No. AF 33(616)-6868
Project No. 7350

= U.S.A.F.
WRIGHT AIR DEVELOPMENT DIVISION,
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

400 - May 1961 - 29-1121

FOREWORD

THIS REPORT WAS PREPARED BY THE RESEARCH DIVISION, COLLEGE OF ENGINEERING, NEW YORK UNIVERSITY UNDER USAF CONTRACT NO. AF 33(616)-6868. THE CONTRACT WAS INITIATED UNDER PROJECT NO. 7350, "REFRACTORY INORGANIC NON-METALLIC MATERIALS", TASK NO. 73500, "CERAMIC AND CERMET MATERIALS DEVELOPMENT". THE WORK WAS ADMINISTERED UNDER THE DIRECTION OF THE MATERIALS CENTRAL, DIRECTORATE OF ADVANCED SYSTEMS TECHNOLOGY, WRIGHT AIR DEVELOPMENT DIVISION, WITH LT. N. M. GEYER ACTING AS PROJECT ENGINEER.

THIS REPORT COVERS WORK CONDUCTED FROM NOVEMBER 1959 TO OCTOBER 1960.

ACKNOWLEDGMENTS

THE AUTHORS ARE GREATLY INDEBTED TO DR. H. BUCKLE AND HIS SUPERIORS OF THE OFFICE NATIONAL D'ETUDES ET DE RECHERCHES AERONAUTIQUES (ONERA), PARIS, FRANCE FOR THEIR GENEROUS ASSISTANCE IN PREPARING PART OF THE COATED SUBSTRATE MATERIAL AND SOME OF THE PHOTOMICROGRAPHS. DR. BUCKLE'S ADVICE IN PURSUING THE MAJOR OBJECTIVES OF THE PROGRAM HAS BEEN INVALUABLE. THANKS ARE ALSO DUE TO MR. H. V. MOSBY OF THE FLAME DEPARTMENT, LINDE COMPANY, INDIANAPOLIS, IND. FOR HIS ARRANGEMENT FOR THE PLASMA ARC FLAME SPRAY COATING EXPERIMENTS.

ABSTRACT

A PRELIMINARY STUDY OF THE FEASIBILITY OF PROTECTING TUNGSTEN WIRES AGAINST OXIDATION AT 3300°F (1815°C) WAS UNDERTAKEN. A TUNGSTEN DISILICIDE COAT WAS FOUND TO BE THE MOST PROMISING COATING FOR THIS OPERATING TEMPERATURE.

SEVERAL SILICONIZING METHODS WERE GIVEN A CURSORY TREATMENT, INCLUDING VAPOR PLATING AND DIPPING INTO MOLTEN COPPER-SILICON BATH, AND THE SIMPLEST, CEMENTATION, SELECTED FOR CLOSER INVESTIGATION. THIS OPERATION WAS PERFORMED UNDER FLOWING HYDROGEN ATMOSPHERE AND SUCH VARIABLES AS TEMPERATURE, TIME, AND COMPOSITION OF THE CEMENTATION PACK WERE STUDIED AS A MAIN PART OF OUR EXPLORATORY WORK. A SINGLE BRITTLE TUNGSTEN-DISILICIDE (WSi_2) LAYER IS FORMED BY THIS METHOD. THE INHERENT BRITTLINESS OF TUNGSTEN APPEARS FURTHER AGGRAVATED BY THE DEVELOPMENT OF MICRO-CRACKS IN THE LAYER AS WELL AS IN THE SUBSTRATE DURING SILICONIZING.

OXIDATION TESTS USING DIRECT ELECTRICAL RESISTANCE HEATING WERE PERFORMED. IT WAS FOUND THAT PACK-SILICONIZED WIRES CAN WITHSTAND OXIDATION AT 3300°F IN STILL AIR FOR PROLONGED PERIODS UP TO AND EXCEEDING 10 HRS. THIS IS ACCOMPLISHED WITHOUT ANY DESTRUCTION OF THE COATING IN THE HIGH TEMPERATURE ZONE OWING TO THE FORMATION OF A VISCOUS GLASSFILM ON THE SURFACE. A PRONOUNCED TENDENCY TOWARD SELF-HEALING IS A USEFUL PROPERTY OF THIS TYPE OF COAT.

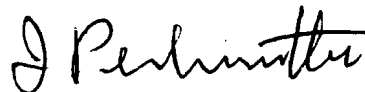
A SERIOUS DRAWBACK OF THE DISILICIDE COAT, HOWEVER, IS ITS LOW TEMPERATURE OXIDATION ("DISILICIDE PEST") WHICH OCCURS IN PARTS EXPOSED TO TEMPERATURES BETWEEN 1200° AND 2280°F (650°-1250°C) FOR PROLONGED PERIODS. IT CAUSES A DESTRUCTION OF THE DISILICIDE LAYER OVER A PERIOD OF 5 TO 15 HRS, DEPENDING ON COATING THICKNESS. IT WAS THE ACTUAL LIFE DETERMINING FACTOR IN THOSE TESTS WHERE OTHER FAILURES CAUSED BY IMPROPER TECHNIQUE HAD BEEN ELIMINATED.

PRELIMINARY ATTEMPTS TO DEPOSIT ZrO_2 ON TOP OF SILICONIZED WIRES BY MEANS OF PLASMA ARC SPRAY METHOD REMAINED LARGELY UNSUCCESSFUL BECAUSE OF POOR ADHESION. WHERE BONDING WAS OBTAINED, NO IMPROVEMENT IN LIFE UNDER HIGH TEMPERATURE OXIDIZING CONDITIONS COULD BE ASCERTAINED.

PUBLICATION REVIEW

THIS REPORT HAS BEEN REVIEWED AND IS APPROVED.

FOR THE COMMANDER:



I. PERLMUTTER
CHIEF, PHYSICAL METALLURGY BRANCH
METALS AND CERAMICS LABORATORY
MATERIALS CENTRAL

TABLE OF CONTENTS

	PAGE
I. INTRODUCTION AND BACKGROUND	1
A. GENERAL	1
B. OXIDATION OF UNCOATED TUNGSTEN	1
C. PROTECTIVE COATINGS ON TUNGSTEN	1
D. COATING TECHNIQUES	5
E. OXIDATION TESTS AT HIGH TEMPERATURES	7
II. EXPERIMENTAL PROCEDURE	9
A. SUBSTRATE	9
B. DIP-SILICONIZING	9
C. SILICONIZING BY MEANS OF VAPOR PLATING	10
D. SILICON CEMENTATION	10
E. OXIDATION TESTS	12
III. EXPERIMENTAL RESULTS AND ANALYSIS	14
A. COATINGS FORMED BY CEMENTATION	14
B. COATINGS FORMED BY OTHER METHODS	16
C. OXIDATION TESTS OF SILICONIZED WIRES	16
D. SILICONIZED WIRES WITH EXTERNAL FLAME SPRAYED ZrO_2 COATING	19
IV. SUMMARY AND CONCLUSIONS	19
A. GENERAL	19
B. APPLICATION OF COATINGS	20
C. HIGH TEMPERATURE PROPERTIES	21
D. CONCLUSIONS	22
V. REFERENCES	23

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	FLOW DIAGRAM OF HYDROGEN PURIFICATION	31
2	SCHEMATIC LAYOUT OF PACKSILICONIZING ARRANGEMENT	32
3	LAYER THICKNESS VS SILICONIZING TIME	33
4	RADIAL CRACKS IN WSi_2 COATING - 200X, ETCH. $K_3Fe(CN)_6 + NaOH$	34
5	LONGITUDINAL CRACKS IN WSi_2 COATING - 200X, ETCH. $K_3Fe(CN)_6 + NaOH^2$	34
6	WSi_2 LAYER, DISCONTINUITY CAUSED BY MELTING OF THE ENERGIZER, 200X, ETCH. $K_3Fe(CN)_6 + NaOH$	35
7	WSi_2 COATING BEFORE TESTING	36
8	FORMATION OF A W_3Si_2 INTERMEDIATE LAYER (AFTER 1-1/2 HR. TESTING)	36
9	GRAIN SIZE OF THE WSi_2 LAYER SHOWN IN FIG. 7	36
10	GRAIN SIZE OF THE WSi_2 LAYER AFTER OXIDATION TEST (1-1/2 HR. AT $3100^\circ F$) ²	36
11	WSi_2 COATING BEFORE TESTING	37
12	FORMATION OF W_3Si_2 INTERMEDIATE LAYER AND GLASSY SURFACE (AFTER TESTING)	37
13	GRAIN SIZE OF THE WSi_2 LAYER SHOWN IN FIG. 11	37
14	GRAIN SIZE OF THE WSi_2 LAYER AFTER TESTING	37
15	CONVERTED DISILICIDE LAYER AFTER 10 HR. OXIDATION TEST, 500X	38
16	LAYER MOLTEN BENEATH THE GLASS LAYER AFTER 3 HR. TEST TIME AND OXIDATION TEST CONTINUED TO 10 HR. TEST TIME, 500X	38
17	THERMAL CYCLING OF THICK WSi_2 COATED WIRE (AFTER 17 MINUTE HEATING IN THE SECOND CYCLE)	39
18	THERMAL CYCLING OF THICK WSi_2 COATED WIRE (AFTER 1 HR. 37 MINUTES IN THE SECOND CYCLE)	39

LIST OF ILLUSTRATIONS (CONTINUED)

FIGURE		PAGE
19	CROSS SECTION OF PINHOLE FAILURE, 150X	40
20	SURFACE OF SAMPLES THAT FAILED BY LIQUID PHASE FORMATION	41
21	PHOTOMICROGRAPH OF THE LIQUID PHASE FAILURE, 200X, ETCH. $K_3Fe(CN)_6$ + NaOH	41
22	LOW TEMPERATURE OXIDATION OF A 35μ - DISILICIDE COATING	42

LIST OF TABLES

TABLE	PAGE
I. MELTING AND BOILING POINTS OF ENERGIZER SALTS	26
II. LAYER THICKNESSES IN MICRONS PRODUCED BY DIFFERENT SILICONIZING PACKS	27
III. OXIDATION TEST RESULTS - FAILURES CAUSED BY LOCAL IMPERFECTION	28
IV. OXIDATION TEST RESULTS - FAILURES CAUSED BY FUSION	29
V. OXIDATION TEST RESULTS - FAILURES CAUSED BY DISCILIIDE PEST	30

I. INTRODUCTION AND BACKGROUND

A. GENERAL

UNDER CONTRACT No. AF 33(616)-5735, PROJ. No. 8-(8-7350), TASK No. 73500 AN INVESTIGATION OF PROTECTIVE METALLIC COATINGS ON TUNGSTEN WAS PERFORMED (1). THE TARGET WAS TO OBTAIN PROTECTION AT 3000°F (1650°C) AGAINST OXIDATION FOR 10 HOURS IN STILL AND FLOWING AIR. THE INVESTIGATION REPORTED HERE IS A CONTINUATION OF THAT EFFORT. HOWEVER, THE REQUIREMENTS OF RESISTANCE AGAINST OXIDATION WERE RAISED TO 3300°F (1815°C) FOR 10 HOURS IN STILL AND FLOWING AIR.

B. OXIDATION OF UNCOATED TUNGSTEN

THE OXIDATION BEHAVIOR OF TUNGSTEN HAS BEEN THE SUBJECT OF NUMEROUS INVESTIGATIONS. IN AIR, LOW TEMPERATURE OXIDATION IS VERY SLOW, AND TUNGSTEN REMAINS BRIGHT FOR SEVERAL HOURS UP TO 600°F (315°C). ABOVE 600°F, OXIDE LAYERS ARE FORMED RATHER QUICKLY (2). WITHIN THE TEMPERATURE RANGE OF 600° TO 1800°F (980°C), SEVERAL TUNGSTEN OXIDES ARE OBTAINED INCLUDING WO_2 , W_4O_{11} AND WO_3 (3,6). THE OXIDE LAYERS FORMED ARE GENERALLY NOT PROTECTIVE BECAUSE OF POROSITY, MAINLY AS A RESULT OF CONVERSION OF DENSE LAYERS TO POROUS OXIDE FORMS (7). AGREEMENT ABOUT THE OXIDATION RATES IS NOT COMPLETE IN THE LITERATURE (2,4,8), AT LEAST IN PART BECAUSE OF THE HIGH DEPENDENCE OF THE OXIDATION RATE ON THE COMPOSITION (ESPECIALLY THE MOISTURE CONTENT) OF THE OXIDIZING ATMOSPHERES USED BY THE DIFFERENT INVESTIGATORS. ABOVE 1800°F THE TUNGSTEN SURFACE OXIDES VOLATILIZE CONSIDERABLY (7) CAUSING AN ACCELERATED OXIDATION OF THE TUNGSTEN SUBSTRATE. AT HIGH PARTIAL PRESSURES OF WATER VAPOR, VOLATILIZATION OCCURS AT A CONSIDERABLY LOWER TEMPERATURE. INCREASING MOISTURE CONTENT IN THE OXIDIZING ATMOSPHERE ALSO INCREASES THE VOLATILIZATION RATE (9,10). THE VOLATILIZATION RATES FOR DIFFERENT COMPOSITION OF THE OXIDIZING MEDIUM AND DIFFERENT TEMPERATURES ARE WELL ESTABLISHED (8,11,12).

C. PROTECTIVE COATINGS ON TUNGSTEN

1. CLASSIFICATION:

BECAUSE OF THE POOR OXIDATION RESISTANCE, APPLICATION OF TUNGSTEN IN AIR AT ELEVATED TEMPERATURE REQUIRES PROTECTIVE COATINGS ON THE METAL. THERE ARE THREE PRINCIPAL POSSIBILITIES OF PROTECTION. ONE APPROACH IS THE USE OF COATINGS OF HIGH MELTING, INTRINSICALLY OXIDATION RESISTANT METALS OR ALLOYS. ANOTHER WAY IS THE APPLICATION OF COMPOUNDS WITH OXYGEN, SUCH AS GLASSES AND CERAMICS, TO THE SURFACE OF THE TUNGSTEN SPECIMEN. A THIRD POSSIBILITY IS THE FORMATION OF OXIDATION RESISTANT INTERMETALLIC COMPOUNDS WITH THE TUNGSTEN SUBSTRATE ITSELF ON ITS SURFACE. COMBINATION OF THESE THREE TYPES OF COATINGS MIGHT SOMETIMES BE THE BEST SOLUTION OF A COATING PROBLEM.

2. METALLIC COATINGS:

THE HIGH SERVICE TEMPERATURE SPECIFIED RAISES SEVERE PROBLEMS, ESPECIALLY FOR THE APPLICATION OF METALLIC PROTECTIVE COATINGS. THERE ARE ONLY A FEW METALS

MANUSCRIPT RELEASED FOR PUBLICATION 1 NOVEMBER 1960 AS A WADD TECHNICAL REPORT.

WHICH HAVE A MELTING POINT ABOVE 3300°F AND UNFORTUNATELY, MOST OF THEM FORM VOLATILE OXIDES AT ELEVATED TEMPERATURE, EXPOSING THE PURE METAL SURFACE TO OXIDATION. IN THESE CASES VERY HIGH OXIDATION RATES PREVAIL AT 3300°F. AN EXCEPTION ARE THE HIGH MELTING MEMBERS OF THE PLATINUM GROUP, WHICH BEHAVE UNDER CERTAIN CONDITIONS LIKE NOBLE METALS.

NONE OF THE OXIDES FORMED ON PLATINUM GROUP METALS ARE STABLE ABOVE 2100°F (1150°C) (10,13). MOST INVESTIGATORS AGREE TODAY THAT ABOVE THIS TEMPERATURE OXIDES ARE FORMED ON PLATINUM GROUP METALS WHICH IMMEDIATELY VOLATILIZE OR DECOMPOSE (14). HOWEVER, THE OXIDATION RATES ARE RELATIVELY LOW AND SOME OF THESE METALS WOULD POSSIBLY BE SUITABLE FOR LAYERS OXIDATION RESISTANT IN THE 10-HOUR RANGE, AT TEMPERATURES CONSIDERABLY ABOVE 2100°F, IF ONLY THE RATE FACTOR WERE CONSIDERED, AND NOT OTHER MECHANISMS SUCH AS DIFFUSION, BRITTLE INTERMEDIATE PHASES, AND THE LIKE.

THERE REMAINS ONLY CHROMIUM AND SOME OF ITS ALLOYS IN PRACTICAL USE WHICH FORM OXIDE LAYERS OF SOME STABILITY AT TEMPERATURES ABOVE 2000°F (1095°C) (15). HOWEVER, THE PRACTICAL PROTECTION LIMIT OF SUCH COATINGS, E.G. OF ALLOYS OF THE TYPE Fe-Cr-Al, IS TODAY ABOUT 2700°F (16,17). (A Mo-Si-Cr-B-Al ALLOY PROTECTED COLUMBIUM AT 2730°F (1500°C) FOR 108 HOURS (16))

THE HIGH TEMPERATURE APPLICATION OF METALLIC COATINGS RAISES TWO CONTRADICTORY REQUIREMENTS. THE DIFFUSIVITY OF TUNGSTEN THROUGH THE PROTECTIVE COATING SHOULD BE VERY LOW IN ORDER TO RETAIN THE EFFECTIVENESS OF THE PROTECTION. ESPECIALLY THE OXIDATION BEHAVIOR OF THE PLATINUM GROUP METALS IS, DUE TO THEIR OXIDATION MECHANISMS AT THESE TEMPERATURES, VERY SENSITIVE TO IMPURITIES. ON THE OTHER HAND, THE EXTREMELY LOW TEMPERATURE COEFFICIENT OF THERMAL EXPANSION OF TUNGSTEN IN COMPARISON TO ALL OTHER METALS YIELDS BONDING DIFFICULTIES BETWEEN LAYER AND SUBSTRATE. A CONSIDERABLE DIFFUSION BETWEEN SUBSTRATE AND LAYER WOULD BE NECESSARY TO PROVIDE A GRADUAL CHANGE OF THE COEFFICIENT. IN ORDER TO SOLVE THIS PROBLEM, INTERMEDIATE LAYERS WERE INTRODUCED IN ORDER TO SERVE AS BOTH A DIFFUSION BARRIER AND A LAYER WITH AN INTERMEDIATE EXPANSION CHARACTERISTIC (1). HOWEVER, AT THESE HIGH TEMPERATURES INTERMEDIATE LAYERS RAISE NEW PROBLEMS (SUCH AS FORMATION OF LOW MELTING EUTECTICS) WHICH BECOME THE MORE CRITICAL THE GREATER THE NUMBER OF COMPONENTS INVOLVED. SINCE THE SPECIFIED SERVICE TEMPERATURE IS VERY CLOSE TO THE MELTING POINT OF MOST OF THE COATING METALS UNDER INVESTIGATION, THE DIFFUSION BARRIER AND LOW MELTING PHASES CONSTITUTE THE MAJOR PROBLEMS. RECENTLY, SOME INVESTIGATIONS ABOUT DIFFUSION BARRIERS WERE INITIATED (18) AND NUMEROUS PUBLICATIONS EXIST ABOUT THE TWO AND THREE PHASE SYSTEMS OF THE HIGH MELTING METALS (19,25,28). CONNECTED WITH THESE PROBLEMS IS ALSO THE POSSIBLE FORMATION OF BRITTLE INTERMETALLIC COMPOUNDS AS INTERMEDIATE LAYERS (26,27,31). AS A RESULT OF THESE DIFFICULTIES THE TEMPERATURE LIMIT OF THIS TYPE OF COATING SEEMS TO LIE BELOW 3000°F (1650°C) FOR ANY PROLONGED TIMES OF EXPOSURE TO OXIDIZING ATMOSPHERE.

3. STABLE OXIDE COMPOUNDS:

GLASSES HAVE SEVERAL PROPERTIES WHICH MAKES THEM INTERESTING AS OXIDATION PROTECTIVE MATERIALS. THEY DO NOT REACT WITH AN OXIDIZING ATMOSPHERE, ARE USUALLY INERT VIS-A-VIS THE SUBSTRATE, AND ARE PRACTICALLY IMPERVIOUS TO OXYGEN. A PERFECT GLASS FILM IS THEREFORE ABSOLUTELY PROTECTIVE AGAINST OXIDATION EVEN ABOVE ITS FUSION TEMPERATURE, AS SHOWN BY EXPERIMENT (29). HOWEVER, ALL GLASSES ARE VERY BRITTLE

AT ROOM TEMPERATURE AND MOST OF THEM HAVE A SOFTENING AND MELTING POINT BELOW 3300°F (1815°C). THE MOST SUITABLE BASIC GLASS TYPE IS QUARTZ (SiO_2), WHICH HAS A SOFTENING TEMPERATURE OF 1800°F (980°C) AND A MELTING POINT OF ABOUT 3100°F (1705°C) (30). FOR A SUCCESSFUL COATING IT IS THEREFORE NECESSARY TO INCREASE THE MELTING POINT OF THE GLASS BY MEANS OF ADDITIONS, E.G. ZrO_2 , ZIRCON OR K_2O (16,29). HIGHER MELTING GLASS TYPES ON AN Al_2O_3 OR Ta_2O_5 BASIS HAVE ALSO BEEN REPORTED (16,32). THOUGH IT IS FORTUNATELY POSSIBLE WITH THESE GLASS TYPES TO MATCH THE THERMAL EXPANSION COEFFICIENT OF THE TUNGSTEN SUBSTRATE, NO GLASS LAYERS OF THIS TYPE SATISFACTORY FOR PROTECTIVE COATINGS COULD BE OBTAINED AS YET, MAINLY DUE TO THEIR INFLEXIBILITY AND BRITTLINESS AT ROOM TEMPERATURE (29).

