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WRITTEN BY: P. Bliss

APPROVED BY: P. Bliss

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1. Introduction

Material and component development work at Pratt & Whitney Aircraft, CANEL, has demanded increasingly better thermocouples - thermocouples with better accuracy at higher temperatures for longer times. Inpile operation has focused attention on transmutation of elements sufficient to cause decalibration during the required test periods. The problem of contamination of refractory sheath materials exposed to liquid alkali metals was an unexpected blessing, because the by-product of adequate contamination control was the out-of-pile thermoelectric stability we needed. I am confident that fabrication and quality control techniques presently known to us will permit the indefinite use of Chromel/Alumel at temperatures approaching its melting point (2500F). Fig. 1 shows the proven capability of CANEL fabricated thermocouples to date.

2. Fabrication

In order to achieve the dependability indicated, the most rigorous quality control is necessary on all raw materials and throughout the process. While design details differ, the fabrication and material control are no less stringent for Chromel/Alumel than for refractory metal thermocouples. The quality of alumina required for insulation has been a challenge to all suppliers, yet deviation from our specifications has caused significant deterioration in performance. (Copies of our ceramic, sheath and wire specifications appear in the appendix; also copies of typical thermocouple specifications.)

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PROVEN THERMOCOUPLE CAPABILITY AT P & WA CANEL

TYPE	SHEATH	ENVIRONMENT	°F	HOURS ^③	REMARKS
C/A	St. St.	INERT GAS	2000	10000	COMPLETE
C/A	Cb-1Zr	INERT GAS	2000	10000	COMPLETE
C/A	Cb-1Zr	INERT GAS	2200	2500	CONTINUING ①
W-5Re/W-26Re	Cb-1Zr	INERT GAS	2000	10000	COMPLETE
W-5Re/W-26Re	Cb-1Zr	INERT GAS	2300	5325	CONTINUING
W-5Re/W-26Re	Cb-1Zr	INERT GAS	2800	1000	CONTINUING
W-3Re/W-25Re	Cb-1Zr	INERT GAS	2000	10000	COMPLETE
Mo/Cb	Cb-1Zr	INERT GAS	2000	8420	CONTINUING
W-5Re/W-26Re	Cb-1Zr	LITHIUM	2200	2800	CONTINUING
W-5Re/W-26Re	Cb-1Zr	NaK	2000	2300	CONTINUING ②
C/A	Cb-1Zr	NaK	2200		CONTINUING ②
Mo/W-26Re	Cb-1Zr	INERT GAS	2000	10000	COMPLETE

1 THESE THERMOCOUPLES PREVIOUSLY ACCUMULATED 10000 HRS @ 2000F

2 ADDITIONAL EXPERIENCE OBTAINED TO 6000 HRS FROM INPILE TESTS

3 AS OF FEB. 1, 1965

Fig. 2 shows a typical CANEL fabricated liquid metal thermocouple. This happens to be a non-grounded Chromel/Alumel thermocouple designed to measure temperatures up to 2200F for 10,000 hours inpile. The plug used at the measuring junction has been found necessary in all thermocouples for extended high temperature use in liquid metal. Without it acceptable oxygen levels in the weld metal (compatible with liquid metal) cannot be maintained. Tantalum is used for the plug and for a sheath liner in the Chromel/Alumel thermocouple to prevent the formation of a columbium-nickel eutectic, with resulting sheath leakage.

The reference end of the thermocouple must be hermetically sealed, as shown, or the surrounding atmosphere will diffuse down the sheath and result in sheath failure and thermoelement decalibration. The "bamboo split" type of sheath failure is shown dramatically in Fig. 3. This type of failure was unfortunately typical before hermetic seals were used. The unit shown had operated for 3500 hours at 1950F before disassembly. Less dramatic failures still resulted in thermoelement decalibration.

