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# BASIC FACTORS CONTROLLING PEST IN HIGH TEMPERATURE SYSTEMS

by



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## INTRODUCTION

In a previous study,[1] we showed that pest failure in polycrystalline molybdenum disilicide is due to preferential oxidation in highly stressed areas in the neighborhood of Griffith flaws. The absence of pest failure at temperatures above a critical limit was ascribed to the onset of plastic deformation in the silicide, which provides a flaw rounding mechanism that counteracts the flaw sharpening effect of oxidation.

There are many empirical formulations reported in the literature for overcoming or delaying pest failure in molybdenum disilicide coating systems. On the basis of the fundamental mechanism proposed above, it might be expected that the various additives to molybdenum disilicide have the effect of lowering the ductile-brittle transition temperature of the silicide matrix. To test this hypothesis, monolithic bodies of the composition of some of the best pest-resistant coatings were fabricated by cold-pressing and sintering, and creep tested. As expected, deformation was observed at lower temperatures than had been found for pure polycrystalline $MoSi_2$.

A phenomenon superficially similar to pest in $MoSi_2$ has also been observed in aluminide systems, notably in $CbAl_3$. In order to test whether a similar fundamental mechanism is operative, crystals of $CbAl_3$ were fabricated by Czochralski growth from the melt, and were tested for delayed failure in air, under the conditions where pest is normally encountered. The results to date confirm that the rate of pest failure is indeed dependent on applied stress level.

## EXPERIMENTAL

### Materials Preparation

#### $CbAl_3$

Polycrystalline boules of columbium aluminide were pulled from a melt by the Czochralski crystal growth technique. Starting materials were high purity aluminum (99.997%) and columbium (99.9%). A 60 g charge, containing 2% excess aluminum to compensate for evaporation losses during growth, was loaded into a pyrolytic boron nitride crucible. The columbium was in the form of 1/4" cylindrical rod, cut into 1" lengths. The aluminum was used as a monolithic block of appropriate weight. Prior to placement in the crucible, the surfaces of the columbium rods were ground with 400 grit silicon carbide paper, then washed and rinsed in methanol using ultrasonic action. The rods were stored under methanol prior to use. The aluminum pieces were cleaned and stored similarly.

The crucible charge was melted under a 70 psig argon atmosphere by radiation from an inductively heated graphite susceptor surrounding the Boron nitride crucible. Prior to the actual growth run, each charge was melted and allowed to react. This melt was then cooled and removed from the crucible. The outer surfaces of the reacted charge were ground with silicon carbide paper to remove minor amounts of columbium oxide. The cleaned ingot was broken into several pieces, loaded back into the crucible, and remelted.

For the actual growth runs, a 1/16" diameter boron nitride rod was used as a starting seed. Growth rates were of the order of 1"/hour. A typical as-grown boule of $CbAl_3$ is shown in Figure 1.

Preparation of crack-free boules of $CbAl_3$ proved extremely difficult. None of the usual oxide and low cost high temperature crucible materials were found to be satisfactory for crystal growth. The pyrolytic boron nitride crucibles react very little with the melts, and several runs are possible with each crucible. However, during growth copious amounts of aluminum vapor escape from the melt and fall back into the melt surface as $Al_2O_3$, inspite of the relatively high pressure, high purity argon atmosphere. The oxide scum limits the time of the growth runs, since the oxide grains act as nucleating sites for spurious grain growth, leading eventually to microcracking of the boules. Sufficient crack free lengths could be grown, however, for the desired delayed failure experiments.