QUITE A FEW METAL AND NONMETAL OXIDES (CERAMICS) ARE KNOWN TO POSSESS GOOD HIGH TEMPERATURE PROPERTIES (30). HOWEVER, ATTEMPTS TO APPLY TO TUNGSTEN PLAIN CERAMIC COATINGS AS PROTECTIVE LAYERS MEET WITH DIFFICULTIES IN SEVERAL RESPECTS. FOR ONCE, TECHNIQUES OF APPLYING AND GENERATING AN IMPERVIOUS LAYER ARE NOT SUFFICIENTLY DEVELOPED. ANOTHER PROBLEM STEMS FROM THE FACT THAT SOMETIMES A REACTION TAKES PLACE BETWEEN THE SUBSTRATE AND THE LAYER (29). HOWEVER, SOME IMPROVEMENT IN THIS TYPE OF OXIDATION PROTECTION WAS RECENTLY REPORTED ALONG LINES OF GLASS FRITTED ZIRCONIA OR ZIRCONIA-ENRICHED GLASS COATINGS (29). ADDITIONAL USEFUL COATING TECHNIQUES FOR CERAMICS HAVE BEEN REPORTED FROM EUROPE (31). ANOTHER SUGGESTED TECHNIQUE FOR FORMATION OF DENSE CERAMIC LAYERS IS THE DEPOSITION OF OXIDES FROM THE GAS PHASE (32) BUT SO FAR ITS PRACTICAL APPLICABILITY FOR TUNGSTEN COATINGS COULD NOT BE PROVED (29). SOME SUCCESS HAS BEEN REPORTED IN USING SPRAYED METAL-METAL OXIDE MIXTURES SUCH AS Ni-MgO , $\text{Cr-Al}_2\text{O}_3$, $\text{Al-Al}_2\text{O}_3$ (33).

A USEFUL PROPERTY OF ALL GLASS AND CERAMIC COATINGS IS THEIR SELF-HEALING PROPERTY IF EXPOSED ABOVE THE SOFTENING TEMPERATURE.

4. OXIDATION RESISTANT INTERMETALLIC COMPOUNDS:

MANY INTERMETALLIC COMPOUNDS HAVE A RELATIVELY HIGH MELTING POINT, AND THE BEHAVIOR AND TECHNOLOGY OF SOME OF THE HIGHER MELTING BORIDES, CARBIDES, NITRIDES, ALUMINIDES, AND SILICIDES HAVE BEEN THOROUGHLY INVESTIGATED (34,37). MANY OF THESE COMPOUNDS ALSO POSSESS REASONABLY GOOD HEAT AND OXIDATION RESISTANCE AND ARE THEREFORE POTENTIAL MATERIALS FOR PROTECTIVE COATINGS IN HIGH TEMPERATURE APPLICATIONS. THE OXIDATION RESISTANCE OF THESE COMPOUNDS IS ALWAYS BELIEVED TO BE BASED ON THE FORMATION OF AN IMPERVIOUS OXIDATION PRODUCT ON THE SURFACE WHOSE EXISTENCE CAN BE SOMETIMES EFFECTIVELY DETECTED.

SUCH INVESTIGATIONS PERFORMED ON BORIDES, HAVE RELATED ESPECIALLY TO APPLICATIONS REQUIRING RESISTANCE TO BORON OXIDE (16). PROTECTIVE PROPERTIES OF SiB_6 HAVE BEEN REPORTED UP TO 3500°F (1925°C) DUE TO THE FORMATION OF A VERY STABLE BOROSILICATE GLASS ON THE SURFACE (33,38,39).

THOUGH THERE ARE NO SUCCESSFUL APPLICATIONS KNOWN OF CARBIDES AS HIGH TEMPERATURE PROTECTIVE COATINGS ON REFRACTORY METALS, A LIMITED OXIDATION RESISTANCE HAS BEEN ESTABLISHED FOR CARBIDES OF Hf, W, Ti, Si AS COATING MATERIALS FOR GRAPHITE IN ROCKET NOZZLE APPLICATIONS. INVESTIGATIONS OF THE OXIDATION BEHAVIOR OF SiC AS COMPARED TO OTHER CARBIDES SHOW ITS RESISTANCE TO AIR AT ELEVATED TEMPERATURE (IN THE ORDER OF 3500°F) TO BE THE BEST OF THE GROUP, THOUGH STILL ONLY FAIR (16,40).

PLAIN COATINGS OF ALUMINIDES AND NITRIDES HAVE RECEIVED LITTLE ATTENTION, BUT ARE SOMETIMES USED IN COMPLEX COATING SYSTEMS (16).

THE MOST PROMISING INTERMETALLIC COMPOUNDS ARE THE SILICIDES. THEIR RESISTANCE TO OXIDATION WAS THEREFORE INVESTIGATED IN THE CASE OF MOST OF THE REFRACTORY METALS, AND IT WAS FOUND THAT THE FORMATION OF A GLASSY SURFACE IS AN IMPORTANT PRE-REQUISITE. WITH INCREASING IMPORTANCE OF TUNGSTEN AND PARTICULARLY MOLYBDENUM AS STRUCTURAL MATERIALS, INTENSIVE STUDIES WERE UNDERTAKEN OF THE SILICIDES OF THESE METALS AS POTENTIAL PROTECTION MATERIALS. IN THE TWO SYSTEMS, THE COMPOUNDS WSi_2 AND W_3Si_2 , AND $MoSi_2$, Mo_3Si_2 AND Mo_3Si , RESPECTIVELY, OCCUR. BUT ONLY THE INTER-METALLIC COMPOUNDS HIGH IN SI, I.E. WSi_2 AND $MoSi_2$, RESPECTIVELY, ARE RESISTANT TO HIGH TEMPERATURE OXIDATION AND FORM A GLASSY COATING. A DISADVANTAGE OF THIS TYPE OF COATING IS THE HIGH EMBRITTLEMENT OF BOTH THE DISILICIDE AND THE GLASS THAT IS FORMED. MICROHARDNESS TESTS HAVE SHOWN WSi_2 TO HAVE THE HIGHEST HARDNESS FOLLOWED BY $MoSi_2$, W_3Si_2 , AND Mo_3Si (42). THIS IMPLIES THAT WSi_2 IS ALSO THE MOST BRITTLE COMPOUND OF THE GROUP.

THE OXIDATION RESISTANCE OF SOLID SOLUTIONS BETWEEN WSi_2 AND $MoSi_2$ IS INFERIOR IN ALL RESPECTS TO THAT OF EITHER COMPOUND (41). THE TEMPERATURE LIMIT OF THE SILICIDE COATINGS IS THAT OF EUTECTIC FORMATION BETWEEN WSi_2 AND W_3Si_2 AT $3750^\circ F$ ($2065^\circ C$), AND BETWEEN $MoSi_2$ AND Mo_3Si_2 AT $3100^\circ F$ ($1705^\circ C$), RESPECTIVELY (41,43). THEREFORE, AT $3300^\circ F$ ($1815^\circ C$) ONLY WSi_2 IS USEFUL AS A PROTECTIVE COATING. IN ORDER TO OBTAIN THE HIGHEST POSSIBLE EFFECTIVENESS OF SUCH A COATING, A LAYER CONSISTING PRINCIPALLY OF WSi_2 AND A MINIMAL INTERMEDIATE LAYER OF W_3Si_2 IS DESIRED. EXTERNAL LAYERS OF PURE SI DO NOT OFFER PROTECTION BECAUSE OF LOW MELTING ($2550^\circ F$) EUTECTIC FORMS BETWEEN SI AND WSi_2 (41).

SEVERAL PROCESSES HAVE BEEN REPORTED PRODUCING THE DESIRED DIFFUSION LAYER (16,41,44,45). BECAUSE OF THEIR BRITTLINESS DIFFUSED LAYERS ALWAYS HAVE FISSURES. AT SERVICE TEMPERATURE, HOWEVER, A SELFHEALING EFFECT THROUGH A DIFFUSION PROCESS PREVAILS (42). FOR $MoSi_2$ THE OXIDATION AND PROTECTION MECHANISMS HAVE BEEN THOROUGHLY ESTABLISHED (43). IT IS REPORTED THAT A PROTECTIVE OXIDE LAYER IS ALREADY FORMED AS LOW AS $1300^\circ F$ ($705^\circ C$). ITS PROTECTION IS MAINLY DUE TO THE FORMATION OF AN ADHERENT MO-RICH OXIDE LAYER, WHEREAS SI FORMS A FLUFFY SILICA. WITH INCREASING TEMPERATURE A SOLUTION OF THIS METAL OXIDE IN SILICA STARTS TO OCCUR AND A LOW MELTING GLASS IS FORMED AT ABOUT $2500^\circ F$ ($1370^\circ C$). THROUGH VOLATILIZATION OF THE METAL OXIDE AT STILL HIGHER TEMPERATURE THE MELTING POINT OF THE GLASS IS INCREASED (43). MORE RECENTLY, IT WAS FOUND THAT AN OXYGEN GRADIENT EXISTS WITHIN THE FORMED GLASS PHASE WHICH MIGHT RANGE FROM SiO AT THE METAL-GLASS INTERFACE TO SiO_2 ON THE OUTER-MOST SURFACE. IF THE SILICON CONTENT IN THE $MoSi_2$ LAYER WAS HIGH SO AS TO CAUSE A PRONOUNCED SiO LAYER ON THE INTERFACE, BLISTERING WAS OBSERVED AT HIGHER TEMPERATURES BECAUSE OF THE HIGH VAPOR PRESSURE OF SiO (45). BELOW $1300^\circ F$ ($705^\circ C$) AND STARTING AS LOW AS $600^\circ F$ ($316^\circ C$), A CATASTROPHIC OXIDATION OF $MoSi_2$ (THE SO-CALLED "DISILICIDE PEST") WAS REPORTED BUT NO SATISFACTORY EXPLANATION FOR THIS PHENOMENON COULD BE ADVANCED (43,45). ALTHOUGH THE GLASSY SURFACE FORMED UPON OXIDATION AT HIGH TEMPERATURE DEVELOPED CRACKS DURING COOLING, PERFECT PROTECTION OF THE $MoSi_2$ AFTER REHEATING WAS REPORTEDLY OBTAINED DUE TO AN EXCELLENT SELFHEALING ABILITY OF THIS GLASS COATING (43,45). A POSSIBILITY OF PREVENTING THE DISILICIDE PEST BY PREFORMATION OF THE GLASSY SURFACE THROUGH CONTROLLED OXIDATION AT THE PROPER TEMPERATURE WAS SUGGESTED BY THE SAME AUTHOR.

IN THE CASE OF TUNGSTEN, THE DISILICIDE PEST WAS ALSO DETECTED IN W_{Si_2} (29), BUT THE SELFHEALING EFFECT COULD NOT BE OBSERVED, NOR COULD THE DISILICIDE PEST BE PREVENTED BY MEANS OF PREOXIDIZING THE SURFACE TO A GLASSY FILM (29).

THESE DEFICIENCIES IN THERMAL CYCLING RESISTANCE AND LOW TEMPERATURE OXIDATION RESISTANCE LEAD TO ATTEMPTS TO FORM COMPOUND COATINGS ON SILICONIZED TUNGSTEN. A CERAMIC COATING ON TOP OF A SILICONIZED TUNGSTEN SUBSTRATE GAVE IMPROVED OXIDATION RESISTANCE AS COMPARED TO PLAIN CERAMIC COATINGS BUT THE DIFFICULTIES EXPERIENCED WITH PLAIN CERAMIC LAYERS ALREADY MENTIONED REMAINED (29). SOME ENCOURAGING RESULTS WITH $MoSi_2-TiB_2$ COATED GRAPHITE BODIES HAVE BEEN REPORTED, THOUGH THESE COATINGS DO NOT APPEAR IMMEDIATELY APPLICABLE TO TUNGSTEN (16).

D. COATING TECHNIQUES

THERE ARE IN THEORY NUMEROUS COATING METHODS AVAILABLE FOR TUNGSTEN SUBSTRATES, INCLUDING MECHANICAL PLATING, ELECTRODEPOSITION, FLAME AND ARC SPRAYING, THE APPLICATION OF A "SOLUTION" OR SUSPENSION WITH SUBSEQUENT FIRING, DIP METHODS, VAPOR DEPOSITION, AND CEMENTATION PROCESSES.

MECHANICAL CLADDING OR PLATING IS ONLY APPLICABLE TO READILY DEFORMABLE METAL SUBSTRATES. MOST OF THE HIGHLY REFRACTORY METALS DO NOT MEET THIS REQUIREMENT. EVEN FOR THE MOST COMMON OF THESE METALS, MOLYBDENUM, EXPERIENCE IN MECHANICALLY CLADDING THIS METAL IS LIMITED. A POSSIBLE APPLICATION OF SUCH METALS AS AL, ZR, ETC. FOR THE SOLE PURPOSE OF SUBSEQUENTLY FORMING ALUMINA OR ZIRCONIA COATINGS, OR USING THE METALS AS AN INTERMEDIATE LAYER FOR BONDING OR GENERATING MORE COMPLEX COATINGS CAN THEREFORE BE SPECULATED UPON.

THE ELECTRODEPOSITION METHOD IS LIMITED TO METALS AND ALLOYS. HOWEVER, MOST METALS CAN BE ELECTROPLATED. THE SUBSTRATE SURFACE CONDITIONS HAVE A GREAT INFLUENCE ON THE ADHERENCE OF THE COATING. ELECTROPLATED LAYERS ARE OFTEN VERY POROUS AND A DENSIFICATION BY MEANS OF FUSION PROCESSES (E.G. HEATING ABOVE THE MELTING POINT OF THE COATING IN AN INERT GAS ATMOSPHERE) IS NECESSARY FOR THESE COATINGS (1). FOR SERVICE TEMPERATURES IN THE $3000-3300^{\circ}F$ ($1650-1815^{\circ}C$) RANGE, METALLIC COATINGS ARE ONLY USEFUL AS INTERMEDIATE LAYERS OR FOR CONVERSION TO PROTECTIVE OXIDES OR INTERMETALLIC COMPOUNDS. THE MOST FREQUENTLY ELECTROPLATED METALS IN THIS CONNECTION ARE CR, AL, NI, TI, ZR, RE, RH IN SINGLE OR MULTIPLE LAYERS (1,19,33).

ANOTHER METHOD OFTEN APPLIED IN HIGH TEMPERATURE WORK IS HIGH TEMPERATURE SPRAYING. THE PRINCIPLE IS TO SPRAY THE DESIRED COATING MATERIAL IN THE FORM OF A STREAM OF HIGHLY HEATED SOLID PARTICLES, DROPLETS, OR VAPOR MIXED WITH A CARRIER GAS OF A HIGH VELOCITY ONTO THE SUBSTRATE. THE COMMON "FLAME SPRAY" EQUIPMENT USUALLY CONSISTS OF A TORCH NOZZLE WHERE A MIXTURE OF FUEL AND OXYGEN ARE ACCELERATED TO A HIGH SPEED AND REACTED TO YIELD A HIGH TEMPERATURE. INTO THIS GAS STREAM CLOSELY SIZED PARTICLES OF THE COATING MATERIAL ARE FED. SOLID ROD INSTEAD OF POWDER MAY BE USED TO FEED THESE GUNS (16,33). FUEL TYPES ARE ACETYLENE AND HYDROGEN. BECAUSE OF THE TEMPERATURE LIMITATION OF THE COMMON FLAME SPRAY METHOD, THE "ARC PLASMA JET FLAME SPRAY TECHNIQUE" WAS DEVELOPED FOR HIGH MELTING INTERMETALLIC COMPOUNDS AND OXIDES. THE COATING MATERIAL IS DISPERSED IN A CARRIER GAS SUCH AS ARGON OR NITROGEN, HEATED IN THE PLASMA OF AN ELECTRICAL ARC AND SUBSEQUENTLY IMPINGED ONTO THE SUBSTRATE TO BE

COATED. WHEREAS AN ACETYLENE OR HYDROGEN GUN OPERATES AT ABOUT 5000°F (2760°C) (33), AN ARC PLASMA CAN PROVIDE TEMPERATURES IN EXCESS OF 20,000°F (11100°C) (46). BY NOW, MOST OF THE COMMON OXIDES, CERAMICS, CERMETS AND INTERMETALLIC COMPOUNDS AND THEIR MIXTURES CAN BE TORCH OR ARC FLAME SPRAYED BUT COATINGS SO PRODUCED OFTEN ADHERE POORLY TO THE SUBSTRATE. DIFFICULTIES ARE ENCOUNTERED WITH MATERIALS WHICH DECOMPOSE OR VOLATILIZE AT HIGHER TEMPERATURES, SUCH AS MgO, OR CERTAIN CARBIDES, NITRIDES AND BORIDES (16,33). BECAUSE OF THE BONDING PROBLEM WITH FLAME SPRAYED COATINGS THE SURFACE CONDITION OF THE SUBSTRATE IS OF IMPORTANCE. IN ORDER TO OVERCOME SOME OF THE DIFFICULTIES CAUSED BY THE LIMITED TEMPERATURE OF THE GAS-OXYGEN SPRAY GUNS, SUCCESS WAS OBTAINED IN USING METAL-METAL OXIDE POWDERS TO PROVIDE BETTER ADHERENCE AND A DENSER COATING. THE OBTAINABLE DENSITIES ARE UP TO 90% ON COMMON FLAME SPRAYED AND UP TO 98% ON ARC PLASMA JET FLAME SPRAYED COATINGS (33). THE RESIDUAL POROSITY OF THE FLAME SPRAYED COATINGS IS DISADVANTAGEOUS FOR PROTECTION OF THE SUBSTRATE AGAINST HIGH TEMPERATURE OXIDATION, BUT FLAME SPRAYED MoSi₂ COATINGS WERE FOUND TO GIVE SIGNIFICANT PROTECTION (16,33).

VERY HIGH MELTING MATERIALS SUCH AS CERAMICS AND CERMETS CAN BE APPLIED AS A COATING BY MEANS OF A LIQUID OR VISCOUS SUSPENSION OR A SOLUTION FOLLOWED BY FIRING. THERE EXISTS CONSIDERABLE EXPERIENCE IN APPLYING SUCH COATINGS FOR LOW TEMPERATURE SERVICE, THE BEST KNOWN TYPE OF THESE COATINGS BEING THE ENAMELS. THE SAME METHOD IS ALSO CONSIDERED USEFUL IN PROVIDING HIGH TEMPERATURE COATINGS (16,33). THE LITERATURE REPORTS ATTEMPTS TO COAT WITH PROMISING CERAMICS, GLASS FRITS, AND CERMETS IN FORM OF SLIPS, WHICH ARE APPLIED EITHER BY MEANS OF DIPPING, SPRAYING OR BRUSHING. SUBSEQUENT FIRING IS PERFORMED EITHER IN VACUUM OR IN INERT GAS ATMOSPHERE, OR BOTH. FIRING TEMPERATURES ARE REPORTED BETWEEN 2000°F AND 3000°F (1095-1650°C). AN INCREASE OF THE ADHERANCE OF SUCH COATINGS BY ADDING TO THE SLIP METALS DIFFUSABLE INTO THE SUBSTRATE HAS BEEN REPORTED (16,19,29). EVEN FOR PLAIN ALUMINIZING, THE SLIP METHOD HAS BEEN APPLIED WITH SUCCESS BY USING AN ALUMINUM POWDER SUSPENSION WITH A SUBSEQUENT DIFFUSION TREATMENT (33).

BESIDES DIPPING SAMPLES TO BE COATED IN CERAMIC SOLUTIONS, COATINGS CAN BE PRODUCED BY MEANS OF DIPPING IN A METALLIC MELT. IN PRINCIPLE, TWO DIFFERENT PROCESSES ARE POSSIBLE. IN ONE, A CLADDING IS FORMED BY THE METAL OF THE MELT. ONLY RELATIVELY LOW MELTING METALS, E.G. ALUMINUM OR ALUMINUM-SILICON ALLOY, CAN BE CLAD IN THIS WAY. FOR HIGHLY REFRACTORY COATINGS IT COULD CONSTITUTE ONLY ONE STEP IN A MORE COMPLICATED COATING TECHNIQUE INVOLVING SUBSEQUENT PREOXIDIZING OR DEPOSITING ADDITIONAL SURFACE LAYERS. IN THE OTHER PROCESS, A HIGH MELTING METAL MIGHT BE INCORPORATED IN A LOW MELTING ALLOY AND IS SELECTIVELY DIFFUSED FROM THE MOLTEN ALLOY INTO THE SUBSTRATE TO BE COATED. HOWEVER, THE COATING MECHANISM IS USUALLY MORE COMPLEX AND BOTH PROCESSES OCCUR (31). THE DIP PROCESS IS REPORTED TO HAVE BEEN APPLIED SUCCESSFULLY IN CHROMIZING AND SILICONIZING A VARIETY OF SUBSTRATES (19,31,50).

VAPOR DEPOSITION CONSISTS ESSENTIALLY OF REDUCING OR DECOMPOSING A VOLATILE COMPOUND OF THE COATING MATERIAL UPON THE HEATED SURFACE OF THE SAMPLE TO BE COATED (32). IN PRINCIPLE, THE VAPOR PLATING PROCESS PERMITS DEPOSITION OF MANY REFRACTORY MATERIALS SUCH AS HIGH MELTING METALS, CERAMICS AND CERMETS. IF THE DEPOSITION OF A DESIRED COMPOUND IS NOT POSSIBLE, ITS FORMATION MIGHT STILL BE PROVIDED BY MEANS OF DEPOSITION OF MULTILAYERS WITH FOLLOWING DIFFUSION OR OXIDATION.

BECAUSE OF ITS EXCELLENT OXIDATION RESISTANCE, THE FORMATION OF TUNGSTEN DISILICIDE BY MEANS OF VAPORPLATING IS OF PARTICULAR INTEREST IN OUR CASE. THE MOST

FREQUENTLY USED METHOD IS THE REDUCTION OF SiCl_4 WITH H_2 ON THE SURFACE TO BE COATED. SINCE THE REQUIRED REDUCTION TEMPERATURES ARE BETWEEN 1500° AND 3300°F (815 - 1815°C) DIFFUSION INTO THE SUBSTRATE IS OBTAINED CONCURRENTLY RESULTING IN FORMATION OF THE DISILICIDE. WHETHER THE DESIRED WSi_2 , OR A COMBINATION WITH W_3Si_2 OR Si OCCURS DURING VAPOR DEPOSITION DEPENDS ON TEMPERATURE, GAS FLOW AND MIXTURE, AND GAS PRESSURE. A CAREFUL PURIFICATION OF THE HYDROGEN AND A SUBSEQUENT DIFFUSION TREATMENT ARE NECESSARY. AT LOW TEMPERATURES DEPOSITION OF FREE SILICON PREDOMINATES. A HIGH FLOW RATE AND A HIGH SiCl_4 CONCENTRATION ALSO PROMOTE SILICON DEPOSITION. AT HIGH TEMPERATURES ONLY A DISPLACEMENT MECHANISM OCCURS. THEREFORE NO FREE SILICON IS FORMED AND THE UPPER TEMPERATURE LIMIT FOR DEPOSITION IS ONLY THE MELTING POINT OF THE EUTECTIC BETWEEN THE TWO SILICIDES.