Our current fabrication procedure is shown as a material flow diagram in Fig. 4. After thorough inspection of materials, the thermoelement is welded. The element is then formed and strung with insulating beads, previously air-baked at 1500F for four hours. This assembly operation is performed in a "clean-room" by operators wearing nylon gloves. The assembly is then loaded into the previously cleaned sheath from the reference end, and the ends of the sheath are crimped lightly to retain the parts. A production lot of assemblies is loaded into a retort, vacuum baked at 400F for four to six hours and purged with purified argon until the effluent gas from the retort contains less than 2.5 and 10 ppm of oxygen and water, respectively. At this point the retort is sealed off and connected to a welding dry box so that the assemblies can be brought into the box without exposure to atmosphere. After seal welding both ends, the assemblies can be removed for swaging, which is done with moly disulphide lubricant and from the junction end. The plug in the measuring junction end is located by X-ray; the assembly is leak checked and cleaned, and is returned to the clean room where the measuring junction end is trimmed and the reference end of the assembly is cut to length. After electrical inspection, the entire assembly is heat treated for two hours at 2200F in clean argon. The assembly is returned to the clean room where the hermetic seal is partially installed by dip brazing the wires into the tubes; and the assembly returned to the weld chamber through the retort where the 400F bake and backfill is repeated to remove atmosphere which may have entered the unsealed end. Maintaining the weld chamber at 2.5 and 10 ppm as before, the measuring junction final weld and the reference end seal braze are made. After checking wire and insulation resistance (10^{12} ohms at 100 VDC and room temperature), the finished thermocouples are removed from the chamber. The measuring junction is locally annealed at 2200F to insure liquid metal integrity, and the thermocouple output is noted at this temperature. Helium at 1000 psig is applied to the outside of the thermocouples for 5-10 minutes in a retort. The

Cb - 1Zr SHEATHED C / A THERMOCOUPLE CONSTRUCTION

FIG 2

FAILURE OF UNSEALED Cb - 1Zr SHEATHED THERMOCOUPLES AFTER 3567 HOURS AT 1950 F IN ARGON

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FIG 3

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THERMOCOUPLE FABRICATION FLOW DIAGRAM

FIG 4

thermocouples are removed, wiped to remove surface helium, and placed in another retort which is evacuated and checked with a mass spectrometer. The thermocouples are X-rayed for wire and plug position, junction weld quality and quality of the hermetic seal installation. The measuring end weld is removed from one piece in the lot for oxygen analysis.

All refractory metal clad thermocouples made at CANEL are made by the same basic process, with variations with wire materials, size, etc. The metal plug is used in liquid metal immersion types only.

Direct assessment of the quality parameters has been used wherever practical; however, some indirect techniques are used. The purge gas is analyzed for oxygen and moisture content because we have no direct method for measuring these contaminants within the alumina. Insulation resistance is used as a vital control on insulation purity because we find that this technique will detect contamination levels lower than other methods, and because it can be measured in the finished product. Also we have observed correlation between low insulation resistance and subsequent decalibration in use. Wire resistance measurements insure continuity and give indication of some types of shorted elements. Zone heating has been used to evaluate homogeneity. Pulse ranging techniques are showing some success in detecting irregularities.

3. Materials Compatibility

Generally, this portion of CANEL's experience is beyond the scope of this paper. Since the great bulk of our thermocouple data concerns Chromel, Alumel, molybdenum, columbium, and the alloys of tungsten and rhenium, I will merely say that alumina, if pure, is compatible with these materials at temperatures at least to 2200F for 10,000 hour periods. This statement probably becomes untrue when certain contaminations exceed a few parts per million. Air and moisture, if not restricted to these very low levels, will result in decalibration and sheath rupture. The thermocouple sealing must be perfect if these contamination levels are to be maintained in operation.

4. Service Experience

Our first indication of trouble with refractory metal sheathed thermocouples coincided with our first use of them - in impile capsules somewhat below 2000F in NaK. Concurrent out-of-pile tests in an argon atmosphere showed similar failure - complete sheath rupture as shown in an earlier slide. It became evident that air, diffusing down the thermocouple from the reference end, attacked the sheath where it was first contacted at an adequate temperature (about 1000F), and being "gettered" there, went no further. Decalibration also occurred when the thermoelements were oxidized. Partial success was achieved by the use of epoxy resin seals at the reference end, but these ma-

materials proved unreliable. With properly sealed assemblies, sheath failures were reduced; but calibration continued to shift due to residual contamination until rigid quality controls on insulation purity and fabrication methods were adopted. Even with our best techniques today, with 10,000 hour stabilities within one percent, the major shift occurs in the first 1000 hours, when residual contamination is being gettered.