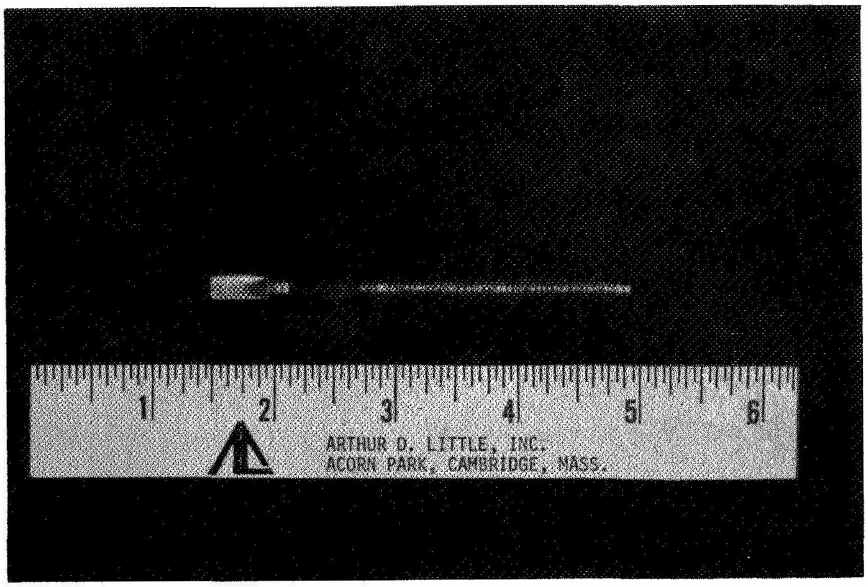


FIGURE 1: AS-GROWN $CbAl_3$ BOULE

Efforts to grow single crystals have thus far been unsuccessful. However, now that the technique for polycrystalline growth is well-developed, areas of single crystal $CbAl_3$ may be cut from the polycrystalline rods, and used as seed material, thus making it possible to nucleate single crystals.

Empirical Coating Formulations

Two of the best pest resistant silicide coating formulations were developed by Solar[2] and are designated NS-1 and NS-4. The reported compositions are as follows:

NS-1 45.5wt% $WSi_2$ - 45.5% $MoSi_2$ - 6% $VSi_2$ - 3% $TiSi_2$
NS-4 65% $WSi_2$ - 26% $MoSi_2$ - 6% $VSi_2$ - 3% $TiSi_2$

Bulk monolithic bodies of these compositions were fabricated by cold-pressing and sintering. 100 gm samples of each composition were weighed out to ±1 mg. The components were blended by tumbling for 80 hours in clean glass jars. To facilitate preparation of the green compacts, a simple three-piece die was constructed from tool steel, with the die-run of the same material as the die body. The whole assembly was heat treated to a hardness of 50 Rc. The cross-section of the die cavity was 1" x 1/2". A maximum compaction stress of 16,000 psi was used to fabricate 1/4" thick "green" compacts with a porosity of about 50%.

The "green" compacts were sintered in a flowing hydrogen atmosphere, in a clear quartz tube, supported within a mullite tube, which was in turn inserted in a glo-bar tube furnace. Water-cooled end plates and sealing gaskets were used. The specimens were placed upon a thin sheet of tungsten, supported on an alumina plate. Temperatures were measured with a Pt-Pt 10% Rh thermocouple, and control was accurate to ±10°C. An initial sintering run with NS-1 was carried out for 20 hours at 1150°C. This heat-treatment was just sufficient to initiate sintering. The second sintering experiment, carried out for 36 hours at 1200°C, resulted in samples of good strength but rather low density, with large volumes of interconnected porosity. All remaining runs were carried out at 1240°C. Figure 2 shows the structure of an NS-4 composition sintered for

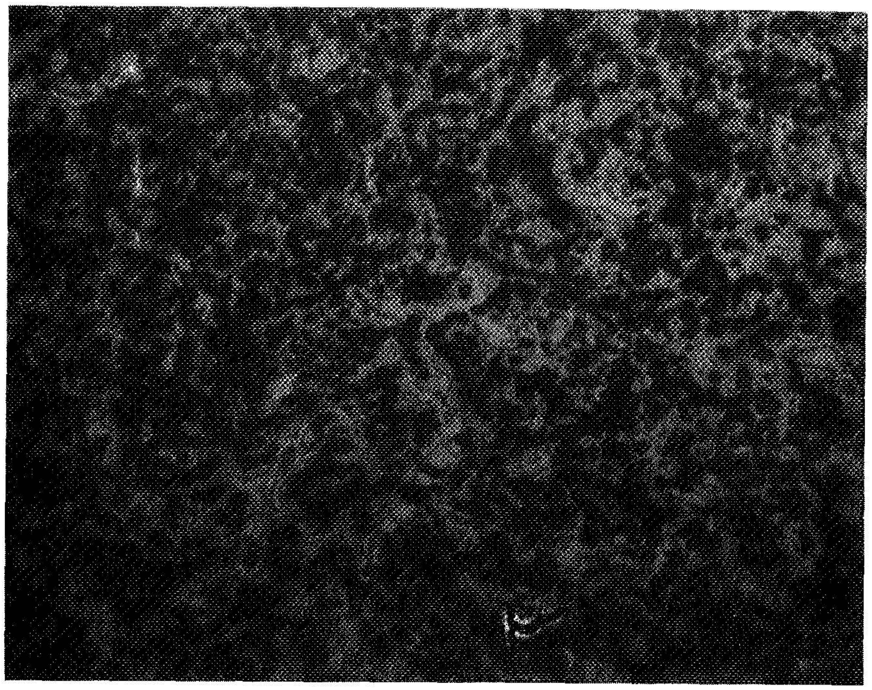

FIGURE 2: PHOTOMICROGRAPH OF SAMPLE OF NS-4
SINTERED IN HYDROGEN AT 1240°C FOR 36 HOURS
Unetched - Magnification X200