MOST EXPERIENCE HAS BEEN COLLECTED ON MOLYBDENUM, AND EXCELLENT RESULTS WERE OBTAINED WITH RESPECT TO OXIDATION RESISTANCE AT HIGH TEMPERATURE (16,32,33,42,44,47). THE LITERATURE CONTAINS ONLY LIMITED REFERENCE TO SILICON VAPORPLATING OF TUNGSTEN (33). RECENTLY SOME SUCCESS WAS OBTAINED IN PROVIDING PROTECTION AGAINST OXIDATION AT 3300°F BY THIS METHOD (29).

AN ADDITIONAL ASPECT OF POTENTIAL INTEREST IS THE VAPOR DEPOSITION OF REFRACTORY OXIDES SUCH AS ZrO_2 , Al_2O_3 , ETC., BUT THE MERITS OF THIS APPROACH REMAIN TO BE PROVEN (29,32).

THE CEMENTATION METHOD IS BASED ESSENTIALLY ON A DIFFUSION PROCESS. THE SAMPLE TO BE COATED IS PACKED IN A POWDER OF THE COATING MATERIAL MIXED WITH AN ENERGIZER SUCH AS A HALIDE OR AMMONIUM COMPOUND. A INERT FILLER SUBSTANCE MAY BE ADMIXED. THE COATING PROCESS OCCURS AT THE TEMPERATURE NECESSARY FOR DIFFUSION. THE PACK IS SUBJECTED TO A HYDROGEN FLOW, OR MAY BE CONTAINED IN A SEALED VESSEL. IT IS NOT DEFINITELY ESTABLISHED WHETHER THERE ARE VOLATILE COMPOUNDS OF THE COATING MATERIAL FORMED WHICH DECOMPOSE OR ARE REDUCED ON THE SURFACE TO BE COATED, OR IN A SIMPLE DIFFUSION-TYPE PROCESS THE ENERGIZER SALT OPERATES ONLY AS A CATALYST. FOR CHROMIZING THE CEMENTATION METHOD HAS BEEN ADVANCED TO AN INDUSTRIAL SCALE AS CAN BE RECOGNIZED FROM THE MANY REPORTS PUBLISHED (16,33). HOWEVER, THESE CHROMIZED COATINGS ARE NOT USEFUL AT TEMPERATURES APPROACHING 3000 - 3300°F (1650 - 1815°C). (16,19). RECENTLY THE CEMENTATION METHOD HAS BEEN PERFECTED FOR INDUSTRIAL SILICONIZING OF MOLYBDENUM (DURAK MG AND W-2) WITH GOOD RESULTS REPORTED (16). AN OBVIOUS ADVANTAGE OF PACK SILICONIZING IS ITS APPLICABILITY TO MORE COMPLICATED SHAPES THAN POSSIBLE FOR VAPORPLATING, AS THE PARTS ARE BETTER SUPPORTED AND UNDERGO LESS DISTORTION DURING THE TREATMENT.

E. OXIDATION TESTS AT HIGH TEMPERATURES

THE PERFORMANCE SPECIFICATIONS FOR THIS PROJECT REQUIRE TEST SPECIMENS TO BE HEATED TO 3300°F (1815°C) IN STILL AND FLOWING AIR. SEVERAL TESTING SYSTEMS FULFILLING THESE REQUIREMENTS SHOULD BE DISCUSSED HERE SHORTLY.

INDIRECT ELECTRICAL RESISTANCE HEATING OF THE SPECIMEN TO 3300°F , E.G. IN A MUFFLE OR TUBE FURNACE, POSES PROBLEMS OF FURNACE CONSTRUCTION AND ELEMENT LIFE, ESPECIALLY WITH A HIGHER AIR FLOW AROUND THE SPECIMEN.

GAS FIRED MUFFLES CAN PROVIDE THE STILL AIR ATMOSPHERE AND HAVE A HIGHER TEMPERATURE LIMIT THEN ELECTRICALLY HEATED FURNACES. TESTS PERFORMED AT 3300°F WITH SUCH EQUIPMENT SHOW ITS OPERATIONAL CAPABILITY (29).

THE TEMPERATURE REQUIREMENTS CAN BE MET EASILY BY EXPOSING THE SAMPLE DIRECTLY TO A FLAME. NOZZLE-SHAPED SAMPLES IN PARTICULAR CAN BE ADEQUATELY TESTED BY THIS METHOD SINCE A HIGH GAS FLOW CAN BE PROVIDED. THE FUELS ARE SOLID, LIQUID OR GASEOUS AND ARE BURNED WITH OXYGEN. THE ATMOSPHERE SURROUNDING THE SAMPLE IS NOT AIR BUT THE EXHAUST GAS. THE POSSIBLE EXCESS OXYGEN AMOUNT IS A FUNCTION OF THE TEMPERATURE REQUIRED. HOWEVER, AT 3300°F AN OXYGEN CONCENTRATION EQUAL TO THAT OF AIR CAN BE PROVIDED WITH THE PROPER FUEL (16,33).

CONCURRENTLY WITH THE DEVELOPMENT OF ARC PLASMA SPRAY UNITS THE POSSIBILITY OF USING AN ARC PLASMA FOR HIGH TEMPERATURE TESTING HAS BECOME IMPORTANT. THE USE OF AIR AS AN ENVIRONMENT IS POSSIBLE AND HIGHEST TEMPERATURES CAN BE PRODUCED (3). ARC PLASMA TESTING EQUIPMENT IS BEING DEVELOPED AT THIS TIME AND CERTAIN OF ITS MECHANISMS SUCH AS IONIZATION OR DISSOCIATION OF THE GASES USED FOR THE TEST ARE BEING INVESTIGATED (16).

FROM THE VIEWPOINT OF THE ULTIMATE APPLICATION OF THE COATINGS TO BE DEVELOPED, TEST FACILITIES WHERE THE HEAT IS PRODUCED AT THE COATING-ATMOSPHERE INTERFACE WOULD BE MOST ADVANTAGEOUS. ONE APPROXIMATION TO SERVICE CONDITIONS CONSTITUTES A GAS FIRED MUFFLE TEST SET-UP WHERE THE SAMPLE SURFACE TO BE TESTED IS HEATED TO TEMPERATURE ALMOST ENTIRELY BY RADIATION. IN THIS CASE, ONLY THE AIR IMMEDIATELY SURROUNDING THE SAMPLE IS HEATED BY CONVECTION SINCE AIR IS UNABLE TO RECEIVE HEAT BY RADIATION. HOWEVER, IT IS TO BE RECOGNIZED THAT BY NECESSITY THERE IS ALWAYS A CONSIDERABLE TEMPERATURE STEP IN THE DIRECTION HOTTER SAMPLE SURFACE VS. COOLER SURROUNDING (FLOWING) AIR. MOREOVER, A DESIRABLE TEMPERATURE GRADIENT FROM THE COATING TO THE SUBSTRATE CORE IS ELIMINATED WITH ATTAINMENT OF EQUILIBRIUM CONDITIONS SINCE IT IS HARD TO PROVIDE A COOLING OF THE SAMPLE CORE. THE SAME WOULD BE TRUE FOR EXTERNAL ELECTRICAL HEATING.

IF TESTING IS CARRIED OUT IN A FLAME OR IN AN ARC PLASMA, THE SURFACE OF THE COAT IS HEATED BY THE SURROUNDING GAS ITSELF. BECAUSE OF THE GEOMETRICAL ARRANGEMENT, A COOLING OF THE SAMPLE CORE IS EASIER. THIS COOLING ASSUMES A TEMPERATURE STEP BETWEEN COATING SURFACE AND SURROUNDING MEDIUM OF ABOUT THE SAME ORDER BUT OPPOSITE DIRECTION AS THE ONE MENTIONED ABOVE. IN THIS CASE A TEMPERATURE GRADIENT WITHIN THE SAMPLE MIGHT ALSO BE PROVIDED DEPENDING ON DETAILS OF THE SET-UP. AS FAR AS THE HEAT DISTRIBUTION IS CONCERNED, THIS PRINCIPLE MIGHT BE A CLOSER APPROACH TO ACTUAL SERVICE CONDITIONS. A DRAWBACK OF THE FLAME AND ARC METHODS, HOWEVER, IS THE FACT THAT THE ATMOSPHERE SURROUNDING THE SAMPLE IS ALTERED BY THE EXHAUST GASES OR BY IONIZATION EFFECTS, RESPECTIVELY.

THE LEAST ACCURATE TEST CONSIDERING ALL OF THESE ASPECTS IS BASED ON DIRECT ELECTRICAL RESISTANCE HEATING. HERE THE HEAT IS PRODUCED WITHIN THE SAMPLE AND CONDUCTED TO THE SURFACE CAUSING A REVERSE TEMPERATURE GRADIENT WITHIN THE COATING. IT WILL BE SHOWN LATER THAT THIS GRADIENT MAY UNDER CERTAIN CIRCUMSTANCES BE NEGLECTED, BUT IT INCREASES WITH SAMPLE CROSS SECTION, NONMETALLIC LAYER THICKNESS AND INCREASED AIR FLOW. THE DIRECT RESISTANCE HEATING OF THE TEST SAMPLE, HOWEVER, HAS CONSIDERABLE ADVANTAGES OVER THE OTHER METHODS, AS IT IS SIMPLE, EASY TO MANIPULATE AND PROVIDES GOOD OPPORTUNITY FOR TEMPERATURE MEASUREMENTS AND SURFACE CONTROL DURING TESTING.

AT THE TEST TEMPERATURE UNDER CONSIDERATION, TEMPERATURE MEASUREMENTS CAN ONLY BE PERFORMED BY MEANS OF AN OPTICAL PYROMETER. CORRECT MEASUREMENTS ARE SOMEWHAT PROBLEMATIC BECAUSE OF THE UNKNOWN EMISSION COEFFICIENT AT TEST TEMPERATURE OF THE MATERIAL FORMED ON THE SAMPLE SURFACE DURING OXIDATION. MOREOVER, DIRECT CALIBRATION OF THE PYROMETER WHILE SIGHTING THE SO COATED SAMPLE AT TEMPERATURE IS DIFFICULT, AS CONVENTIONAL CALIBRATION METHODS APPEAR INAPPLICABLE IN THIS CASE.

II. EXPERIMENTAL PROCEDURE

A. SUBSTRATE

AS IN THE PRECEDING INVESTIGATION (1), TUNGSTEN WIRES 0.080 IN. (2MM) IN DIAMETER WERE USED AS SUBSTRATES. THE LENGTH WAS GENERALLY 12 IN. (30 CM) BUT MOST WIRES WERE CLIPPED TO 8 IN. (20 CM) FOR OXIDATION TESTING, THE ENDS BEING USED FOR METALLOGRAPHY AND OTHER TESTS. ALL WIRES HAD A GROUND FINISH.

PRELIMINARY TESTS COMPARING COATING AND OXIDATION PROPERTIES OF TUNGSTEN WIRES WITH DIFFERENT THORIA CONTENT FROM 0 TO 2.0% SHOWED NO NOTICEABLE DIFFERENCE IN PERFORMANCE. HENCE, MATERIAL WITH 1.8-2% ThO_2 WAS USED FOR THE MAIN PART OF THE INVESTIGATION. A TYPICAL ANALYSIS OF GASEOUS IMPURITIES OF THE SUBSTRATES IS:

0.235% O_2

0.0006% H_2

0.0009% N_2

CLEANING TREATMENTS WERE TRIED AS FOLLOWS:

- (1) 40 SEC. ANODIC CLEANING IN "OAKITE SOLUTION No. 90 AS PREVIOUSLY DESCRIBED (1).
- (2) 2 MIN. ANODIC CLEANING UNDER THE SAME CONDITIONS.
- (3) CLEANING IN CCl_4 .

THE ANODIC CLEANING WAS EMPLOYED IN EARLIER WORK AS PREVIOUSLY USED FOR ELECTROLYTIC PLATING. HOWEVER, IT WAS OBSERVED IN PACK SILICONIZING THAT WIRES CLEANED IN CCl_4 FORMED THICKER DISILICIDE LAYERS THAN THOSE ANODICALLY CLEANED.

NO OTHER PRETREATMENTS WERE PERFORMED.

B. DIP-SILICONIZING

A PRELIMINARY STUDY WAS MADE TO ADAPT FOR TUNGSTEN THE LEBEAU PROCESS (50) OF SILICON DIFFUSION FROM A COPPER-SILICON ALLOY BATH TO THE SUBSTRATE.

ACCORDING TO THE LOWEST MELTING EUTECTIC IN THE TWO-PHASE SYSTEM A Cu-Si, AN ALLOY WITH 16 WT.% Si WAS PREPARED BY FIRST FUSING A MASTER ALLOY OF 30% Si. FOR MELTING, A NICHROME-WOUND ELECTRICAL FURNACE AND 1-1/2 IN. OUTSIDE DIA. AND 18 IN. LONG CRUCIBLE WERE EMPLOYED, WHICH COULD ACCOMMODATE THE 12 IN.-LONG WIRES. THE ALLOY WAS MOLTEN IN AIR UNDER A BORAX SLAG. SINCE THE HEAT CAPACITY OF THE FURNACE AND THE SIZE OF THE CRUCIBLE WERE LIMITED, NO APPRECIABLE OVERHEATING OF THE MELT WAS POSSIBLE. EVEN SMALL ADDITIONS OF SOLID MATERIAL CAUSED A TEMPORARY FREEZING OF THE MELT, WHICH IN TURN RESULTED IN OXIDATION OF THE ADDED SOLID ALLOY. THESE NEWLY FORMED OXIDES DISSOLVED IN THE SLAG CAUSING A VERY HIGH VISCOSITY OF THE LATTER. DUE TO THIS SLOW AND PROLONGED MELTING DOWN OPERATION CRUCIBLE FAILURES OCCURRED FREQUENTLY. IT BECAME APPARENT AFTER A FEW TRIAL HEATS THAT THE CRUCIBLE MATERIALS (ALUNDUM AND GRAPHITE) DID NOT WITHSTAND THE SEVERE OPERATING CONDITIONS OF THE PROCEDURE USED. SINCE A CONSIDERABLE IMPROVEMENT IN APPARATUS AND TECHNIQUE APPEARED NECESSARY AND THE APPROACH HAD BEEN GIVEN A LOW PRIORITY IN THE PROGRAM, THE DECISION WAS MADE TO HALT THIS LINE OF ENDEAVOR IN FAVOR OF THE MORE EASILY MANAGEABLE CEMENTATION PROCESS.

C. SILICONIZING BY MEANS OF VAPOR PLATING

THE FREQUENTLY REPORTED METHOD BASED ON THE REDUCTION OF SiCl_4 (29,32,44) WAS EMPLOYED IN ANOTHER EXPLORATORY STUDY OF SILICIDE COATING TECHNIQUES. HYDROGEN PURIFIED AS SHOWN IN FIG. 1 WAS SATURATED WITH TECHNICALLY PURE SiCl_4 AT ROOM TEMPERATURE, SUBSEQUENTLY MIXED WITH PURE HYDROGEN IN AN APPROXIMATIVE RATIO 1:1 AND INTRODUCED TO THE PLATING CHAMBER CONTAINING THE HEATED SAMPLE TO BE SILICONIZED.

SEVERAL EXPERIMENTS WERE CONDUCTED WITH TUNGSTEN WIRES THAT WERE MOVED PARALLEL TO THEIR AXIS THROUGH A NOZZLE THROUGH WHICH A STREAM OF SiCl_4 -HYDROGEN GAS MIXTURE WAS PASSED CONCURRENTLY. IT WAS HOPED THAT BY THIS PROCEDURE SURFACE DEPOSITS OF MORE UNIFORM THICKNESS AND QUALITY COULD BE OBTAINED AT A LOWER STATIC GAS PRESSURE WITHOUT EMPLOYING VACUUM EQUIPMENT. DIRECT ELECTRICAL RESISTANCE HEATING OF THE TUNGSTEN WIRE SAMPLE WAS DIFFICULT TO ADAPT TO THE SET-UP MAINLY BECAUSE OF HIGH CURRENT REQUIREMENTS AND THE NECESSARY GAS-TIGHT SEALS PERMITTING MOVEMENT OF THE WIRE WITHOUT LEAKAGE OF THE CORROSIVE SiCl_4 GAS. HIGH FREQUENCY HEATING WAS ATTEMPTED WITHOUT SUCCESS BECAUSE OF THE SMALL DIAMETER OF THE WIRE AND THE NECESSARILY CONSIDERABLY LARGER DIAMETER OF THE PLATING CHAMBER. EXTERNAL HEATING BY MEANS OF A NICHROME-WOUND ELECTRIC FURNACE WAS THEN RESORTED TO. THIS SET-UP, HOWEVER, IMPOSED A TEMPERATURE LIMITATION OF 2000°F (1095°C).

A TENDENCY FOR THE SILICON TO DEPOSIT ON THE WALL OF THE VYCOR PLATING CHAMBER RATHER THAN ON THE TUNGSTEN WIRE SAMPLES, AS WELL AS PERPETUAL DIFFICULTIES WITH THE SEALS AND THE MOVING MECHANISM UNDER THE STRONGLY CORROSIVE ATMOSPHERE CONDITIONS FORCED DISCONTINUATION OF THIS APPROACH DURING THE PERIOD ALLOWED FOR THE INVESTIGATION.

D. SILICON CEMENTATION

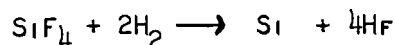
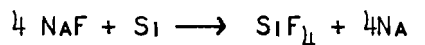
SIMPLICITY OF ARRANGEMENT AND APPLICABILITY TO COMPLICATED SHAPES WERE THE MOST OBVIOUS REASONS TO CONCENTRATE ON THIS METHOD OF PRODUCING SILICIDE COATINGS ON THE TUNGSTEN WIRES.

THE PACKS EMPLOYED USUALLY CONSISTED OF SILICON POWDER (99.80% Si, .01% Fe, 325 MESH), AN ENERGIZER SALT AND, INITIALLY, ALUMINA AS A FILLER. CHLORIDES, FLUORIDES, AND AMMONIUM SALTS WERE EMPLOYED AS ENERGIZER. THE MELTING AND BOILING POINTS OF THESE COMPOUNDS ARE GIVEN IN TABLE 1.

FIG. 2 SHOWS A DIAGRAM OF THE PRINCIPAL SET-UP EMPLOYED FOR THESE EXPERIMENTS. SILICONIZING WAS PERFORMED IN A HYDROGEN ATMOSPHERE OF 5 TO 30 CFT/HR FLOW RATE. THE HYDROGEN PURIFICATION USED WAS THE SAME EMPLOYED FOR VAPORPLATING (FIG. 1). THE WIRES WERE PLACED EITHER IN CONVENTIONAL COMBUSTION BOATS OR IN 12 MM DIA. VYCOR TUBES LOOSLY FILLED WITH THE PACK SUBSTANCE. THE PACKS WERE EXPOSED TO TEMPERATURE UNDER HYDROGEN FLOW IN A SOFT INCLINED 52 MM DIA. VYCOR TUBE SURROUNDED BY A NICHROME-WOUND ELECTRICAL RESISTANCE FURNACE. TEMPERATURE, HYDROGEN FLOW, AND ESPECIALLY PACK COMPOSITION WERE VARIABLES SUBJECT TO METHODOICAL INVESTIGATION. IN EARLY EXPERIMENTS THE PACKS WERE HEATED UP WITH THE FURNACE, BUT THE TIME REQUIRED TO REACH EQUILIBRIUM AT REACTION TEMPERATURE WAS ABOUT THREE HOURS. IT WAS REASONED THAT THIS SLOW HEATING CYCLE CAUSED PREMATURE EVAPORIZATION OF CERTAIN ENERGIZER SALTS IN THE PACK BEFORE THE TEMPERATURE FOR THE DIFFUSION OF SILICON INTO THE TUNGSTEN SUBSTRATE WAS REACHED. THEREFORE THE TECHNIQUE WAS CHANGED, AND IN A MAJORITY OF RUNS THE PACKS WERE KEPT IN A COOL SECTION OF THE REACTION TUBE AND PUSHED INTO THE HOT ZONE AFTER HEATING UP THE FURNACE TO THE DESIRED TEMPERATURE. THE TECHNIQUE OF PUSHING THE VESSEL CONTAINING THE PACK INTO THE HOT ZONE PERMITTED OPERATION IN A PERFECTLY PURE HYDROGEN ATMOSPHERE DURING THIS STEP AND THE REACTION TO OCCUR SUBSTANTIALLY AT THE MAXIMUM TEMPERATURE.

ABOVE ABOUT 1800°F (980°C) A REACTION BETWEEN PACK AND VYCOR VESSEL MATERIAL TOOK PLACE. HOWEVER, THERE WERE INDICATIONS THAT THE REACTION OCCURRED ONLY IN A THIN LAYER OF THE PACK NEXT TO THE VYCOR-PACK INTERFACE AND THEREFORE IT APPEARED UNLIKELY THAT THE SILICONIZING PROCESS WAS DISTURBED.

