HIGH TEMPERATURE THERMOCOUPLE

RESEARCH AND DEVELOPMENT PROGRAM

APPENDIX 4

NEW TECHNOLOGY

To

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REPORT OF NEW TECHNOLOGY

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REPORT OF NEW TECHNOLOGY

1.0 GENERAL

The items described below are classified, to the best knowledge of ACL as new Technology, as defined by N.A.S.A.'s interpretation of the "New Technology" reporting clause in the contract. All items were described in monthly progress reports.

2.0 REPORTABLE ITEMS

2.1 Method of Nickel Brazing Tungsten to Tungsten, & to Tungsten Rhenium Alloys

2.1.1 **Problem:** Brazing drawn Tungsten wire to thin-wall thermochemically formed Tungsten tubing, or to other Tungsten wire, or Tungsten-Rhenium alloys to Tungsten. Previous attempts to perform the brazement had resulted in serious oxidation of the Tungsten or the alloy, with accompanying deterioration. Various brazing materials had been tried without success.

2.1.2 **The Solution:** Thin Tungsten wire (.020" dia. or less) can be cold-formed, but will not withstand re-bending. In joining Tungsten wire to a Tungsten tube approximately .260 inch dia., the Tungsten wire is first coiled to the outside diameter of the tube. In ACL's application, two to six turns were used. Care must be taken to avoid reverse bending the wire. A mandrel should be used to lay the coil. The coil is then slipped over the tube to the desired location. A second coil of

2.1.2 The Solution: (Cont'd.)

Nickel wire of the same diameter as the Tungsten wire is made, and is threaded on the tube between the coils of Tungsten. The assembly is then placed in an oven purged with clean Argon gas, and the oven is brought up to temperature while the part is being observed. As the Nickel is seen to flow, the oven is held at that temperature for approximately thirty seconds, then power is cut off and the part permitted to cool. No flux is used, since wetting is accomplished without it.

2.1.3 Notes: This process was used in approximately thirty instances without failure. If the refractory metal parts are massive enough to permit surface oxidation, the same result can be obtained by torch brazing. However, extreme care is required, and an experienced technician, to avoid excessive oxidation. Since Tungsten is subject to recrystallization, each joint must be carefully examined with a microscope to assure that the wire is intact.

2.2 <u>Technique for surface grinding thermochemically formed, thin-wall Tungsten tubing.</u>

2.2.1 Problem: Thermochemically formed Tungsten tubing, in the as-received condition, has a surface consisting of sharply defined peaks and valleys, as seen in a microscopic examination of radial cross sections. Collapse strength was lower than desired, and the failure mode was typical in that, once started, cracks were

2.2.1 Problem: (Cont'd.)

self-propagating. Ordinary grinding resulted in nuclei for grain growth.

2.2.2 The Solution: With the part carefully mounted, even cuts were taken over the surface with a fine grit wheel or belt sander. The grinding was performed slowly to avoid heating the part. The surface was examined with a microscope periodically during the process. No cut was made more than .005 below the deepest "valley" in the surface.

2.2.3 Notes: Compression tests showed that the collapsing strength of the tube was approximately doubled. The mode of failure changed from the typical self-propagating crack, with large pieces remaining when the tube collapsed, to a sudden tube failure with a multitude of very small pieces resulting. Ductility was not improved at ambient temperatures. Parts thus treated did, however, resist nucleization and exhibited a brittle to ductile transition temperature of approximately 370°C.

2.3 "Technique for Fabricating Mandrels for Forming Deposited Tungsten Parts

2.3.1 The Problem: The formation of deposited parts over a mandrel or positive die is almost as old as the art of casting. The separation, or removal, of the mandrel over which thermochemically deposited Tungsten is formed, however poses problems not immediately seen by the engineer. Foremost among these is

2.3.1 The Problem: (Cont'd.)

the absolute removal of steel from the interior of the finished part. This is required because Tungsten is soluble in molten steel and if any steel remains in the part when it is heated above the melting temperature of the steel, a catastrophic failure can result.

2.3.2 The Solution: Mild steel mandrels were formed to the interior shape of the part to be formed. Every effort is made to use a one-piec mandrel. After machining, the mandrel is polished to a # 6 or better finish, and is 100% examined with at least 40X binocular microscope. No depressions or irregularity can be tolerated. In symmetrical parts, the dimensions should be such that a small but finitely larger diameter is at the back end of the part. The effect of coefficients of thermal expansion, at room temperature and at forming temperature, must be taken int account. In most cases, the mandrel can then be withdrawn after formation. If the mandrel should stick in the part, it must not be forced. The steel can be etched out with hot, concentrated Hydrochloric acid, which readily attacks the stee but does not attack either the Tungsten or the Tungsten-Rhenium alloys.

2.3.3 Notes: In formation of unsymmetrical, or irregularly shaped parts, the mandrel must be etched away, to leave the formed part. After etching, it is necessary to flush the part as often as

2.3.3 Notes: (Cont'd.)

necessary, and perform a simple qualitative analysis to assure that no steel remains.