Further dramatic illustration of the effectiveness of these fabrication controls on Chromel/Alumel thermocouples is given by an operation in the capsule fabrication procedure. The thermocouple sheaths are brazed through a columbium bulkhead with a 2500F braze. Although the thermoelement materials are left with an as-cast microstructure, no parasitic junction is created by this inhomogeneity; and the 10,000 hour reliability is not impaired.

With the masking effect of contamination removed, transmutation of the thermoelement became a problem. Inpile capsules were built with one Chromel/Alumel and three W-5 Re/ W-26 Re thermocouples so that the transmutation shift in the tungsten/rhenium could be evaluated and, hopefully, corrected for. The results showed a great deal of scatter, as shown in Fig. 5. The normalized difference in indicated temperature between a tungsten/rhenium thermocouple and the Chromel/Alumel thermocouple is plotted against cycle hours in the MTR. Since these were not primarily thermocouple tests, flux, spectrum, and gradients of flux and temperature are not comparable between tests; however, the decalibration of the tungsten/rhenium thermocouples is evident. Since, at this point, out-of-pile tests had indicated the reliability of Chromel/Alumel at these temperatures, the use of tungsten/rhenium thermocouples for inpile testing was discontinued.

Completed and current testing at CANEL is shown in Fig. 6. At this time we have completed formal 10,000 hour testing on 53 thermocouples at temperatures up to 2000F in controlled thermocouple tests, in addition to service application experience. We now have on test 150 thermocouples scheduled for 10,000 hour testing at temperatures up to 2600F.

5. Development Work

The major development goal at the present time is to find a radiation-resistant thermoelectric pair for temperatures at least up to 2600F, compatible with a columbium sheath, and suitable for vacuum, gas, and lithium environments. Our prime candidate at the moment is molybdenum/columbium, which shows promise up to at least 3000F. CANEL work has shown stability within one-half percent for 8500 hours at 2000F, in limited testing. No irradiation testing has been done to date, but the cross section references are encouraging. Wire selection

DECALIBRATION OF W-5Re/W-26Re THERMOCOUPLES IN SEVERAL TEST CAPSULES OPERATED IN THE MTR

P&WA CANEL THERMOCOUPLE DEVELOPMENT

Cb-1Zr SHEATHED THERMOCOUPLE TESTS

COMPLETED TESTS

TYPE	QUAN	ENVIRONMENT	°F	HOURS*
C/A	20	INERT GAS	2000	10000
W-5Re/W-26Re	16	INERT GAS	2000	10000
W-3Re/W-25Re	10	INERT GAS	2000	10000
Mo/W-26Re	7	INERT GAS	2000	10000

IN PROGRESS TESTS

C/A	20	INERT GAS	2200	750
C/A	20	INERT GAS	2200	1075
C/A	10	INERT GAS	2200	150
C/A	7	INERT GAS	2200	2500
C/A	20	INERT GAS	2300	425
W-5Re/W-26Re	5	INERT GAS	2800	1000
W-5Re/W-26Re	20	INERT GAS	2300	5325
Mo/Cb	20	INERT GAS	2500	220
Mo/Cb	10	INERT GAS	2000	8420
C/A	3	INERT GAS	2200	3600
W-5Re/W-26Re	3	INERT GAS	2200	3600
W-5Re/W-26Re	6	LITHIUM	2200	2800
W-5Re/W-26Re	6	LITHIUM	2200	2300
W-5Re/W-26Re	6	NaK	2000	2300

* AS OF FEB. 1, 1965

is critical because both elements are strongly positive (with respect to platinum). Small variations in molybdenum purity are strongly reflected in the calibration.

Better methods of predicting the decalibration effect of transmutation are needed. Post-irradiation composition of thermoelements agrees reasonably well with calculated values; however, the extent of decalibration due to these differential changes in composition cannot be predicted. Since post-test calibration is difficult and gradient effects cannot be predicted, it is desirable to start with materials whose transmutation, if any, will not decalibrate the thermocouple.

None of us who have been concerned with this program looks on thermocouple pyrometry as a simple technique anymore. We feel that the state-of-the-art of high temperature stability has been much advanced in the past few years, through scrupulous attention to purity. We believe that much could be done to improve the stability of other thermoelements by similar attention. As usual, in engineering work, need must be carefully balanced against academic interest.

NOTE: Referenced specifications in this report are as follows:
CS-1831-F, CSP-1902-B, CS-1750-A, CSP-1905-A, CS-2048-B,
CSP-1913-C