SINCE THE EXACT SILICONIZING MECHANISM IN A PACK REACTION SYSTEM IS NOT KNOWN WITH CERTAINTY THE INFLUENCE OF HYDROGEN CONCENTRATION IN THE PACK ATMOSPHERE IS PROBLEMATIC. IT HAS BEEN ESTABLISHED THAT AN ENERGIZER SALT PROMOTES METAL DIFFUSION PROCESSES, SUCH AS CHROMIZING, EVEN IN THE COMPLETE ABSENCE OF A REDUCING AGENT. ON THE OTHER HAND IT IS QUITE POSSIBLE THAT A REACTION OF THE ENERGIZER SALT WITH A REDUCING AGENT ENHANCES THE DIFFUSION PROCESS. IF FOR INSTANCE NAF IS ADDED TO THE PACK AS ENERGIZER SALT, A REDUCTION MECHANISM SUCH AS



MIGHT OCCUR, WHICH WILL REQUIRE A CERTAIN HYDROGEN FLOW IN ORDER TO GIVE OPTIMUM SILICONIZING CONDITIONS. ON THE OTHER HAND, IF THIS IS NOT A MECHANISM THAT PROMOTES THE SILICONIZING PROCESS, THE VAPOR PRESSURE OF THE ENERGIZER SALT SHOULD BE AS HIGH AS POSSIBLE AND THE HYDROGEN ATMOSPHERE NEED THEN ONLY BE SUFFICIENT TO MAINTAIN AN OXYGEN FREE ATMOSPHERE, I.E. TO PREVENT ANY BACK DIFFUSION OF AIR INTO THE SYSTEM SINCE OXYGEN IS EXTREMELY DETRIMENTAL TO THE DIFFUSION PROCESS. WITHIN THE AVAILABLE TIME, NOT ENOUGH EXPERIMENTS COULD BE PERFORMED TO OBTAIN A COMPLETE PICTURE ABOUT THE HYDROGEN INFLUENCE ON THE ENTIRE SILICONIZING MECHANISM.

SINCE ESSENTIALLY NO DIFFUSION OF SILICON INTO TUNGSTEN OCCURS BELOW 1600°F (870°C), THIS WAS THE LOWER TEMPERATURE LIMIT CHOSEN FOR THE CEMENTATION EXPERIMENTS. TEMPERATURE AND PACK COMPOSITION WERE SELECTED IN SUCH A WAY THAT SUBLIMATION OF THE SALT OCCURRED AT A RATE PERMITTING THE MAIN PART OF THE ENERGIZER TO BE CONSUMED WITHIN THE TIME REQUIRED FOR SILICONIZING, WHILE THE TEMPERATURE WAS SUFFICIENTLY HIGH FOR THE SILICON DIFFUSION PROCESS, I.E. BETWEEN 1650-2010°F (900 AND 1100°C).

THE EFFECTIVENESS OF NUMEROUS PACK COMPOSITIONS AND RATIOS OF SILICON TO ENERGIZER WAS INVESTIGATED METHODICALLY AND THE RESULTS ARE DISCUSSED IN THE NEXT SECTION.

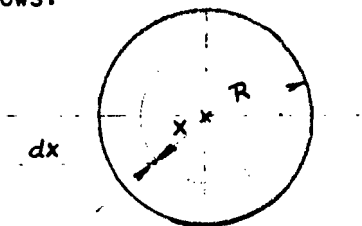
E. OXIDATION TESTS

THE TEST FACILITY USED, BASED ON DIRECT ELECTRICAL RESISTANCE HEATING OF THE SAMPLE WIRE, HAS BEEN PREVIOUSLY DESCRIBED (1) IN CONNECTION WITH THE EARLIER PHASE OF THE PROGRAM. THE EQUIPMENT AVAILABLE HAD FIXED WATER COOLED COPPER BLOCKS AS TERMINALS AND NO PROVISIONS TO USE MERCURY AS A LIQUID CONTACT. COMPENSATION FOR THE THERMAL EXPANSION OF THE WIRE WAS ACCOMPLISHED BY MEANS OF A PURELY MECHANICAL SLIDING CONTACT BETWEEN WIRE AND COPPER BLOCK, SOMETIMES CAUSING A CLAMPING CONTACT RESISTANCE WITHIN THE ELECTRICAL HEATING SYSTEM AMOUNTING TO TEMPERATURE CHANGES WITHIN THE RANGE OF ABOUT $\pm 70^\circ\text{F}$. OCCASIONAL GREATER FLUCTUATIONS RESULTED IN A COMPLETE BREAK OF THE CONNECTION AND THEREFORE A DISCONTINUATION OF THE TEST.

TEMPERATURE MEASUREMENTS WERE PERFORMED BY OPTICAL PYROMETER. A CORRECTION OF THE PYROMETER READINGS TAKING INTO ACCOUNT THE EFFECTS OF THE WIRE'S EMISSION COEFFICIENT IS PROBLEMATIC. FROM DATA FOUND IN THE LITERATURE (29,48,49) AN EMISSION COEFFICIENT BETWEEN 0.7 AND 0.9 CAN BE ESTIMATED. THIS GIVES AN UNCERTAINTY IN THE CORRECTION FACTOR OF $\frac{1}{4}\sqrt{0.7}$ TO $\frac{1}{4}\sqrt{0.9} = 0.92$ TO 0.97. IN OUR EXPERIMENTS THE UPPER LIMIT 0.97 WAS USED IN ORDER TO MAKE SURE THAT THE WIRES WERE REALLY HEATED TO THE SPECIFIED SURFACE TEMPERATURE OF 3300°F (1815°C).

THE TEMPERATURE DISTRIBUTION ALONG THE WIRE WAS OBSERVED TO BE CONSTANT FOR A 3 TO 4 IN. LENGTH IN THE CENTRAL PART OF THE WIRE.

IN ORDER TO ESTIMATE THE RADIAL TEMPERATURE GRADIENT WITHIN THE WIRE, A ROUGH CALCULATION OF HEAT CONDUCTION WAS PERFORMED. CONSIDERING ONLY A TEMPERATURE GRADIENT NORMAL TO THE WIRE SURFACE, THE EQUATION FOR HEAT CONDUCTION CAN BE WRITTEN AS FOLLOWS:



$$dT = \frac{Q(x)}{\sum_i F(x)} dx \quad (1)$$

dT = TEMPERATURE DIFFERENCE BETWEEN $x = 0$ AND $x = x_1$

$Q(x)$ = HEAT PRODUCED WITHIN THE CYLINDER $r = x$ AND LENGTH $L = 1$

$F(x)$ = SURFACE OF THE CYLINDER $r = x$, $L = 1$

= CONDUCTIVITY, FOR TUNGSTEN $\sim 0.269 \text{ CAL/CM}^2/\text{SEC}/^\circ\text{C/CM}$

FOR GLASS $\sim 0.2 \times 10^{-2} \text{ CAL/CM}^2/\text{SEC}/^\circ\text{C/CM}$

IN STILL AIR THE AVERAGE CURRENT NECESSARY TO MAINTAIN 1815°C ON THE WIRE WAS $I = 160 \text{ AMP}$. ASSUMING THAT AS AN APPROXIMATION THE CURRENT DENSITY i WITHIN THE WIRE CROSS SECTION IS CONSTANT, WE CAN WRITE

$$i = \frac{I}{R^2} \pi \quad (2)$$

THE HEAT PRODUCED WITHIN THE CYLINDER $\left\{ \begin{matrix} L = 1 \\ r = x \end{matrix} \right\}$ IS THEREFORE

$$Q(x) = i^2 \cdot \rho \cdot x^2 \cdot \pi \quad (3)$$

BEING THE ELECTRICAL RESISTIVITY

IT FOLLOWS FROM (2) AND (3) THAT

$$Q(x) = \frac{I^2}{R^4 \cdot \pi^2} \cdot \rho \cdot x^2 \cdot \pi \quad (4)$$

AND (4) AND (1) GIVE INTEGRATED

$$\Delta T = \frac{i^2 \cdot \rho}{4 \int \cdot R^2 \cdot \pi^2} \left(1 - \frac{x^2}{R^2} \right), \text{ OR}$$

WITH 1 WATT = 0.239 CAL

$$\rho = 66 \times 10^{-6} \Omega \text{ CM}$$

$$\lambda = 0.269 \text{ CAL/CM}^2/\text{SEC}/^\circ\text{C/CM}$$

$$R = 0.1 \text{ CM}$$

$$I = 160 \text{ AMP.}$$

$$\Delta T_{\text{TUNGSTEN}} = 3.82 \left(1 - \frac{x^2}{R^2} \right)$$

THIS MEANS THAT THE CALCULATED TEMPERATURE DIFFERENCE WITHIN THE 2 MM DIA. PLAIN TUNGSTEN WIRE 3300°F (1815°C) AT STILL AIR BETWEEN CORE AND SURFACE IS $\sim 4^\circ\text{C}$.

IF THE GLASS LAYER ON THE SURFACE IS TAKEN INTO CONSIDERATION THE TEMPERATURE GRADIENT IN IT WOULD BE ABOUT 2 ORDERS GREATER THAN IN UNCOATED TUNGSTEN BECAUSE

OF THE MUCH LOWER CONDUCTIVITY OF THE GLASS. ASSUMING A GLASS LAYER THICKNESS OF 10^{-3} CM

$$\Delta T_{\text{GLASS}} = 4 \times 10^{+2} \left(1 - \frac{(10^{-1} - 10^{-3})^2}{10^{-2}} \right) = 8^\circ\text{C}$$

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. COATINGS FORMED BY CEMENTATION

1. GENERAL:

IN GENERAL, ONLY A SINGLE LAYER OF WSi_2 WAS FORMED BY THIS PROCESS AND IN NO INSTANCE COULD EVEN A THIN INTERMEDIATE LAYER OF W_3Si_2 BE OBSERVED. HENCE, THE TYPE OF LAYER PRODUCED IN PACK SILICONIZING SEEMS TO BE INDEPENDENT OF THE CONDITIONS PREVAILING DURING THE OPERATION. FURTHERMORE, NO SURFACE LAYER OF PURE SILICON WAS MICROSCOPICALLY DETECTED, THOUGH THIS IS NO ABSOLUTE PROOF OF ITS ABSENCE. BECAUSE OF ITS BRITTLINESS, A PURE SILICON DEPOSIT MIGHT PEEL OFF DURING METALLOGRAPHIC SPECIMEN PREPARATION OR THE SILICON MAY BE DEPOSITED IN POWDER FORM.

2. EFFECT OF TEMPERATURE:

EXPERIMENTS PERFORMED AT 1650°F (900°C) SHOW THAT AT THIS TEMPERATURE DIFFUSION IS ALREADY CONSIDERABLE. NOT ENOUGH RELIABLE TRIAL RUNS WERE POSSIBLE FOR A QUANTITATIVE DETERMINATION OF THE EFFECT OF SILICONIZING TEMPERATURE ON THE LAYER THICKNESS FORMED FOR A CONSTANT TIME. HOWEVER, ON THE BASIS OF THE EXPERIMENTS PERFORMED, WE OBSERVED THAT THE SILICONIZING TEMPERATURE IN THE RANGE FROM 1650 TO 1920°F (900 TO 1050°C) DOES NOT GREATLY INFLUENCE THE FORMATION RATE OF THE DISILICIDE LAYER.

3. EFFECT OF TIME:

THE LAYER THICKNESS AS A FUNCTION OF TIME IS VERY MUCH DEPENDENT ON THE PACK COMPOSITION, AS SHOWN IN FIG. 3. THIS RELATIONSHIP EXISTS AS LONG AS THE RATE OF DIFFUSION OF SILICON INTO THE SUBSTRATE, WHICH IS DETERMINED BY THE PARABOLIC DIFFUSION LAW, IS GREATER THAN THE RATE OF FORMATION OF DIFFUSIBLE SILICON BY THE ENERGIZER AT THE SURFACE OF THE SUBSTRATE. AS LONG AS FLOWING HYDROGEN ATMOSPHERE IS EMPLOYED, THE FORMATION RATE IS ALWAYS SMALLER THAN THE DIFFUSION RATE DURING THE INITIAL PART OF THE PROCESS SINCE THE LATTER, BECAUSE OF $\frac{dx}{dt} = \frac{1}{x}$ OR $\frac{1}{\sqrt{t}}$, IS ∞ FOR $t = 0$. HOWEVER, FOR A VERY ACTIVE ENERGIZER IT MIGHT BE POSSIBLE THAT AFTER A SHORT TIME THE FORMATION RATE IS HIGHER THAN THE DIFFUSION RATE AND THE LAYER GROWTH IS GOVERNED BY DIFFUSION. SINCE THE ENERGIZER IS CONSUMED IN THIS PROCESS AT LEAST IN PART THROUGH THE FLOWING HYDROGEN, THE RATE OF FORMATION OF DIFFUSIBLE SILICON DECREASES TO ZERO AFTER A LIMITED TIME, I.E. AFTER A CERTAIN TIME THE FORMATION RATE MUST AGAIN BE THE DETERMINING FACTOR FOR LAYER GROWTH, EVEN WITH A VERY ACTIVE ENERGIZER. THIS TIME IS REACHED THE FASTER, THE HIGHER THE REACTIVITY OR VOLATILITY AND THE SMALLER THE AMOUNT OF THE ENERGIZER. OPTIMUM PACK COMPOSITION THEREFORE CHANGES WITH SCHEDULED TIME ALLOWED FOR THE SILICONIZING PROCESS.

THOUGH OUR CEMENTATION EXPERIMENTS WERE BASED ON THESE THOUGHTS, WE COULD NOT PERFORM ENOUGH OF THEM FOR A COMPLETE EVALUATION OF THESE FACTORS. FOR INSTANCE, IF THE HIGHEST LOCATED CURVE IN FIG. 3 WOULD BE DETERMINED FOR A CERTAIN LENGTH BY DIFFUSION, THEN PACKS WITH A COMPOSITION IN THE VICINITY OF THOSE INDICATED SHOULD LIE EXACTLY ON THE SAME CURVE WITHIN THE STATED TIME RANGE.

4. EFFECT OF PACK COMPOSITION:

DIFFERENT PACK COMPOSITIONS WERE INVESTIGATED. THE LAYER THICKNESS OBTAINED ARE TABULATED IN TABLE II.

WHEREAS THE SURFACE APPEARANCE OF LAYERS PRODUCED IN DIFFERENT PACKS VARY WIDELY, METALLOGRAPHIC SECTIONS OF THE SILICONIZED WIRES SHOW ALWAYS EXACTLY THE SAME KIND OF A SINGLE LAYER WITH RADIAL AND LONGITUDINAL CRACKS, TYPICAL FOR A WSi_2 COATING. FIG. 4 AND 5 SHOW SUCH A TYPICAL PICTURE OF A TUNGSTEN WIRE, PACK SILICONIZED BY H. BUCKLE OF O.N.E.R.A., PARIS, FRANCE. THOUGH THERE IS ALWAYS A SHARP BOUNDARY BETWEEN LAYER AND SUBSTRATE, THE SILICIDE COATING IS ADHERENT AND IN NO INSTANCE COULD A SPALLING BE DETECTED.

ALUMINA POWDERS OF DIFFERENT GRAIN SIZES (RANGING FROM LINDE "B" TO 20 MESH ALUNDUM) WERE INVESTIGATED AS FILLER SUBSTANCE, BUT IN MOST CASES THESE PACKS WERE INFERIOR TO PACKS WITHOUT A FILLER, SINCE THE RESULTING COATINGS WERE THINNER AND MORE DISCONTINUOUS.

IT WAS FOUND TO BE IMPORTANT TO KEEP THE PACK DRY BECAUSE OF THE HYDROSCOPIC BEHAVIOR OF SOME ENERGIZER SALTS, ESPECIALLY KF. MOISTURE CAUSES A HARDENING OF THE PACK MAKING RECOVERY OF INTACT WIRES AFTER SILICONIZING DIFFICULT.

IF THE ENERGIZER SALT MELTS AT THE SILICONIZING TEMPERATURE, A DISCONTINUOUS COATING IS FORMED WHICH AFTER SILICONIZING HAS SALT OR FILLER INCLUSIONS FROM THE PACK AND AREAS WITH SOLIDIFIED SALT FILMS. UNDER THE MICROSCOPE, THE TYPICAL SINGLE DISILICIDE LAYER IS VISIBLE UNDERNEATH, BUT IT IS DISCONTINUOUS (FIG. 6). THESE MOLTEN SALT INCLUSIONS WERE ESPECIALLY APPARENT WITH KF. FURTHER INVESTIGATIONS WERE THEREFORE CONCENTRATED ON OTHER SALTS WITH A HIGH MELTING POINT, SUCH AS NAF OR NaCl, OR WITH A SUBLIMATION POINT BELOW THE SILICONIZING TEMPERATURE, SUCH AS THE AMMONIUM SALTS NH_4Br , NH_4I , NH_4Cl . PACKS CONTAINING ONLY AMMONIUM SALT ENERGIZER RESULTED IN SILICIDE LAYERS WITH A SMOOTH SURFACE, BUT THE THICKNESS OBTAINABLE WAS VERY SMALL. THE MOST PLAUSIBLE MECHANISM FOR THIS PHENOMENON IS THAT BECAUSE OF THE LOW SUBLIMATION POINT OF THE AMMONIUM SALTS THIS TYPE OF ENERGIZER IS CONSUMED AT AN EARLY STAGE OF THE PROCESS, SO THAT NO DIFFUSIBLE SILICON IS AVAILABLE ANYMORE FOR THE EXTENDED TIME NECESSARY FOR THE DIFFUSION PROCESS.

OF THE HIGH MELTING SALTS, NAF AND NaCl WERE MORE THOROUGHLY INVESTIGATED AS THEY CONSTITUTED THE MOST PROMISING ENERGIZERS. IT WAS FOUND THAT AT FURNACE TEMPERATURES AS HIGH AS 270°F (130°C) ABOVE THE MELTING POINT OF THE SALTS EMPLOYED, NO DETRIMENTAL MOLTEN PHASE WAS APPARENTLY FORMED, WHICH MAY BE ATTRIBUTED TO A TEMPERATURE GRADIENT CAUSED BY CERTAIN ENDOTHERMIC REACTIONS WITHIN THE PACK. HOWEVER, HEATS WITH ENERGIZER CONCENTRATIONS IN THE PACK BELOW 10 WT.-% INDICATE THAT EVEN THESE HIGH MELTING SALTS ARE CONSUMED WITHIN 4 TO 8 HR AT SILICONIZING TEMPERATURE.

THE EFFECT OF A LOWER HYDROGEN FLOW RATE COULD NOT BE ESTABLISHED WITHIN THE TIME AVAILABLE FOR THIS INVESTIGATION, BUT SUCH STUDY MIGHT BEAR RESULTS OF INTEREST. IN OUR EXPERIMENTS, NAF WAS FOUND TO BE THE MOST SUITABLE ENERGIZER. NaCl CAUSED THINNER COATINGS PROBABLY BECAUSE OF A FASTER VOLATILIZATION. INCREASING THE NAF CONTENT IN THE PACK UP TO 10 WT.%, IMPROVED THE WSi_2 COATING; AT 40 WT.% NAF, HOWEVER, A FUSED SALT LAYER AND A SLIGHTLY THINNER COATING WAS OBTAINED.

THE BEST RESULTS IN OUR EXPERIMENTS WERE OBTAINED WITH A PACK COMPOSITION OF 10% NAF AND 5% NH_4Cl ADDED TO THE SILICON POWDER. ADDITIONS OF AMMONIUM SALTS TO THE HIGHER MELTING ENERGIZERS ALWAYS IMPROVED THE CONTINUITY OF THE WSi_2 LAYERS, WHICH MIGHT BE DUE TO A FORMATION OF A POROUS PACK AND THE REMOVAL OF ANY REMAINING AIR FROM IT. THE MAXIMUM LAYER THICKNESS OBTAINED BY US WAS 38μ ; THE COATINGS FORMED WERE CONTINUOUS AND HAD A METALLIC SURFACE; SOMETIMES THEY DISPLAYED A THIN FILM OF A POWDER DEPOSIT ABOVE THE CONTINUOUS LAYER. EMPLOYING THE SAME PROCESS, H. BÜCKLE WAS ABLE TO PRODUCE LAYERS UP TO 90μ THICK BUT THESE DISPLAYED INCREASINGLY ROUGH AND CHECKED SURFACES.

B. COATINGS FORMED BY OTHER METHODS

BECAUSE OF THE HIGH PRIORITY GIVEN TO, AND THE ENCOURAGING RESULTS ACHIEVED WITH THE CEMENTATION METHOD, EXPERIMENTAL WORK WITH THE DIP AND VAPOR PLATING METHODS WAS LIMITED TO A FEW EXPLORATORY TRIALS. THE MAIN EFFORT IN THIS RESPECT WAS SPENT ON DEVELOPING VARIOUS APPARATUS AND TECHNIQUES, AND ACTUAL RESULTS ON COATINGS REMAINED INCOMPLETE AND INCONCLUSIVE.

C. OXIDATION TESTS OF SILICONIZED WIRES

I. GENERAL:

TUNGSTEN WIRE FAILURES OCCURRING IN HIGH TEMPERATURE OXIDATION TESTING CAN BE DIVIDED IN THREE MAIN GROUPS, (1) OXIDATION DUE TO PINHOLES OR OTHER SMALL INSUFFICIENTLY COATED AREAS, (2) DESTRUCTION OF THE LAYER THROUGH FORMATION OF A LIQUID PHASE, AND (3) THE DISILICIDE PEST IN LOW TEMPERATURE AREAS AS DESCRIBED IN SECTION I. IN THE MAIN, OXIDATION TESTS WERE PERFORMED IN STILL AIR; PARALLEL TESTS IN FLOWING AIR WERE SCHEDULED, BUT COULD NOT BE COMPLETED IN THE AVAILABLE TIME. BECAUSE OF A VARIETY OF CAUSES FOR LOSSES OF COATED WIRES DURING SILICONIZING, HANDLING AND CLAMPING IN THE OXIDATION TEST RIG, ONLY A FRACTION OF THE ORIGINAL WIRES UNDERWENT ACTUAL HIGH TEMPERATURE OXIDATION TESTS. WIRES PREPARED IN OUR LABORATORY WERE AUGMENTED BY A SUBSTANTIAL NUMBER PREPARED BY DR. BÜCKLE AT ONERA.