2.4 Method of Mounting a Tungsten Part in a Stainless Steel Body

2.4.1 The Problem: A method was sought whereby a thin-wall Tungsten thermocouple stem could be gripped securely in a stainless steel body without 1.) exerting excessive compressive stresses on the Tungsten tube 2.) overheating the Tungsten by brazing 3.) endangering the Tungsten by proximity to molten steel during a welding process.

2.4.2 The Solution: A Tungsten slug, machined to the double truncated conical shape shown in ACL Drawing No. 4735-21, was assembled to the forming mandrel as pictured. During the thermochemical formation process, the slug is made an integral part of the sheath assembly. The stainless steel body was machined internally to receive the front conical surface of the Tungsten slug. The threaded nut was machined with its internal configuration such that it matched the aft conical surface of the slug. When the nut is tightened, the load is taken by the slug, rather than the thin wall of the sheath. At the same time, the sheath was centered in the body, with excellent alignment.

2.4.3 Notes: In the as-received condition, minor irregularities were seen in the conical surfaces. Light surface grinding served to remove

2.4.3 Notes: (Cont'd.)

the irregularities, thus providing smooth mating surfaces. Light surface grinding was also required in some instances on the outside diameter of the plug section, to permit clearance of the major diameter of the internal body threads. A special spanner was made to tighten the internal nut.

This method was used in some fifteen assemblies and functioned without failure. Other schemes incorporating various compression type fittings, working directly on the tubular sheath, failed in more than 70 percent of the installations.

2.5 Techniques for Eliminating Electrical Insulation in the Hot Zone of a Coaxial Thermocouple

2.5.1 The Problem: No suitable high temperature electrical insulators were available for use above about 4200°F. The thermocouple tip was required to function above 5000°F. A means was required to permit use of the thermocouple at these elevated temperatures.

2.5.2 The Solution: Tests performed from 300°F to above 4000°F revealed that current leakage between conductor was not significant, in this requirement if the physical angularity between conductors was about 8°, at about 37 millivolts. The atmosphere was varied between air and Argon with no discernible effect. The ACL Type 4735 probes were so fabricated in a coaxial configuration. The center conductor was Tungsten 26% Rhenium, the sheath was

2.5.2 The Solution: (Cont'd.)

thermochemically formed Tungsten. Magnesia and Beryllia were both used to locate the center conductor with respect to the sheath. Their use was restricted to a zone where the temperature would not exceed 4000°F. The no-insulation length was approximately 1.6 inches, measured from the inside of the thermocouple tip.

The maximum physical spacing within the sheath was .065 inch between the outside of the .020 center conductor and the inside of the sheath.

Probes so constructed were calibrated to within 1% of the ideal curve for Tungsten vs Tungsten 26% Rhenium at temperatures from 4000°F to 5000°F.

2.6 <u>Method of Calibrating High Temperature Thermocouples in an Arc-heated, Black Body Furnace</u>

2.6.1 The Problem: It was required to calibrate high temperature thermocouples in an inert atmosphere at temperatures between ambient and 6000°F. Existing furnaces of this temperature capability did not provide either the degree of control, or accessibility necessary. Neither time nor money permitted obtaining a specialized calibration oven from an outside source.

2.6.2 The Solution: An existing ACL pot-oven, used in a previous project, was modified for the required use. The oven, before modification,

2.6.2 The Solution: (Cont'd.)

is described as follows: The body of the oven was machined from graphite, and all surfaces were coated with plasma-sprayed Zirconium Oxide. A stepped lid, also of graphite and coated with Zirconium Oxide, provided a top closure. The pot incorporated a side port for an optically flat quartz window for optical pyrometer observations, a side port 180° away for an arc feed, bottom electrical connections to the power supply, argon supply ports to both the optical port and the pot, and water cooling coils on the bus connection. The whole assembly was mounted on a tripod base.

In original use a graphite crucible was located in the center of the pot, a heliarc torch was introduced through its side port, and an arc was established against the wall of the graphite crucible. Temperatures between 5000°F and 6000°F were easily attained.

In the modification, the graphite crucible was replaced with a thermochemically formed Tungsten cavity tube, closed at one end. Two holes were eloxed in the tube; one at the bottom, .125 dia. for argon feed, the other a viewing port in the side wall of .062 dia., located such that when mounted in the oven, the hole center was in line with the center of the quartz window. As in the original, the heliarc was fired against the outside wall of the Tungsten cavity. The cavity receptor was dimensioned such

2.6.2 The Solution: (Cont'd.)

that the heliarc fired directly opposite the side viewing port. In use, the thermocouple junction was positioned within the aperture of the hole.

2.6.3 Notes: In operation, the oven was purged with Argon prior to use. The thermocouple, mounted on a laboratory stand, was introduced into the cavity and fixed in position such that the junction area was centered in the viewing port aperture. A Pyrometer Company, Model 95C, Micro-optical Pyrometer was set up with a short focal length lens and was focused on the thermocouple tip. Auxiliary lighting was required for accurate focusing. Appropriate shields were set up as protection against ultraviolet from the arc. The arc was then drawn, and power adjusted for the desired rate of temperature rise. The 65µ filter in the optical pyrometer was inserted, and the thermocouple was observed for brightness match.