THE OXIDATION TEST RESULTS ARE SUMMARIZED IN TABLES III TO V. IN INITIAL TESTS THE TIME FOR HEATING THE COATED WIRES TO $3300^{\circ}F$ ($1815^{\circ}C$) WAS 20 MINUTES; IT WAS LATER DECREASED TO 5 MINUTES, AS IT WAS THOUGHT THAT A FASTER HEATING PROVIDES A THICKER WSi_2 LAYER DURING THE PERIOD OF A GLASS FORMATION, SINCE A GROWTH OF AN INTERMEDIATE W_3Si_2 LAYER DURING TESTING WAS OBSERVED. IN ALL CASES, COOLING TO BELOW RED HEAT OCCURRED WITHIN 10 SECONDS.

AS CAN BE SEEN FROM TABLE IV A VISIBLE GLASS FILM WAS ALREADY FORMED FOR A HEATING PERIOD OF 5 MINUTES AND ONE MINUTE AT $3000^{\circ}F$ ($1650^{\circ}C$). FIG. 7 SHOWS AN ABOUT 40 SINGLE WSi_2 LAYER BEFORE TESTING; AS CAN BE SEEN FROM THE PHOTOMICROGRAPH THE DIFFUSED LAYER AS WELL AS THE SUBSTRATE DISPLAYED A SERIES OF CRACKS. FIG. 9 AND

13 SHOW WITH POLARIZED ILLUMINATION THE FINE GRAINS OF THIS LAYER. ANOTHER HIGH MAGNIFICATION (FIG. 11) SHOWS THAT THERE IS REALLY NO INTERMEDIATE W_3Si_2 LAYER BEFORE TESTING. FIG. 8 AND 12 SHOWS THE GROWTH OF THE INTERMEDIATE W_3Si_2 LAYER AFTER ABOUT 1.5 HR HEATING IN AIR AT 3100°F (1700°C). THE W_2Si LAYER IS REDUCED AND A THICK W_3Si_2 LAYER IS FORMED CONSUMING BOTH SUBSTRATE AND W_2Si LAYER. MICROHARDNESS TESTS HAVE GIVEN EVIDENCE THAT THE BOUNDARY WITHIN THE INTERMEDIATE LAYER DOES NOT INDICATE ANOTHER PHASE, BUT IS A TAMMAN-TYPE RESISTANCE BOUNDARY (51). FIG. 12 AND 14 SHOW AT HIGH MAGNIFICATION THE GLASS LAYER FORMED ON TOP. THE APPRECIABLE GRAIN GROWTH IN THE W_2Si LAYER DURING TESTING IS NOTICEABLE IF FIG. 14 IS COMPARED WITH FIG. 13 OR FIG. 16 WITH FIG. 9 RESPECTIVELY. FIG. 15 AND 16 SHOW THAT THE W_2Si LAYER AFTER 10 HR TESTING IS COMPLETELY CONVERTED TO W_3Si_2 WITH A GLASSY LAYER ON TOP.

2. THERMAL CYCLING:

W_2Si LAYERS UP TO ABOUT 50 μ THICKNESS FORMED GLASS LAYERS, WHICH GENERALLY DID NOT CRACK DURING COOLING. THESE WIRES SHOULD THEREFORE BE FAIRLY RESISTANT TO THERMAL CYCLING. ON THE OTHER HAND, IN GLASS LAYERS FORMED ON W_2Si LAYERS THAT WERE THICKER THAN 50 μ , CRACKS ALWAYS OCCURRED DURING THE RAPID TEMPERATURE CHANGE ENCOUNTERED IN COOLING. THESE LAYERS ARE EXPECTED TO FAIL IN THERMAL CYCLING. OXIDATION USUALLY STARTS IN THE CRACKS OF THE GLASSY LAYER AND YELLOW WO_3 IS FORMED MARKING THE CRACK PATTERN (FIG. 17). SOMETIMES THIS OXIDATION PROCESS IS SLOWED DOWN BY A VISCOUS FLOW EFFECT OF THE GLASS AND OXIDATION OCCURS AT A MUCH REDUCED RATE THROUGH OTHER DEFECTS WHICH ARE TEMPORARILY OPENED AND CLOSED THROUGHOUT THE CYCLE. A LOWER, BLUE COLORED OXIDE DISSOLVED IN THE GLASS IS FORMED DURING THIS PROCESS, WHICH CAN GO ON FOR HOURS, UNTIL IT FINALLY CAUSES A BREAK THROUGH IN AN AREA OF AGGLOMERATION OF BLISTERS (FIG. 18).

3. PINHOLE FAILURES:

OUR HYPOTHESIS FOR PINHOLE FAILURES ENVISAGES A MECHANISM WHEREBY THE FAILURE AREA CANNOT BE SEALED OFF BY A DIFFUSION TYPE HEALING OF THE DISILICIDE LAYER. BECAUSE A HOLE OF CONSIDERABLE SIZE HAS DEVELOPED IN THE SUBSTRATE (FIG. 21), THE INCREASED OXIDATION AREA CAUSES A HIGH VAPOR PRESSURE OF WO_3 IN THE SMALL HOLE ON THE SURFACE AND A SEALING IS NOT POSSIBLE THROUGH THE GLASS FORMED IN THE MEANTIME. HOWEVER, THROUGH IMPROVED TECHNIQUE OF COATING AND A CERTAIN MINIMUM LAYER THICKNESS IT SEEMS POSSIBLE TO PREVENT PINHOLE FAILURES.

TESTED WIRES FAILED BY PINHOLES ARE TABULATED IN TABLE III. NO CONNECTION COULD BE DETECTED BETWEEN SURFACE FAILURES OBSERVED BEFORE TESTING AND PINHOLE FAILURES IN TESTING.

4. FORMATION OF A LIQUID PHASE:

THE TYPE OF FAILURE ASSOCIATED WITH DESTRUCTION THROUGH THE FORMATION OF A MOLTEN PHASE AT THE SURFACE OR INTERFACE OF COATING AND SUBSTRATE IS SHOWN IN FIG. 20. THIS REACTION WAS OBSERVED TO START IN AN AS-MEASURED TEMPERATURE RANGE FROM 2800°F (1540°C) UP TO 3540°F (1950°C). FORMATION OF THE $Si-W_2Si_2$ EUTECTIC CANNOT EXPLAIN THIS PHENOMENON SINCE THIS WOULD OCCUR AT A CONSIDERABLY LOWER TEMPERATURE. IT IS UNLIKELY THAT THE TEMPERATURE MEASUREMENTS WERE SO FAR IN ERROR THAT THE TRUE TEMPERATURES CORRESPONDED TO THE MELTING POINT OF THE $W_2Si_2-W_3Si_2$ EUTECTIC (3705°F, 2040°C);

MOREOVER, THIS WOULD NOT EXPLAIN THE WIDESPREAD TEMPERATURE RANGE OBSERVED FOR THE START OF MELTING IN DIFFERENT HEATS, ALWAYS MEASURED WITH THE SAME INSTRUMENT UNDER IDENTICAL CONDITIONS. THE ONLY EXPLANATION THAT APPEARS REASONABLE ON THE BASIS OF THE LIMITED EXPERIMENTAL DATA IS THE EXISTENCE OF AN UNKNOWN THIRD COMPONENT IN THE WSi_2 LAYER, WHICH LOWERS THE MELTING POINT OF THE W_3Si_2 - WSi_2 EUTECTIC. THIS THIRD COMPONENT MIGHT BE OXYGEN ITSELF OR NITROGEN DISSOLVED IN WSi_2 . A PARTIAL CONFIRMATION OF THIS HYPOTHESIS MIGHT BE THE PHOTOMICROGRAPH IN FIG. 21. IT SHOWS THAT THE CATASTROPHIC OXIDATION, WHICH FOLLOWS THE MELTING OF SUCH A LAYER FORMS A EUTECTIC ON THE SURFACE. IF THE GLASS LAYER FORMED IS THICK ENOUGH BEFORE REACHING THE MELTING TEMPERATURE OF THE WSi_2 LAYER, FUSION OF THE TERNARY EUTECTIC MIGHT OCCUR UNDER THE GLASS WITHOUT NECESSARILY DESTROYING THE GLASS FILM AND CAUSING OXIDATION OF THE SUBSTRATE (FIG. 16). SAMPLES THAT FAILED IN OXIDATION TESTS BY FORMATION OF A LIQUID PHASE ARE GIVEN IN TABLE IV.

THE SURFACE APPEARANCE OF WIRES WITH GOOD TEST RESULTS VARIED CONSIDERABLY AND THERE WAS NO ADVANCE DISTINCTION POSSIBLE BETWEEN MORE AND LESS OXIDATION RESISTANT WIRES.

5. Low Temperature Oxidation:

MANY OF OUR TESTS WERE PREMATURELY ARRESTED BECAUSE OF A BREAKTHROUGH IN A LOW TEMPERATURE REGION OF THE WIRE NEAR ONE OF THE TERMINALS. THESE FAILURES WERE THE RESULTS OF THE SO-CALLED DISILICIDE PEST, A LOW-TEMPERATURE OXIDATION PROCESS WHICH WAS MADE THE SUBJECT OF A SPECIAL INVESTIGATION. SILICONIZED TUNGSTEN WIRES WERE CUT INTO 1-INCH SECTIONS AND HEATED IN AIR IN AN ELECTRICALLY HEATED MUFFLE FURNACE AT DIFFERENT TEMPERATURES. THE WEIGHT GAIN OF THE SAMPLES WAS USED AS A MEANS TO DETERMINE THE LOWEST TEMPERATURE AT WHICH AN OXIDIZING REACTION OCCURRED (FIG. 22). IT COULD BE SEEN FROM THE SURFACE OF THE WIRES SHOWN IN THE DIAGRAM OF FIG. 22 THAT THE UNCOATED ENDS HAVE NO SIGNIFICANT INFLUENCE ON THE DETERMINATION OF THE STARTING TEMPERATURE OF THE OXIDATION PROCESS (DISILICIDE PEST) WHICH WAS FOUND TO BE ABOUT $1200^{\circ}F$ ($650^{\circ}C$). THE POWDERY YELLOW OXIDE PRODUCT OF THE SURFACE HAD GREATLY RESEMBLED WO_3 . THIS SIMILARITY WAS CONFIRMED BY THE HIGH VOLATILITY OF THE OXIDE ABOVE $1830^{\circ}F$ ($1000^{\circ}C$) AS INDICATED BY A WEIGHT DROP AND CLEAN SURFACE OF THE SAMPLE. THE UPPER TEMPERATURE LIMIT OF THE DISILICIDE PEST REACTION EXCEEDED THE CAPACITY OF THE MUFFLE FURNACE AND COULD NOT BE DETERMINED WITH THE SAME ACCURACY.

ATTEMPTS WERE MADE TO MEASURE THE TEMPERATURE ON THE UPPER BOUNDARY OF THE DISILICIDE PEST ZONE DURING A NORMAL HIGH TEMPERATURE TEST IN OUR DIRECT RESISTANCE HEATING FACILITY. ONLY AN APPROXIMATE MEASUREMENT IN THE ORDER OF $2280^{\circ}F$ ($1250^{\circ}C$) WAS OBTAINED IN THIS WAY, WHICH WILL REQUIRE CONFIRMATION IN TESTS EMPLOYING SUITABLE FURNACE EQUIPMENT. HOWEVER, THIS VALUE IS CLOSE TO THE VOLATILIZATION TEMPERATURE OF THE OXIDE FORMED IN THE LOW TEMPERATURE AREA. THUS, IT MIGHT WELL BE POSSIBLE THAT A VOLATILIZATION OF A TUNGSTEN RICH OXIDE IS A NECESSARY MECHANISM FOR THE FORMATION OF A PROTECTIVE LAYER. IN MOST INSTANCES A CONSIDERABLE DISTANCE COULD STILL BE OBSERVED ON THE WIRE BETWEEN UPPER DISILICIDE PEST TEMPERATURE BOUNDARY AND THE FIRST ZONE OF VISIBLE GLASS FORMATION. TESTED WIRES WITH FAILURES CAUSED BY DISILICIDE PEST ARE GIVEN IN TABLE V.

EXPERIMENTS DESIGNED TO PREVENT THIS LOW TEMPERATURE OXIDATION BY PREOXIDIZING AT HIGH TEMPERATURE IN ORDER TO FORM A GLASSY SURFACE PROTECTIVE IN THE LOW

TEMPERATURE HEAT ZONE WERE NOT SUCCESSFUL. THE GLASS PHASE DISAPPEARED IN THIS TEMPERATURE RANGE AFTER A SHORT TIME OF HEATING AND THE DISILICIDE PEST REACTION COULD NOT BE RETARDED (FIG. 17).

D. SILICONIZED WIRES WITH EXTERNAL FLAME SPRAYED ZrO_2 COATING

ATTEMPTS TO SPRAY ONTO SEVERAL OF THE PACK-SILICONIZED TUNGSTEN WIRES ZrO_2 BY MEANS OF A PLASMA ARC PERFORMED BY THE LINDE CO. WERE NOT VERY ENCOURAGING, MAINLY BECAUSE OF A GENERAL LACK OF GOOD ADHERENCE TO THE WSi_2 LAYER. HOWEVER, IT WAS POSSIBLE TO PERFORM OXIDATION TESTS ON SOME WIRE SECTIONS WHICH DISPLAYED AT LEAST PARTIAL ADHESION OF THE ZrO_2 COAT TO THE WSi_2 SURFACE LAYER. THE RESULTS ARE TABULATED IN TABLE III.

A STUDY OF THE INFLUENCE OF THE EXTERNAL ZrO_2 LAYER ON THE MECHANISM OF FORMING THE GLASSY PHASE FROM THE DISILICIDE LAYER INDICATED THAT THE THICKNESS OF THE ZrO_2 HAS A CERTAIN INFLUENCE. THIN ZrO_2 LAYERS ARE DISSOLVED IN THE GLASS WITHOUT APPARENT DETRIMENTAL EFFECTS ON THE HIGH TEMPERATURE OXIDATION BEHAVIOR. AREAS COVERED WITH A THICK ZrO_2 COAT DISPLAYED PREMATURE FAILURE, APPARENTLY DUE TO A REACTION WITH THE GLASS FORMED ON THE DISILICIDE LAYER (TABLE III).

THE EFFECT OF THE EXTERNAL ZrO_2 LAYER ON THE DISILICIDE PEST-AFFECTED REGIONS COULD NOT BE ASCERTAINED FOR LACK OF SUFFICIENT SAMPLE MATERIAL.

IV. SUMMARY AND CONCLUSIONS

A. GENERAL

AN INVESTIGATION WAS UNDERTAKEN ON THE DEVELOPMENT OF COATINGS ON TUNGSTEN WHICH ARE PROTECTIVE AGAINST OXIDATION AT $3300^{\circ}F$ ($1815^{\circ}C$) FOR PROLONGED TIME. THE MAIN PROBLEMS ENCOUNTERED AT THIS TEMPERATURE ARE (1) EXTREME VOLATILITY OF THE SUBSTRATE OXIDES, (2) IN GENERAL, HIGH DIFFUSIBILITY BETWEEN SUBSTRATE AND COATING, AND (3) LOW MELTING EUTECTICS FORMED BETWEEN SUBSTRATE AND COMPOUNDS OF THE COATING OR BETWEEN THE COMPOUNDS THEMSELVES. BECAUSE OF (2) AND (3) IT IS BELIEVED THAT NO SUITABLE COATING CAN REMAIN A METALLIC LAYER AT THE CITED TEMPERATURE. A SOLUTION OF THE PROBLEM IS BELIEVED POSSIBLE ONLY BY FORMATION OF AN IMPERVIOUS EXTERNAL LAYER OF A REFRACTORY OXIDE OR GLASS-LIKE SUBSTANCE. IT THEREFORE SEEMS UNLIKELY THAT TUNGSTEN CAN BE PROTECTED AGAINST OXIDATION AT HIGH TEMPERATURES WITHOUT FURTHER INCREASING ITS LACK OF DUCTILITY, AT LEAST AT ROOM TEMPERATURE.

THE INTERMETALLIC COMPOUND, TUNGSTEN DISILICIDE (WSi_2), WHICH AT $3300^{\circ}F$ FORMS AN IMPERVIOUS, SiO_2 -RICH, EXTERNAL GLASS LAYER WAS BELIEVED TO BE THE MOST PROMISING MATERIAL FOR THE COATING. HENCE, PRODUCTION AND PROPERTIES OF DISILICIDE LAYERS ON TUNGSTEN SUBSTRATES CONSTITUTED THE MAIN OBJECT OF THE INVESTIGATION. ANOTHER APPROACH, THE APPLICATION OF CERAMIC LAYERS OR REFRACTORY OXIDES ON TOP OF THE DISILICIDE LAYER WAS ONLY SUBJECTED TO PRELIMINARY STUDY BY US.

AS SUBSTRATE, 2% THORIATED .080 IN (2MM) DIAMETER WIRES WITH GROUND FINISH WERE EMPLOYED. A SMOOTH SURFACE OF THE SUBSTRATE WAS A PREREQUISITE FOR THE FORMATION

OF A CONTINUOUS DISILICIDE LAYER. PRELIMINARY INVESTIGATIONS PERFORMED ON WIRES WITH DIFFERENT THORIA CONTENTS, SHOWED NO INFLUENCE OF THE THORIA CONTENT ON SILICONIZING RATE AND OXIDATION RESISTANCE OF SILICONIZED WIRES.

B. APPLICATION OF COATINGS

THREE PRINCIPAL PROCEDURES FOR FORMING A TUNGSTEN DISILICIDE LAYER ON TOP OF A TUNGSTEN SUBSTRATE WIRE WERE UNDER INVESTIGATION, I.E. (1) VAPOR-PLATING, (2) DIP-SILICONIZING, AND (3) CEMENTATION (PACK-SILICONIZING), ALL DIFFUSION-TYPE PROCESSES. IT IS IMPORTANT THAT FORMATION OF A THICK INTERMEDIATE W_3Si_2 LAYER IS PREVENTED, BECAUSE THIS COMPOUND DISPLAYS POOR OXIDATION RESISTANCE AT HIGH TEMPERATURE. AN EXTERNAL SI-LAYER WOULD CAUSE FUSION AND DESTRUCTION OF ANY PROTECTIVE SURFACE LAYER SINCE A LOW MELTING EUTECTIC BETWEEN WSi_2 AND SI FORMS AT 2550°F (1400°C).

WITHIN THE CONTRACT PERIOD IT WAS ONLY POSSIBLE TO INVESTIGATE THE PACK-SILICONIZING METHODS MORE THOROUGHLY. THIS METHOD WAS GIVEN PREFERENCE BECAUSE OF ITS SIMPLICITY AND GREATEST POTENTIAL FOR A PRACTICAL PROCESS. IT APPEARS TO BE THE MOST ECONOMICAL WAY TO PRODUCE UNIFORM DISILICIDE LAYERS ON COMPLICATED TUNGSTEN PARTS. IT SHOULD BE NOTED, HOWEVER, THAT DESPITE THESE APPARENT ATTRIBUTES, COMPARATIVELY LITTLE HAS BEEN PUBLISHED ABOUT SUCCESSFUL WORK IN APPLYING THE METHOD TO TUNGSTEN, THE BULK OF THE REFERENCES BEING RELATED RATHER TO MOLYBDENUM. GENERALLY SPEAKING, THE PROCESS HAS BEEN SUCCESSFUL SOLELY ON AN EMPIRICAL BASIS AND THE REACTION MECHANISM INVOLVING AN ACTIVATING ADDITIVE OR ENERGIZER IN THE SILICON POWDER PACK IS NOT ENTIRELY UNDERSTOOD. IT WAS FELT THAT FURTHER EXPERIMENTAL WORK TO STUDY THE EFFECT OF SOME OF THE VARIABLES OF THE PROCESS WOULD BE REQUIRED AS A PREREQUISITE TO A MORE THOROUGH UNDERSTANDING OF THE BASIC MECHANISM OF THE SILICON CEMENTATION PROCESS AS IT RELATES TO TUNGSTEN.

WIRES WERE SILICONIZED BETWEEN 1650° AND 1920°F (900-1050°C) IN A FLOWING HYDROGEN ATMOSPHERE. THE PACK CONTAINED A 325 MESH HIGH-PURITY SILICON POWDER AS THE SOURCE FOR THE WSi_2 COATING. INITIAL EXPERIMENTS WITH ADDITIONS OF ALUMINA POWDERS OF DIFFERENT PARTICLE SIZE TO THE PACK AS A FILLER SUBSTANCE DID NOT LEAD TO ANY IMPROVEMENTS AND WERE DISCONTINUED. CHLORIDES, FLUORIDES AND AMMONIUM SALTS WERE USED EXPERIMENTALLY AS ENERGIZERS. BECAUSE OF THE STEADY STATE OF HYDROGEN FLOW THROUGH THE PACK AND THE PROLONGED SILICONIZING TIMES REQUIRED TO OBTAIN REASONABLE COAT THICKNESSES (2 TO 8 HR.), HIGH MELTING SALTS WERE FOUND TO BE THE MOST SUITABLE ENERGIZERS. SALTS, WHICH VOLATILIZE OR EVAPORATE BELOW THE SILICONIZING TEMPERATURE (E.G. AMMONIUM COMPOUNDS), ARE CONSUMED IN A SHORT TIME AND BECOME INEFFECTIVE FOR THE DIFFUSION PROCESS. SALTS, LIQUID AT SILICONIZING TEMPERATURE, INTERFERE WITH THE DIFFUSION PROCESS BY FORMATION OF FUSED FILMS ON THE SUBSTRATE. THE MOST EFFECTIVE ENERGIZER WAS FOUND TO BE NAF (MELTING AT 1820°F, 992°C). ADDITIONS OF AMMONIUM SALTS INCREASE THE INTEGRITY (CONTINUITY AND SURFACE APPEARANCE) OF THE COATING. THE OPTIMUM CONCENTRATION OF THE ENERGIZER IN THE PACK DEPENDS ON THE SILICONIZING TIME. FOR PERIODS OF 4 TO 8 HR., THE OPTIMUM CONCENTRATION IS IN THE ORDER OF 10 WT.-%. CLEANING OF THE WIRE BEFORE SILICONIZING HAS A NOTICEABLE INFLUENCE ON THE QUALITY OF THE COAT. IT WAS FOUND THAT WIRES CLEANED WITH CCl_4 GAVE THICKER COATINGS THEN ANODICALLY CLEANED WIRES.

SINGLE WSi_2 LAYERS UP TO 90 μ THICKNESS WERE OBTAINED BY THIS METHOD. NEITHER AN INTERMEDIATE W_3Si_2 NOR AN EXTERNAL SI LAYER COULD BE DETECTED ON THESE

PACK-SILICONIZED WIRES. HOWEVER, THE LAYER AS WELL AS THE SUBSTRATE DEVELOP MICROCRACKS DURING SILICONIZING, WHICH CAUSES A CERTAIN STRUCTURAL WEAKENING OF BOTH.

IN OUR PRESENT INVESTIGATION A LIMITED NUMBER OF FACTORS WERE DETERMINED, MAINLY THOSE RELATING TO COMPOSITIONS OF THE PACK. QUANTITATIVE DETERMINATION OF THE INTERDEPENDENCE OF TIME, TEMPERATURE, ATMOSPHERE, ARRANGEMENT, ETC. WITH CONCENTRATION AND TYPE OF ENERGIZER OR SILICON REMAIN QUESTIONS TO BE SOLVED BY FURTHER RESEARCH. BECAUSE OF THE GREAT VARIETY OF VARIABLES INVOLVED IN THE PROCESS, A BASIC STUDY OF THE KINETICS AND THERMODYNAMICS WOULD ULTIMATELY BE AN ESSENTIAL SUPPORT IN THE INDUSTRIAL DEVELOPMENT OF THIS IMPORTANT PROCESS FOR TUNGSTEN. MOREOVER, SUCH BASIC STUDY WOULD UNDOUBTEDLY ALSO BENEFIT COATING PROCESSES FOR OTHER METALS, SOME OF WHICH ARE ALREADY USED ON A COMMERCIAL SCALE.

THE APPROACH OF DEPOSITING EXTERNAL LAYERS OF REFRACTORY OXIDES ON TOP OF THE DISILICIDE LAYER WAS UNDERTAKEN WITH THE THOUGHT OF INCREASING THE VISCOSITY OF THE FORMED GLASSY LAYER ON TUNGSTEN DISILICIDE. THIS WAS SOUGHT TO BE ACCOMPLISHED WITHOUT INCREASING THE SOFTENING POINT OF THE EXTERNAL LAYER EITHER BY SOLUTION OR BY DISPERSION OF THE REFRACTORY OXIDES IN THE SiO_2 .

ONLY A FEW EXPLORATORY EXPERIMENTS COULD BE MADE TOWARD PURSUING THIS APPROACH. ONE WAY FOLLOWED WAS TO SPRAY ZrO_2 ONTO SILICONIZED TUNGSTEN WIRES BY MEANS OF A PLASMA ARC. NO TRULY SATISFACTORY BOND BETWEEN THE EXTERNAL OXIDE AND THE SILICIDE LAYER COULD BE OBTAINED BY THE TECHNIQUE EMPLOYED, BUT HEATING THE WSi_2 -COATED SUBSTRATE UNDER PROTECTIVE ATMOSPHERE TO VERY HIGH TEMPERATURES MIGHT LEAD TO MORE PROFITABLE RESULTS. OTHER TECHNIQUES SHOWING PROMISE, SUCH AS VAPORPLATING OF OXIDES OR DEPOSITION OF A METAL THAT FORMS A STABLE OXIDE MIGHT BE A USEFUL FIELD FOR FURTHER INVESTIGATION.

C. HIGH TEMPERATURE PROPERTIES

FOR THE OXIDATION TEST PROGRAM, DIRECT ELECTRICAL RESISTANCE HEATING OF THE COATED WIRES, MAINLY WHILE EXPOSED TO STILL AIR, WAS USED. TESTS IN FLOWING AIR WERE NOT GENERALLY EMPLOYED FOR REASONS OF IMPROVED SIMPLICITY OF THE STILL AIR PROCEDURE, INASMUCH AS IT WAS FELT THAT A GLASSY SURFACE FORMED DURING HEATING TO THE TEST TEMPERATURE OF 3300°F (1815°C) WAS SUFFICIENTLY VISCOUS TO MAKE THE CONDITIONS COMPARABLE. THE GLASSY SURFACE WAS USUALLY FORMED ON THE CENTRAL PART OF THE WIRE SUBJECTED TO THE HIGHEST TEMPERATURE. AN INTERMEDIATE W_3Si_2 LAYER DEVELOPED DURING TESTING AT THE EXPENSE OF THE WSi_2 LAYER AND THE SUBSTRATE. THE TEMPERATURE LIMIT FOR PROTECTION WAS FOUND TO BE THE FUSION OF A PHASE BENEATH THE LIQUID EXTERNAL GLASS FILM. NO EXACT MEASUREMENTS OF THIS FUSION TEMPERATURE COULD BE MADE, BUT MELTING FOR DIFFERENT WIRES OCCURRED IN AN AS-MEASURED TEMPERATURE RANGE OF 2800° TO 3540°F (1540° - 1950°C). NO EXPLANATION FOR THIS ERRATIC PERFORMANCE COULD BE FOUND ON THE BASIS OF THE RELATIVELY FEW TESTS MADE. A FURTHER REFINEMENT OF THE CEMENTATION METHOD WOULD DOUBTLESS INCREASE THE REPRODUCIBILITY OF THOSE COATINGS THAT FUSE AT OR NEAR 3540°F .

THOUGH THE COATINGS PRODUCED SHOWED EXCELLENT SELF-HEALING PROPERTIES, OWING TO MECHANISMS OF DIFFUSION IN THE DISILICIDE LAYER AND VISCOUS FLOW IN THE GLASS LAYER, INITIAL PINHOLE FAILURES OCCURRED IN ANOTHER GROUP OF WIRES TESTED. THESE DEFECTS

WERE PROBABLY DUE TO LOCAL IMPURITIES IN THE WSi_2 COATING, AND THIS TYPE OF FAILURE IS BELIEVED TO BE READILY OVERCOME BY METICULOUSLY CLEAN SILICONIZING CONDITIONS AND A THICK ENOUGH DISILICIDE LAYER.

FOR WIRES FREE FROM PINHOLES AND HAVING A HIGH COAT FUSION TEMPERATURE, THE LIFE AT TEST TEMPERATURE WAS GOVERNED BY A MECHANISM OF LOW TEMPERATURE OXIDATION (DISILICIDE PEST), ACTIVE ON THE COOLER END PARTS OF THE WIRE NEAR THE COLD TERMINAL BLOCKS OF THE DIRECT RESISTANCE TEST FACILITY. THIS PHENOMENON IS A SLOW OXIDATION PROCESS OCCURRING IN A TEMPERATURE RANGE FROM ABOUT 1200 TO 2280°F (650°C-1250°C). LAYERS EXPOSED FOR A SHORT TIME TO THIS TEMPERATURE RANGE ARE STILL ABLE TO FORM A PROTECTIVE GLASS SURFACE AFTERWARDS. THE TIME FOR OXIDATION TO PROCEED TO COMPLETE DESTRUCTION IS STRICTLY A FUNCTION OF THE LAYER THICKNESS, WITH COATINGS RANGING FROM 24 TO 90 μ BEING DESTROYED IN THE SENSITIVE TEMPERATURE RANGE AFTER ABOUT 5 TO 15 HR. THE PREVENTION OF THE DISILICIDE PEST ON AREAS HAVING A CONTINUOUS TEMPERATURE GRADIENT UP TO 3300°F SEEMS TO BE A MAJOR PROBLEM. ONLY A THOROUGH INVESTIGATION OF THE MECHANISM OF THIS LOW TEMPERATURE OXIDATION IS EXPECTED TO LEAD TO ITS INHIBITION OR CONTROL ON AN ACCEPTABLE BASIS.

WIRES WITH A HEAVY DISILICIDE COAT (ABOVE 40 μ) DEVELOP DURING COOLING FROM THE TEST TEMPERATURE CRACKS WITHIN THE GLASSY SURFACE. THE SELF-HEALING EFFECT OF THE GLASS LAYER DOES NOT APPEAR TO BE SUFFICIENTLY POTENT TO PROVIDE RESISTANCE TO REPEATED AND DRASTIC THERMAL CYCLING OF SUCH HEAVILY COATED SPECIMENS. WIRES WITH THINNER COATINGS, HOWEVER, DISPLAYED NO CRACKS IN THE GLASSY FILM AFTER TESTING AND MIGHT THEREFORE BE WELL CAPABLE OF RESISTING AT LEAST A LIMITED NUMBER OF THERMAL CYCLES, POSSIBLY EVEN OF THE MORE DRASTIC TYPE.

OXIDATION TESTS CONDUCTED AT 3250°F ON SILICONIZED WIRES WITH A ZIRCONIA SURFACE LAYER SHOWED THAT THIN ZrO_2 LAYERS ARE DISSOLVED IN THE GLASS FILM OF THE DISILICIDE WITHOUT HARM, BUT THICKER ZrO_2 LAYERS CAUSED PREMATURE FAILURE BY A REACTION NOT READILY UNDERSTOOD AT PRESENT.

D. CONCLUSIONS

PROPERLY SILICONIZED TUNGSTEN SUBSTRATES FORM A GLASSY SURFACE AT HIGHER TEMPERATURES AND UNDER RIGOROUSLY CONTROLLED MANUFACTURING CONDITIONS ARE ABLE TO WITHSTAND OXIDATION AT 3300°F (1815°C) IN STILL AIR FOR PROLONGED TIMES UP TO AT LEAST 10 HRS. IT IS BELIEVED THAT A SIMILAR RESULT IS ALSO OBTAINABLE FOR TESTS UNDER FLOWING AIR CONDITIONS UP TO FAIRLY HIGH AIR VELOCITIES BECAUSE OF THE SURFACE TENSION OF THE VISCOUS GLASS FORMED. NO OTHER TYPE OF COATING IS PRESENTLY KNOWN FOR TUNGSTEN WHICH OFFERS THE SAME STABILITY AT 3300°F.

A FURTHER DEVELOPMENT AND REFINEMENT OF THE DISILICIDE COATING SEEMS TO BE DESIRABLE IN SPITE OF CERTAIN SERIOUS DRAWBACKS, SUCH AS LOW TEMPERATURE OXIDATION AND INHERENT BRITTLINESS. WHEREAS THE LOW TEMPERATURE OXIDATION HAS A GOOD CHANCE TO BE OVERCOME BY RESEARCH DIRECTED AT THE UNDERSTANDING OF ITS MECHANISM, THE BRITTLINESS IS A BASIC PROPERTY OF THE LAYER WHICH RENDERS THE SUBSTRATE COMPLETELY UNWORKABLE AFTER SILICONIZING. THE SILICONIZING PROCESS MUST THEREFORE BE APPLICABLE TO PARTS ALREADY IN THEIR FINAL FORM AND THE PACK-TYPE CEMENTATION METHOD APPEARS, AT PRESENT, TO BE THE MOST ADVANTAGEOUS TO EMPLOY.

REFERENCES

1. C. G. GOETZEL, P. S. VENKATESAN, AND R. F. BUNSHAH: WADC TECHNICAL REPORT 59-405.
2. O. KUBASCHEWSKI AND B. E. HOPKINS: OXIDATION OF METALS AND ALLOYS, ACADEMIC PRESS INC., 1953.
3. J. W. HICKMAN AND E. A. GULBRANSEN: TRANS. A.I.M.M.E. 171, PP. 371 (1947).
4. E. A. GULBRANSEN AND W. S. WYSONG: A.I.M.M.E., TECHN. PUBL. NO. 2224 (1947).
5. V. I. ARKHOROV AND YU. D. KOZMANOV: FIZIKA MEALLOV I METALLOVEDENIE, 2, PP. 361, (1956) NR. 2, BRUTCHER TRANSL. #4104.
6. C. J. SUIRTHELLS: "TUNGSTEN," CHAPMAN & HALL LTD., LONDON, 1952.
7. W. W. WEBB, J. T. NORTON AND C. WAGNER: J. ELECTROCHEMICAL SOC., 108 (2), PP. 107 (1956).
8. R. SPEISER: THE OHIO STATE UNIV. REPORT 831-182 (1958), WADC CONTR. AF 33(616)-5721.
9. M. J. POOL, G. R. ST. PIERRE, AND R. SPEISER: MASTER THESIS AT THE OHIO STATE UNIV. (1959).
10. L. BREWER: CHEM. REV., 52, P. 1 (1953).
11. P. E. BLACKBURN, M. HOCH AND H. L. JOHNSTON: J. PHYSICAL CHEM., 62, PP. 769 (1958).
12. T. MILLNER AND J. NEUGEBAUER: NATURE, 163, PP. 601 (1949).
13. J. P. COUGHLIN: "CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY XII. HEATS AND FREE ENERGIES OF FORMATION OF INORGANIC OXIDES," U.S. BUR. MINES, BULL. 542 (1954).
14. R. W. DOUGLAS, F. C. HOLDEN AND R. I. JAFFEE: TECHNICAL PHASE REPORT, 1959 BATTELLE MEMORIAL INST., COLUMBUS, OHIO.
15. T. E. TIETZ, B. A. WILCOX AND J. W. WILSON, FINAL REPORT STANFORD RESEARCH INST., 1959, SRI PROJECT SU-2436.
16. WADD-NASA CONFERENCE, CONVAIR-SANDIEGO, CALIF., JANUARY 1960 (3RD MEETING OF THE HIGH TEMPERATURE INORGANIC REFRACTORY WORKING GROUP).
17. D. E. COUCH, H. SAPHIRO, J. K. TAYLOR, AND A. BRENNER: J. ELECTROCHEM. SOC., 105 (8) PP. 450, (1958).

REFERENCES (CONTINUED)

18. PMD PROJECT No. BSL-1958-112, CONTR. No. AF 33(616)-6354, TASK No. 73120, PROGR. REP. 2, 3, 1959-60, MANUFACTURING LABORATORIES INC., CAMBRIDGE, MASS.
19. E. S. BARTLETT, H. R. OGDEN, AND R. I. JAFFEE: DMIC REPORT #109 (1959) ASTIA AD 210978, OTS PB 151064.
20. R. KIEFFER, K. SEDLATSCHKE AND H. BRAUN, ZEITSCHRIFT FUER METALLKUNDE 50 PP. 19 (1959).
21. G. A. GEACH AND J. E. HUGHES: PLANSEE PROCEEDINGS, 1955 PP. 245.
22. H. BRAUN, R. KIEFFER, AND K. SEDLATSCHKE: PLANSEE PROCEEDINGS, 1958, PP. 264.
23. R. I. JAFFEE, C. T. SIMS, AND J. J. HARWOOD: PLANSEE PROCEEDINGS, 1958, PP. 380.
24. H. BÜCKLE: Z. METALLKDE. 37 (1946) PP. 53.
25. H. BÜCKLE: REVUE D METALLURGIE LIV, #1 (1957) PP. 10.
26. P. GREENFIELD AND P. A. BECK: J. OF METALS, FEB. 1956.
27. K. KIRNER: PLANSEEBERICHT 7, PP. 117 (1959).
28. J. H. BROPHY, P. SCHWARZKOPF, AND J. WULFF: METALLURGY REPORTS 10, #10 (1959) MASS. INST. OF TECHN.
29. C. G. BERGERON, A. L. FRIEDBERG, AND R. C. ANDERSON UNIVERSITY OF ILLINOIS, WADC TECHNICAL REPORT 59-526 PART I & II (1960).
30. G. A. HOFFMAN AND W. J. KNAPP: ASTIA DOCUMENT # AD 206554 (1958).
31. H. BÜCKLE: PLANSEE PROCEEDINGS 1958, PP. 151.
32. C. F. POWELL, I. E. CAMPBELL AND B. W. GONSER: "VAPORPLATING," JOHN WILER & SONS INC. NEW YORK, CHAPMAN & HALL, LIMITED, LONDON, 1955.
33. TECHNICAL MEMORANDUM WCLT TM 58-139 (1958) (SUMMARY OF FIRST HIGH TEMPERATURE INORGANIC REFRACTORY COATINGS WORKING GROUP MEETING).
34. W. G. BRADSHAW AND C. O. MATHEWS: LOCKHEED AIR CRAFT, REPORT LMSD-2466 (JUNE 1958).
35. H. NOWOTNY, E. KIMAKOPOULOU, AND H. KUDIELKA: MONATSHFTE FUER CHEMIE 88, (HEFT 2, 1957) PP. 181.
36. H. NOWATNY, E. PARTHE, R. KIEFFER, AND F. BENESOVSKY: MONATSHFTE FUER CHEMIE 85, (1954) PP. 255.

REFERENCES (CONTINUED)

37. L. BREWER AND O. KRIFORIAN, UNIVERSITY OF CALIFORNIA, AEC UCRL 2544, (1954).
38. O. E. ACCOUNTIUS, H. H. SISTER, AND T. S. SHEVLIN: J. AMER. CERAM. SOC. 37, (1954) PP. 173.
39. H. M. GREENHOUSE, R. F. STOOPS, AND T. S. SHEVLIN: J. AMER. CER. SOC. 37, (1954) PP. 203.
40. M. JONES: WADC TECHNICAL REPORT 57-602 (ASTIA Doc. #AF 150962) FEB. 1958.
41. R. KIEFFER, F. BENESOVSKY AND E. GALLISTL: METALLKUNDE 43 (1952) PP. 284.
42. R. FITZER: PLANSEE PROCEEDINGS 1952, PP. 244.
43. R. FITZER: PLANSEE PROCEEDINGS 1955, PP. 56.
44. AUSTRIAN PAT. NR. 178779 (1953).
45. E. FITZER: PLANSEE PROCEEDINGS, 1958, PP. 175.
46. LINDE PLASMA ARC PLATING, 1959.
47. E. A. BEIDLER, C. F. POWELL AND I. E. CAMPBELL: J. ELECTROCHEM. SOC. JAN. 1951, PP. 21.
48. A. SCHACK: DER INDUSTRIELLE WARMEUEBERGANG, VERLAG STAHLEISEN M.B.H., 1953, PP. 382-84.
49. W. HAILIGENSTAEDT: WAERMETECHINSCH RECHMINGEN. VERLAG STAHLEISEN M.B.H., 1941, PP. 86-95.
50. MM. P. LEBEAU, AND J. FIGUERAS: COMPTES RENDUS, DE L'ACADEMIE DE SCIENCES, 136, (1903) PP. 1329.
51. H. BUCKLE, PRIVATE COMMUNICATIONS.

TABLE I

MELTING AND BOILING POINTS OF ENERGIZER SALTS

ENERGIZER	CHEMICAL FORMULA	MELTING POINT		BOILING POINT	
		°C	°F	°C	°F
AMMONIUM CHLORIDE	NH ₄ Cl	350 ¹⁾	662 ¹⁾	520 ²⁾	968 ²⁾
AMMONIUM BROMIDE	NH ₄ Br	--	--	542 ²⁾	1008 ²⁾
AMMONIUM IODIDE	NH ₄ I	--	--	-- ²⁾	-- ²⁾
SODIUM IODIDE	NaI	651	1204	1300	2372
POTASSIUM IODIDE	KI	723	1333	1330	2426
POTASSIUM BROMIDE	KBr	730	1346	1380	2516
SODIUM BROMIDE	NaBr	755	1391	1390	2534
POTASSIUM CHLORIDE	KCl	790	1454	1500	2732
SODIUM CHLORIDE	NaCl	804	1479	1413	2575
SODIUM FLUORIDE	NaF	992	1818	--	--
POTASSIUM FLUORIDE	KF	857	1575	1502	2736

1) DECOMPOSITION TEMPERATURE

2) SUBLIMATION TEMPERATURE

TABLE II
LAYER THICKNESSES IN MICRONS PRODUCED BY DIFFERENT SILICONIZING PACKS

WT-% PACK TIME INGREDIENTS, AND TEMP. (BAL. Si) OF TREATMENT	40 NAF	10 NAF	10 NAF	10 NAF	5 NAF	5 NAF	3 NAF	3 NAF	3 NAF	10 NaCl	5 NaCl	3 NaCl	10 KF	10 KF	10 KF	5 KF	5 KF	3 KF	5 NaI	5 NH ₄ Cl	5 NH ₄ Cl	5 NH ₄ Br	5 NH ₄ Br	5 NH ₄ I	5 NH ₄ I
			5 NH ₄ Cl	50 Al ₂ O ₃		60 Al ₂ O ₃	2 NH ₄ Cl	2 NH ₄ Br	2 NH ₄ I	5 NH ₄ Cl		2 NH ₄ Cl	50 Al ₂ O ₃	80 Al ₂ O ₃	60 Al ₂ O ₃	2 NH ₄ Cl			60 Al ₂ O ₃		60 Al ₂ O ₃		60 Al ₂ O ₃		
1050°C 8 HR	*) 1)	31	38	34	--	--	--	--	--	8	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	2)	27	32	38	--	--	--	--	--	14	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	3)	34	32	39	--	--	--	--	--	15	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1050°C 4 HR		--	25	--	18	14	--	9	17	12	--	10	10	15	15	--	--	5	0	--	--	--	--	--	--
950°C 2 HR		--	--	--	--	9	5	8	8	--	--	--	--	--	--	5	5	--	--	0	3	1	1	3	3
900°C 2 HR		--	--	--	--	--	--	--	--	--	--	--	--	--	43**)	--	--	--	--	--	--	--	--	--	--
900°C 1 HR		--	--	--	--	--	--	--	--	--	--	--	--	--	11	--	--	--	--	--	--	--	--	--	--
1000°C 1/2 HR		--	--	--	--	--	--	--	--	--	--	--	--	--	9	--	--	--	--	--	--	--	--	--	--

*) 1) 40 SEC ANODICALLY CLEANED

2) 2 MIN " "