When the desired temperature was reached, as indicat l by the brightness match, a scan was taken to assure that there were no excessive gradients between the thermocouple and the wall of the cavity.

The power was initially controlled with the heliarc foot pedal. A large power rheostat was later added to permit fine control at the higher power settings. Operation was straightforward,

2.6.3 Notes: (Cont'd.)

except at temperatures above 4000°F, where care was necessary to prevent excessive heat. Small incremental changes in power setting thus precluded melting the Tungsten cavity.

Other uses foreseen for this apparatus: One such use is in preparing small samples of high melting point materials. Suitable liners, or thimbles, could be inserted in the Tungsten cavity for samples that are not compatible with Tungsten.

2.7 <u>Protection of Tungsten with Deposited Silicon</u>

2.7.1 The Problem: Tungsten has a great affinity for oxygen, and forms a series of oxides from about 600°F up. Since the sheaths of the thermocouples developed in this project are made of Tungsten, it was necessary to extend their life by utilizing a protective coating. Most coatings were unsatisfactory because of 1) their reaction with Tungsten, 2) the formation of eutectics, or 3) thermocouple junction poisoning due to diffusion through the Tungsten.

2.7.2 The Solution: A total solution of this problem was not found. It was possible, however, to extend the life of the Tungsten by coating the sheaths with elemental Silicon. The protection afforded by this means extended the useful life of a Tungsten vs Tungsten 26% Rhenium thermocouple by about ten times in a highly oxidizing atmosphere, as compared with an uncoated sheath. The

2.7.2 The Solution: (Cont'd.)

thickness of the coating was from .003 inch to .005 inch, and was applied by a deposition process developed by San Fernando Laboratories, Pacoima, California.

2.7.3 Notes: Although the coating performed better than any other tried in this project, certain precautions were required. When the thermocouples were run in an Argon, or any inert atmosphere, the Silicon could not combine with Oxygen, since there was none present, to form the two oxides: Silicon Oxide (SiO) and Silicon Dioxide (SiO_2), and would not react with Argon, which is inert.

In one test, run in Argon at about 4000°F, the Silicon melted and flowed down to the tip of the sheath. Like a drop of water, the molten Silicon remained to form a bulbous mass on cooling. This was observed only in the furnace zone of intense heating. Above this zone the Silicon coating was undisturbed.

Without having Oxygen with which to combine, the Silicon reacted with the Tungsten to form Silicides. This was as planned, to take advantage of the oxidation resistance of the Silicide to extend the life of the sheath. However, without Oxygen present to use up excess Silicon, the Silicide continued to form until chemical equilibrium was reached. Thus, the junction between the Tungsten and the Tungsten-Rhenium alloy was "poisoned"

2.7.3 Notes: (Cont'd.)

by the presence of either diffused Silicon, the Silicide, or both. As the junction was "poisoned" a new thermoelectric system was in effect and an output curve, different from that predicted, was seen. This effect is irreversible, and can not be predicted exactly.

If Tungsten thermocouples are to be siliconized, therefore, they must not be run in an inert atmosphere unless they are pre-oxidized to take care of excess Silicon. The Silicon Dioxide forms quite early in the temperature rise, in the presence of oxygen. It melts at 3100°F and, being volatile, is easily driven off. The Silicon Oxide does not melt until 4406°F, and tends to form a tenacious, glassy film.

2.8 Development of an EMF vs Temperature Curve for Tungsten vs Tungsten 26% Rhenium from -320°F to +5400°F

2.8.1 The Problem: Various curves for the Tungsten-Rhenium thermoelectric system are available from Battelle Memorial Institute, Hoskins Mfg. Co., and Englehard Industries. These published curves commonly cover the range 0°F to 4200°F. Since this project required investigation to 5400°F, an extension of the curve was needed. Curves were obtained from Hoskins to about 5000°F and from Englehard to just over 5000°F. The curve above 5000°F was not found, nor was there a curve at temp-

2.8.1 The Problem: (Cont'd.)

eratures below 0°F. ACL felt the low end should be determined because of the possibility of cooling the body of the probe with LN_2 and the possible effect on transitions.

2.8.2 The Solution: ACL took many observations of temperature vs EMF for their series 4700 Thermocouples over the range from 0 - 4200°F, to establish agreement with the published curves. Good agreement was seen. Further calibrations established agreement in the 4000°F to 5000°F range with both the Englehard curve, and a curve obtained from Hoskins by special request. Near the end of the project, several points over 5000°F were established. The highest temperature reached was 5400°F. It is felt that the region from 5000°F to 5400°F should be more thoroughly investigated, although all points taken by ACL agreed with extrapolations of the Hoskins and Englehard data.

At the low end, -320°F to 0°F, ACL established a tentative curve, which was later verified by Hoskins, at ACL's request. The whole curve, from -320°F to 5400°F is included in the ACL Summary Report.