3) CLEANED IN CCL₄

**) DISCONTINUOUS LAYER

TABLE III

TEST	WSi ₂ COAT THICKNESS, μ	TEST TEMP. °F		LIFE TIME		SAMPLE SURFACE		TYPE OF FAILURE	REMARKS
		AS MEAS.	CORR.	HR.	MIN	BEFORE TEST	AFTER TEST		
1	24	3200	3300	1	50	CONTINUOUS	CONTINUOUS GLASSY	CONTACT FAILURE	OPAQUE AREAS IN THE GLASS FORMED
2	26	3160	3260	1	30	ROUGH	CONTINUOUS GLASSY	REACTION WITH TERMINAL, 1910°F	NO CRACKS IN THE GLASS FILM
3	32	3320	3420	0	5	LOCAL DEFECTS	CONTINUOUS GLASSY	REACTION WITH TERMINAL Cu	CRACKS IN THE GLASSFILM
4	32	3150	3250	0	6	LOCAL DEFECTS	GLASSY	PINHOLE OXIDATION	BLISTERING IN THE GLASSFILM
5	45	3180	3280	1	5	ROUGH	GLASSY	CONTACT FAILURE	CRACKS, PEELING AND BLISTERS IN THE GLASSFILM
5A	--	3160	3260	0	20	GLASSY, CRACKS, BLISTERS	DISCONTINUOUS, GLASSY	PINHOLE OXIDATION	SECOND CYCLE OF TEST No. 5 BLUE GLASSFILM WITH BLISTERS
6	65	3200	3300	0	15	ROUGH	CONTINUOUS GLASSY	REACTION WITH TERMINAL, 2400°F	CRACKS IN THE GLASSFILM
6A	--	3190	3290	1	37	GLASSY, CRACKS	CONTINUOUS GLASSY	PINHOLE OXIDATION	SECOND CYCLE OF TEST No. 6 BLUE GLASSFILM WITH BLISTERS
7	24	3140	3230	1	5	DISCONTINUOUS EXTERNAL ZrO ₂ LAYER	CONTINUOUS GLASSY	CONTACT FAILURE	FEW CRACKS IN GLASSFILM, ZrO ₂ DISSOLVED
8	24	3150	3250	0	43	HEAVY EXTERNAL ZrO ₂ LAYER	GLASSY	OXIDATION IN REACTION AREA	CONT. GLASS LIKE SURFACE EXCEPT IN FAILURE AREA

TABLE IV
OXIDATION TEST RESULTS - FAILURES CAUSED BY FUSION

TEST	WSI ₂ COAT THICKNESS, μ	TEST TEMP. °F		LIFE TIME		SAMPLE SURFACE		REMARKS
		AS MEAS.	CORR.	HR.	MIN.	BEFORE TEST	AFTER TEST	
1	12	3300	3400	0	2	LOCAL DEFECTS	OXIDIZED, FUSED AREAS	APPARENT OXIDATION AFTER FUSION
2	24	3000	3090	0	1	ROUGH	DITTO	DITTO
3	24	3000	3090	0	1	ROUGH	PARTLY FUSED, OXIDIZED, REST GLASSY	APPARENT OXIDATION AFTER FUSION
4	24	3160	3260	0	5	ROUGH	PARTLY FUSED, OXIDIZED, REST GLASSY	
5	31	3000	3090	0	10	CONTINUOUS	DITTO	
6	32	3000	3090	0	1	"	FUSED WITH BLISTERS	BEGINNING OF GLASS FORMATION
7	38	3000	3090	0	1	"	DITTO	DITTO
8	70	3200	3300	0	15	ROUGH AND CRACKS	PARTLY FUSED REST GLASSY	CRACKS IN GLASS FILM

TABLE V

OXIDATION TEST RESULTS - FAILURES CAUSED BY DISILICIDE PEST

TEST	WSi ₂ COAT THICKNESS, μ	TEST TEMP. °F		LIFE TIME		SAMPLE SURFACE		TYPE OF FAILURE	REMARKS
		AS MEAS.	CORR.	HR	MIN	BEFORE TEST	AFTER TEST		
1	24	3200	3300	5	10	ROUGH	GLASSY	DISILICIDE PEST	CRACKS AND PEELING IN THE GLASSFILM
2	50	3200	3300	7	50	ROUGH	GLASSY	DISILICIDE PEST, 2350°F	BLISTERS IN THE GLASSFILM, NO CRACKS
3	90	3250	3350	10	0	ROUGH AND CRACKS	GLASSY	WIRE STILL INTACT	CRACKS IN THE GLASSFILM, FUSED INTERMETALLIC LAYER, BEGINNING DISILICIDE PEST

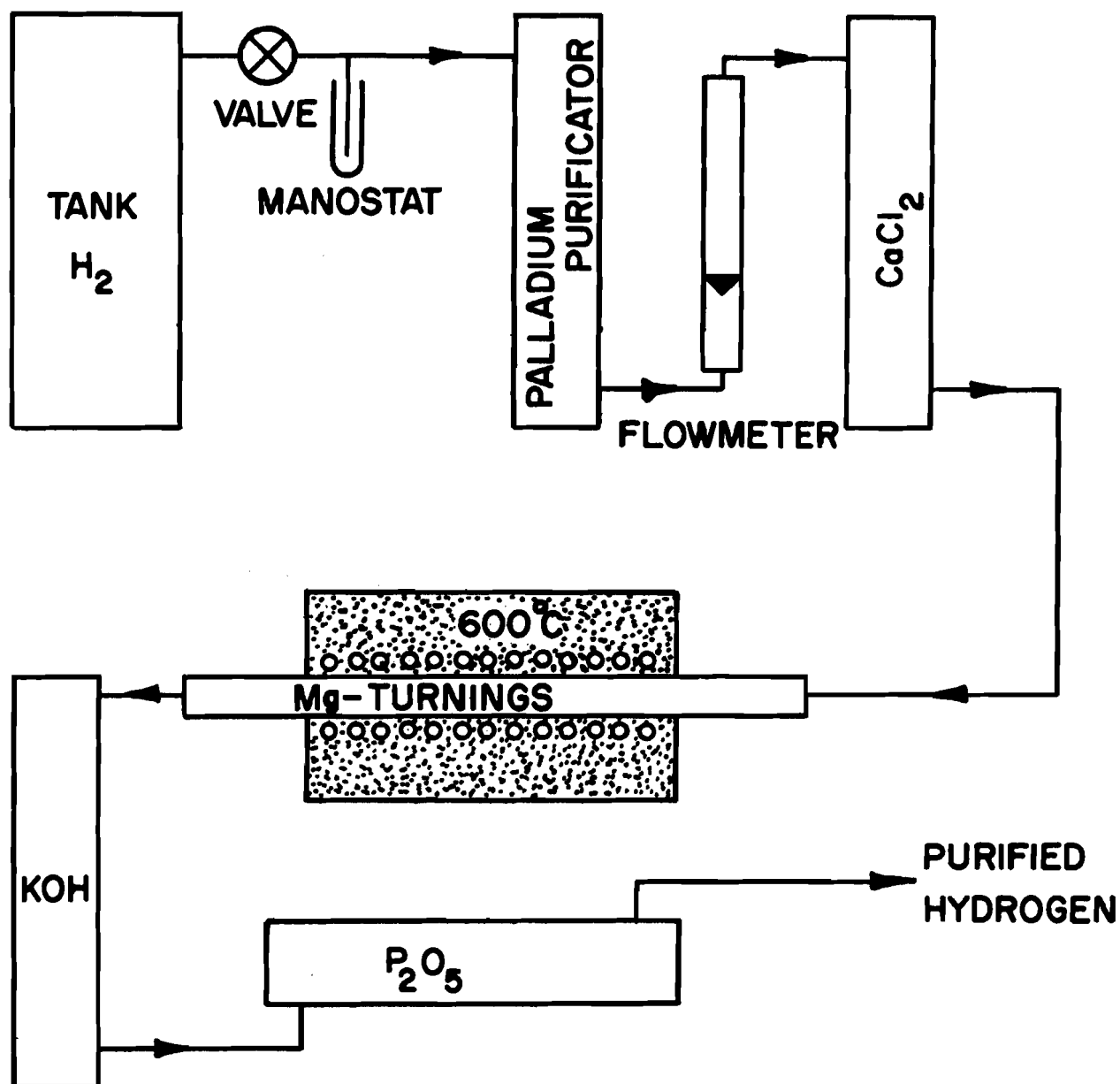


FIG. 1 FLOW DIAGRAM OF HYDROGEN PURIFICATION

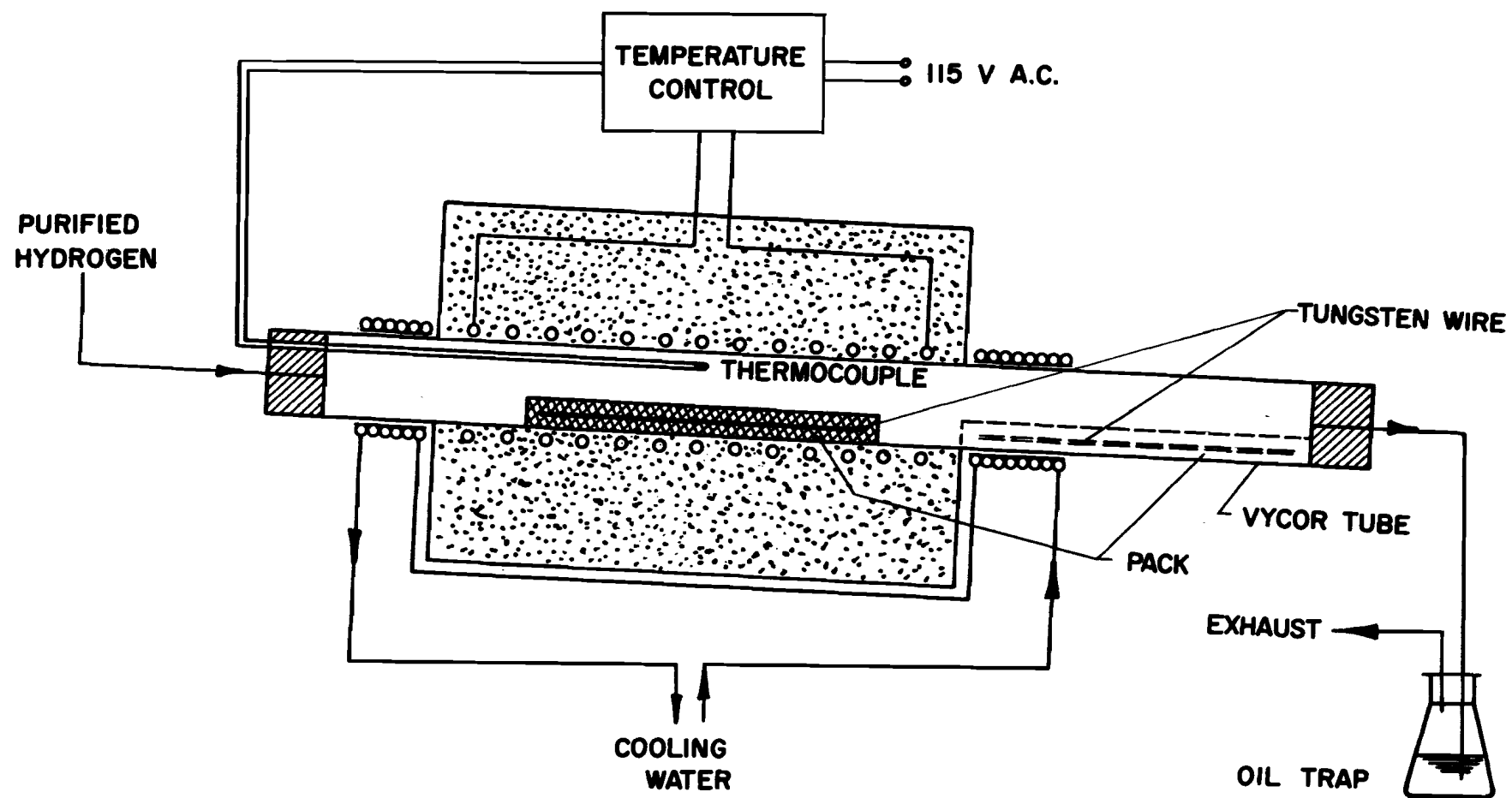


FIG. 2 SCHEMATIC LAYOUT OF PACKSILICONIZING ARRANGEMENT

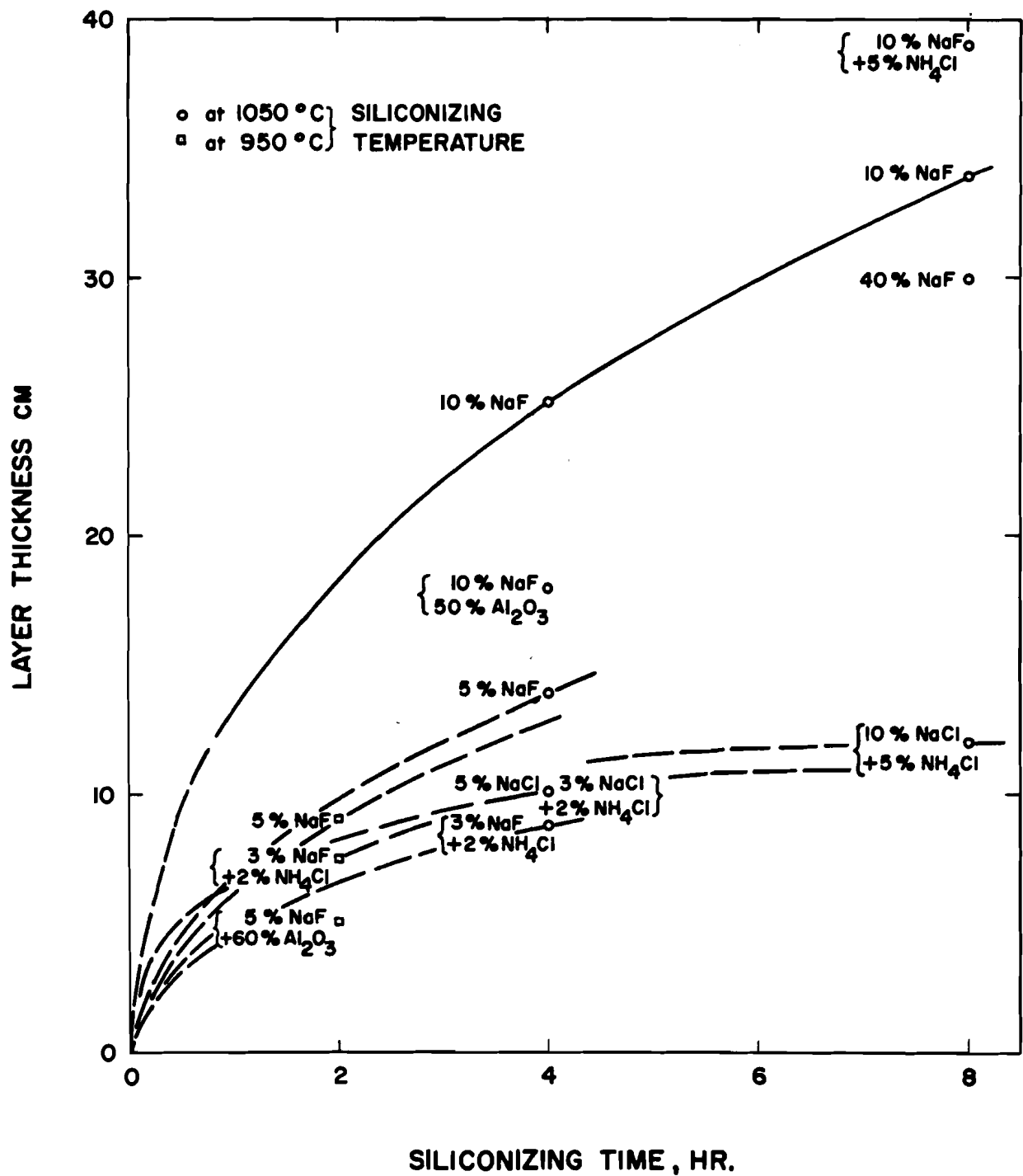


FIG. 3 LAYER THICKNESS VS SILICONIZING TIME
(PACKSILICONIZING)

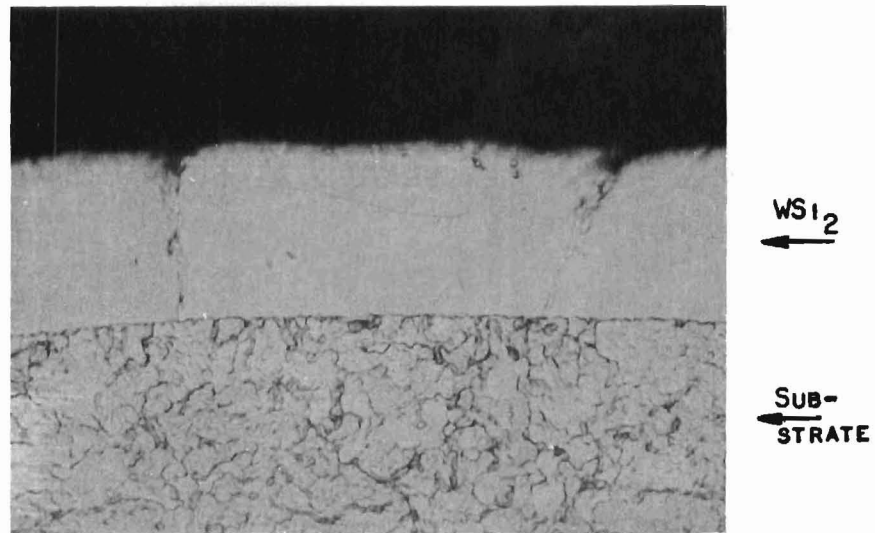


FIG. 4 RADIAL CRACKS IN A WSi_2 COATING
200X, ETCH. $K_3Fe(CN)_6 + NaOH$

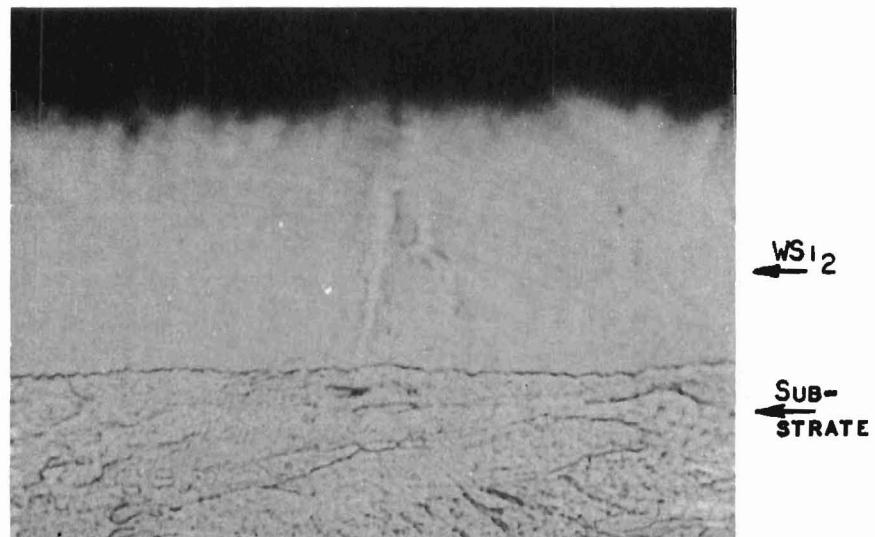


FIG. 5 LONGITUDINAL CRACKS IN A WSi_2 COATING
200X, ETCH. $K_3Fe(CN)_6 + NaOH^2$

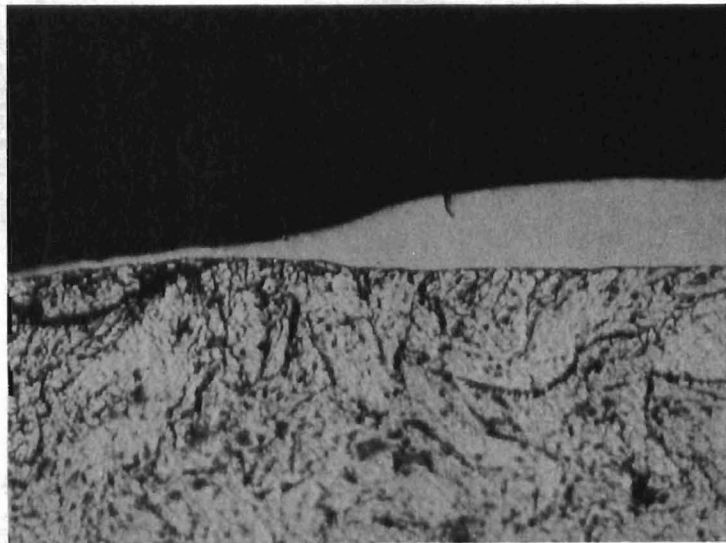


FIG. 6 WSi_2 LAYER. DISCONTINUITY CAUSED BY MELTING
OF THE ENERGIZER, 200X, ETCH. $K_3Fe(CN)_6 + NaOH$

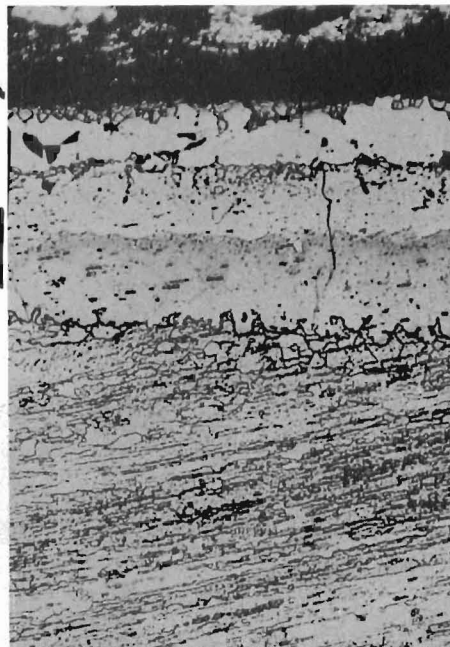
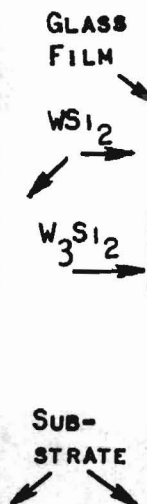


FIG. 7 WSi_2 COATING BEFORE TESTING

FIG. 8 FORMATION OF A W_3Si_2 INTERMEDIATE LAYER (AFTER 1-1/2 HR TESTING)

COMMON ILLUMINATION, 200X

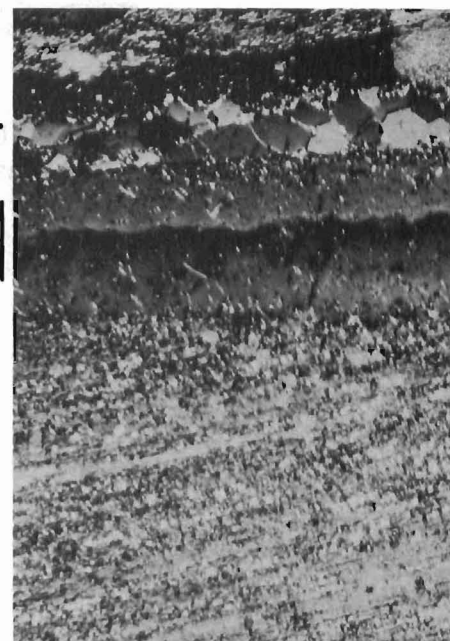
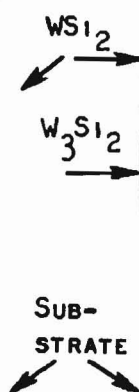
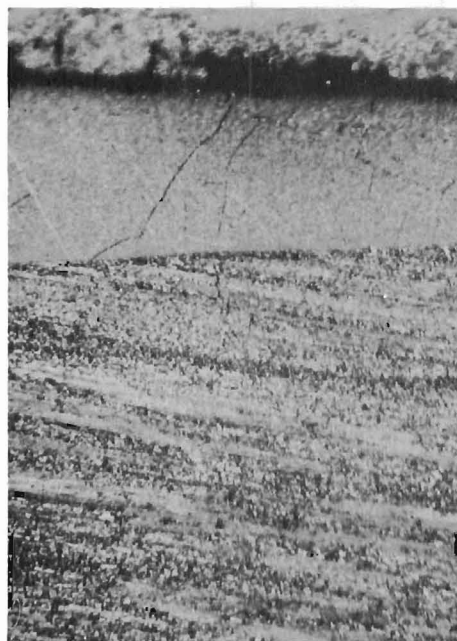


FIG. 9 GRAIN SIZE OF THE WSi_2 LAYER SHOWN IN FIG. 7

FIG. 10 GRAIN SIZE OF THE WSi_2 LAYER AFTER OXIDATION TEST (1-1/2 HR AT 3100°F)

POLARIZED ILLUMINATION, 200X

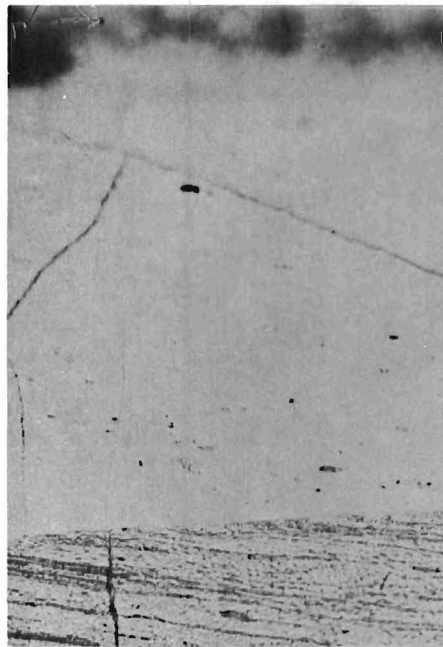


FIG. 11 WSi_2 COATING BEFORE TESTING

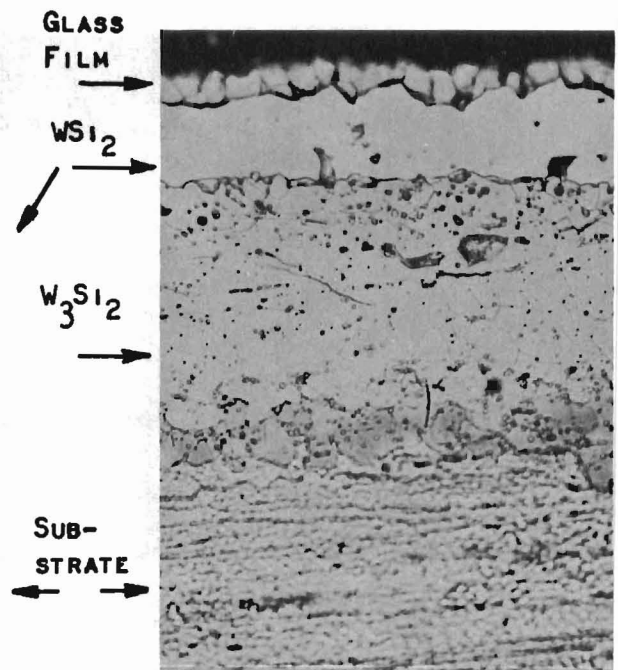


FIG. 12 FORMATION OF W_3Si_2 INTERMEDIATE LAYER AND GLASSY SURFACE (AFTER T.)

COMMON ILLUMINATION, 500X



FIG. 13 GRAIN SIZE OF THE WSi_2 LAYER SHOWN IN FIG. 11

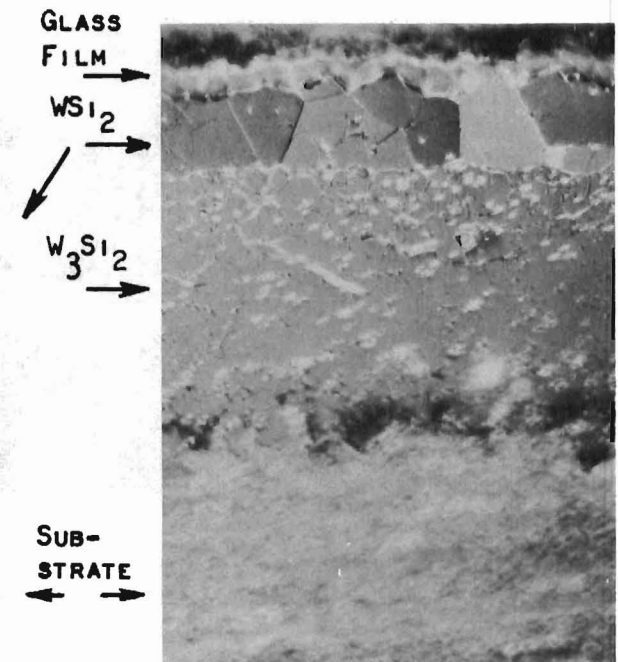


FIG. 14 GRAIN SIZE OF THE WSi_2 LAYER AFTER TESTING

POLARIZED ILLUMINATION, 500X

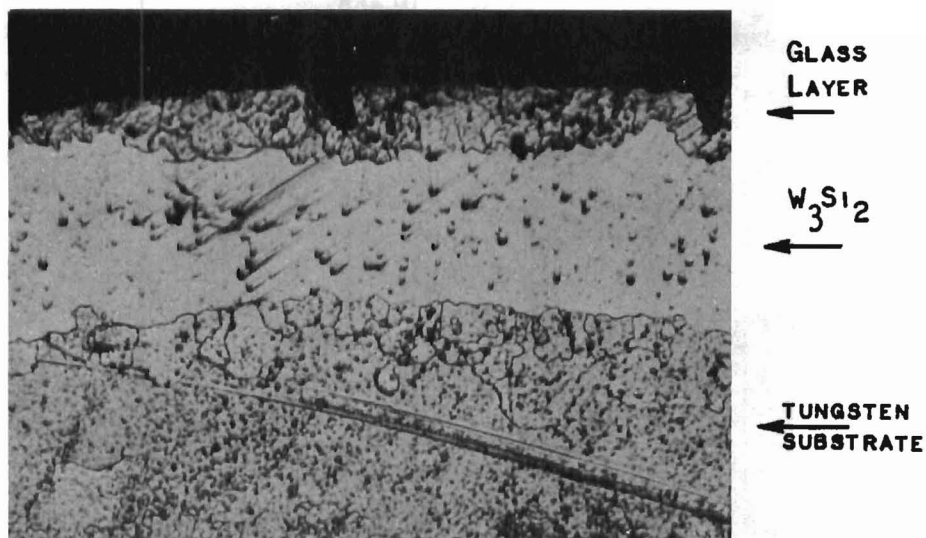


FIG. 15 CONVERTED DISILICIDE LAYER AFTER
10 HR. OXIDATION TEST, 500X

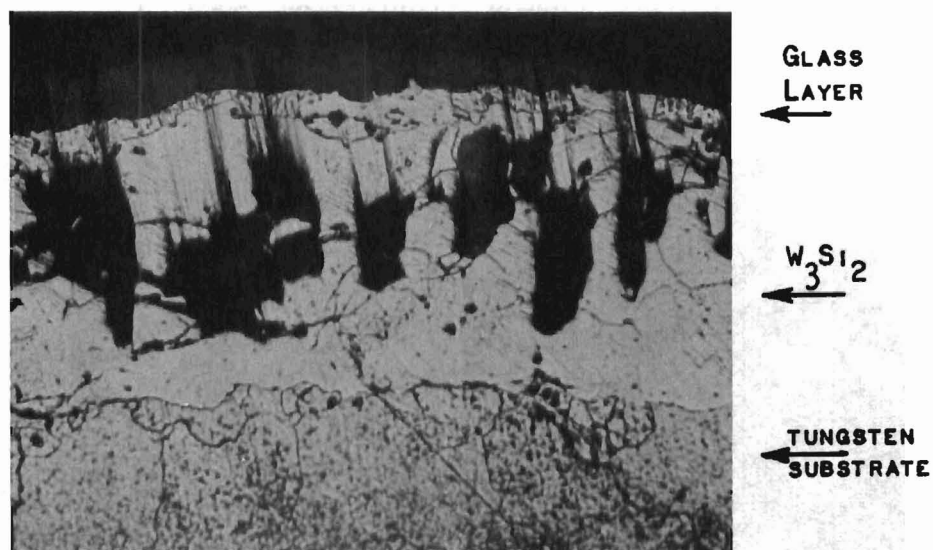


FIG. 16 LAYER MOLTEN BENEATH THE GLASS LAYER AFTER
3 HR. TEST TIME AND OXIDATION TEST CONTINUED
TO 10 HR. TEST TIME, 500X

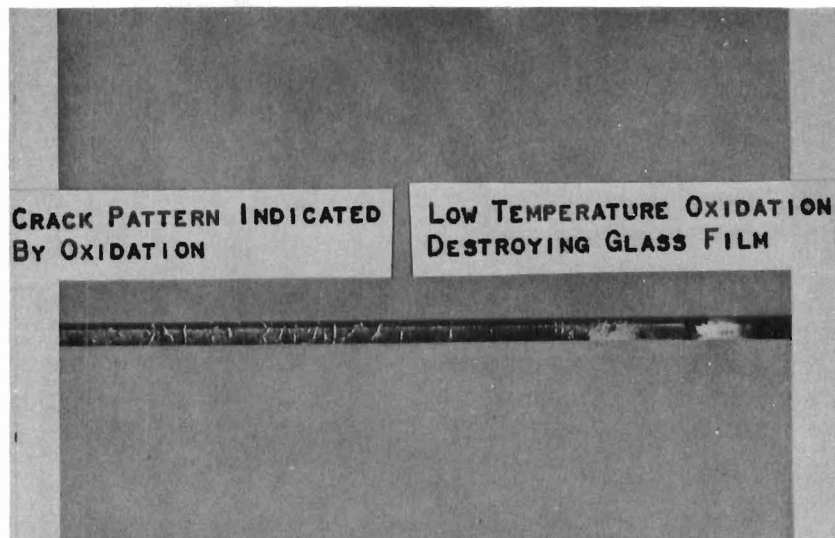


FIG. 17 THERMAL CYCLING OF THICK WSi_2 COATED WIRE
(AFTER 17 MINUTE HEATING IN THE SECOND CYCLE)

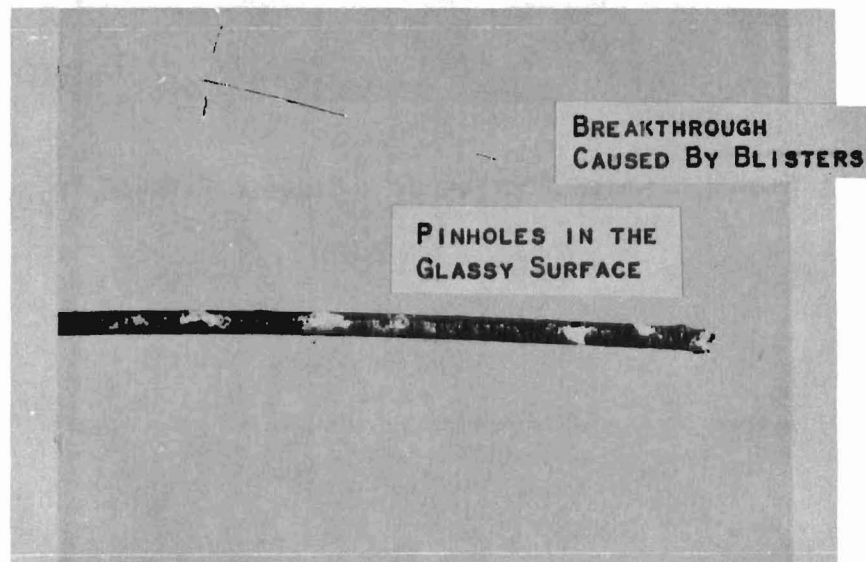


FIG. 18 THERMAL CYCLING OF THICK WSi_2 COATED WIRE
(AFTER 1 HR. 37 MINUTES IN THE SECOND CYCLE)

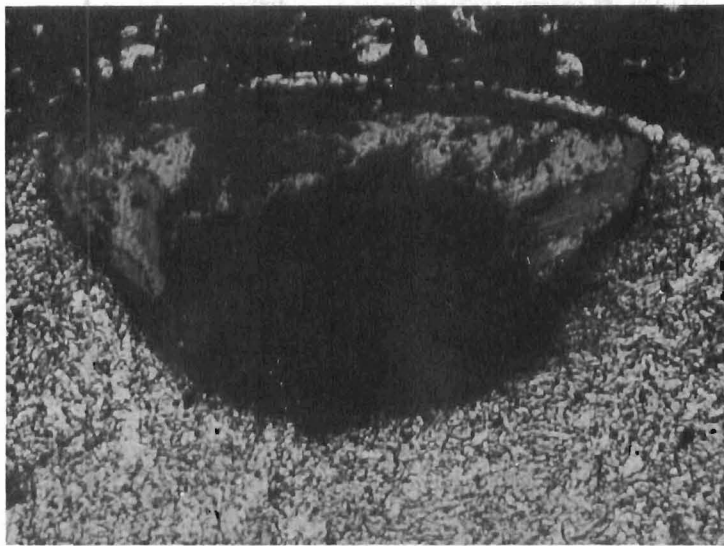


FIG. 19 CROSS SECTION OF A PINHOLE FAILURE, 150X

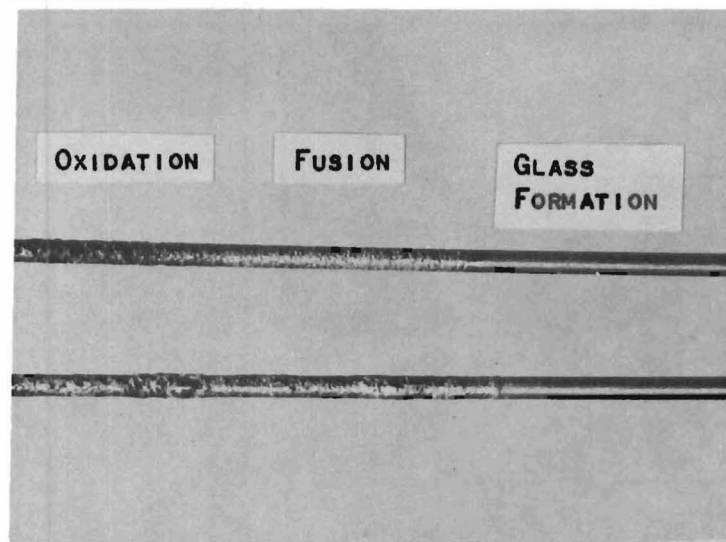


FIG. 20 SURFACE OF SAMPLES THAT FAILED BY LIQUID PHASE FORMATION

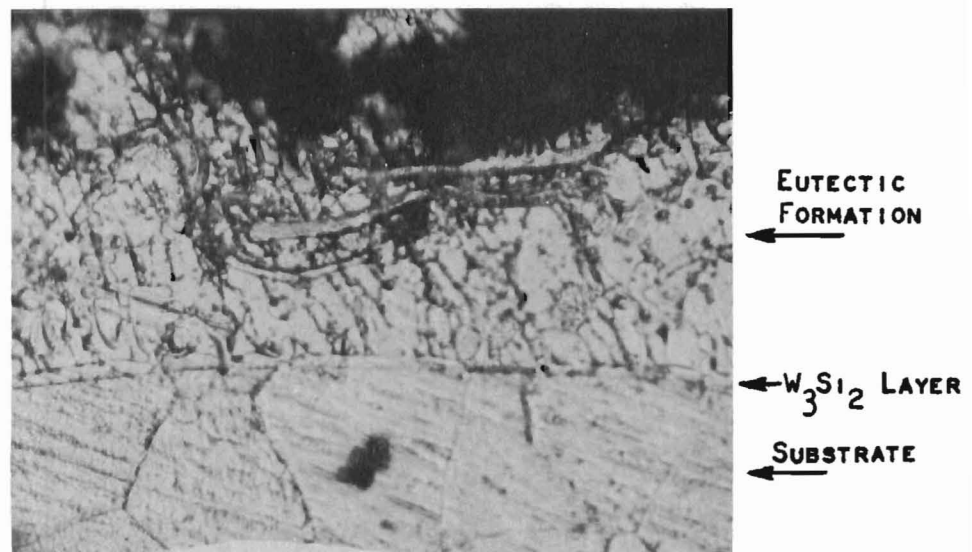


FIG. 21 PHOTOMICROGRAPH OF THE LIQUID PHASE FAILURE,
200X, ETCH. $K_3Fe(CN)_6 + NaOH$

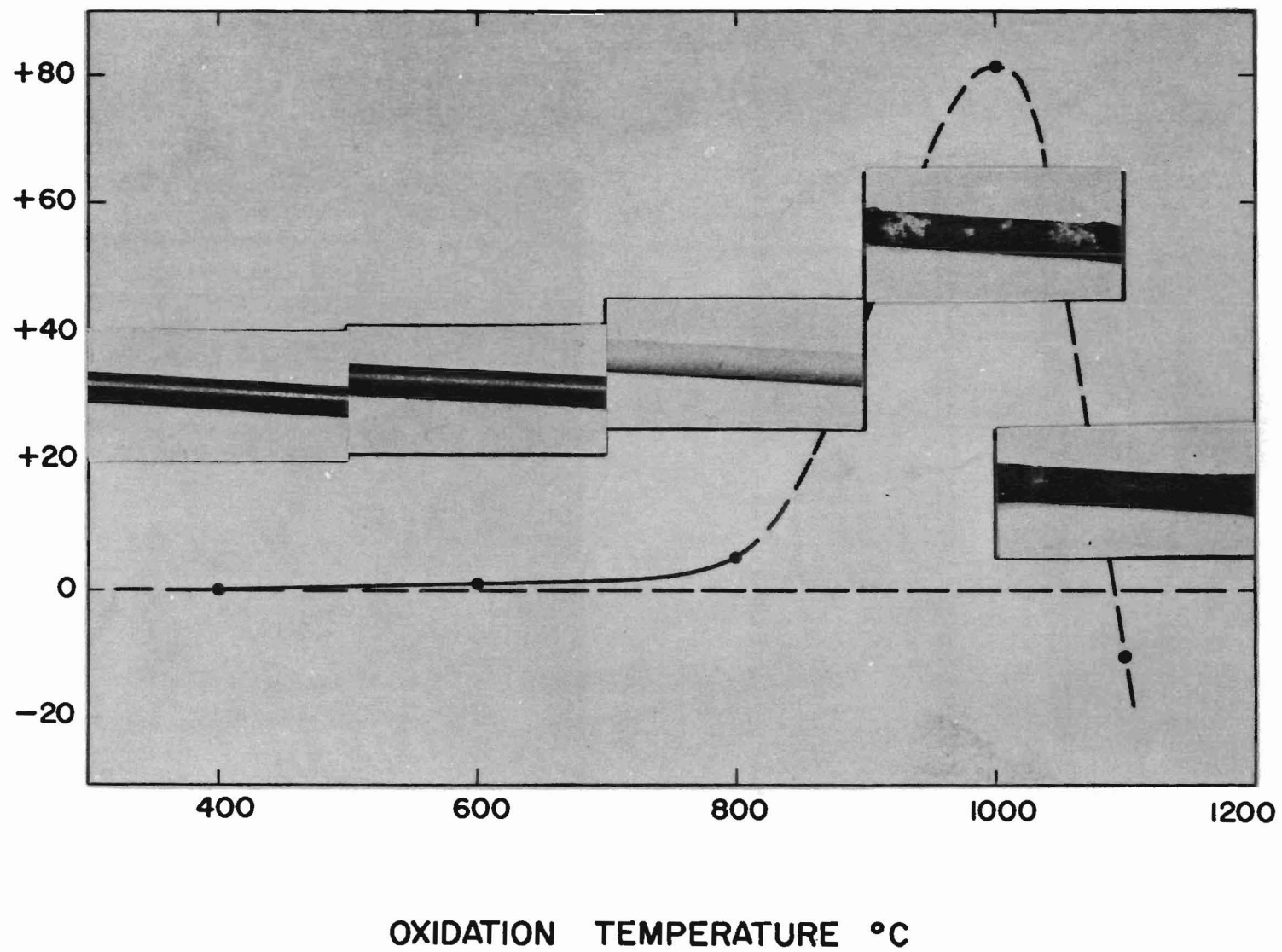
WEIGHT GAIN $10^{-1}\%$ 

FIG. 22 LOW TEMPERATURE OXIDATION OF A
 35μ -DISILICIDE COATING