36 hours. Although the structure is beginning to develop, there is a preponderance of interconnected porosity. Figures 3 and 4 show the structures of NS-1 and NS-4 after 68 hours at 1240°C. It is clear that the NS-1 composition sinters at a slower rate than NS-4. In both cases, however, the porosity is of an isolated nature. The specimens exhibit some surface flaking but the bulk in all instances is very strong and machinable.

For comparison, a photomicrograph of an NS-1 coating (formerly called TNV-7) on a T-222 substrate (Ta-9.6 W-2.4 Hf-0.01C) is shown in Figure 5. The bulk of the coating contains considerable porosity, although there is a fully dense sublayer immediately adjacent to the alloy.

Delayed Failure of $CbAl_3$

Rectangular bar specimens were cut from the as-grown polycrystalline boules with a spark discharge machine. The surfaces were ground on a 300 grit diamond-bonded abrasive wheel, then on successively finer silicon carbide laps down to 600 grit, and finally polished on a high speed 6μ diamond lap. The final size of the specimens was 0.1" x 0.08" x 5/8."

Base level tensile strengths, $S_N$, were measured at 625°C in vacuum. Three rectangular sample bars, selected at random from the cut polycrystalline boules, gave an average $S_N$ of 31,400 $\pm$ 4800 psi.

Delayed failure experiments have been carried out in air at two temperatures within the pest range for $CbAl_3$. Rectangular bars were four-point dead-weight loaded in tension at a fraction $S/S_N$ of the base level strength. As oxidation proceeded, the $CbAl_3$ substrate weakened and eventually failed. The time to failure at 700°C, as indicated in Figure 6, is accelerated by the applied stress. At 625°C, where the rate of surface oxidation is less than at 700°C, a longer time is required for failure at a given $S/S_N$ level. The results thus far are entirely analogous to those obtained for $MoSi_2$ at the lower temperatures characteristic of the pest phenomenon in this material. A similar failure mechanism is thus indicated, with oxidation occurring preferentially at the tips of Griffith flaws, resulting in flaw sharpening with time, and eventual delayed failure.

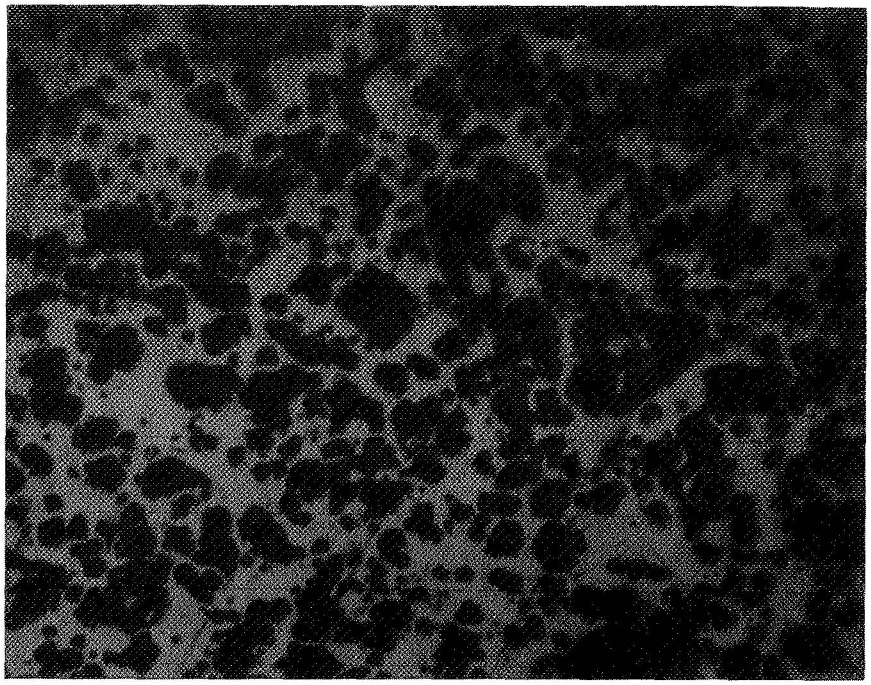

FIGURE 3: NS-1 SINTERED AT 1240°C FOR 68 HOURS
UNETCHED - MAGNIFICATION X200

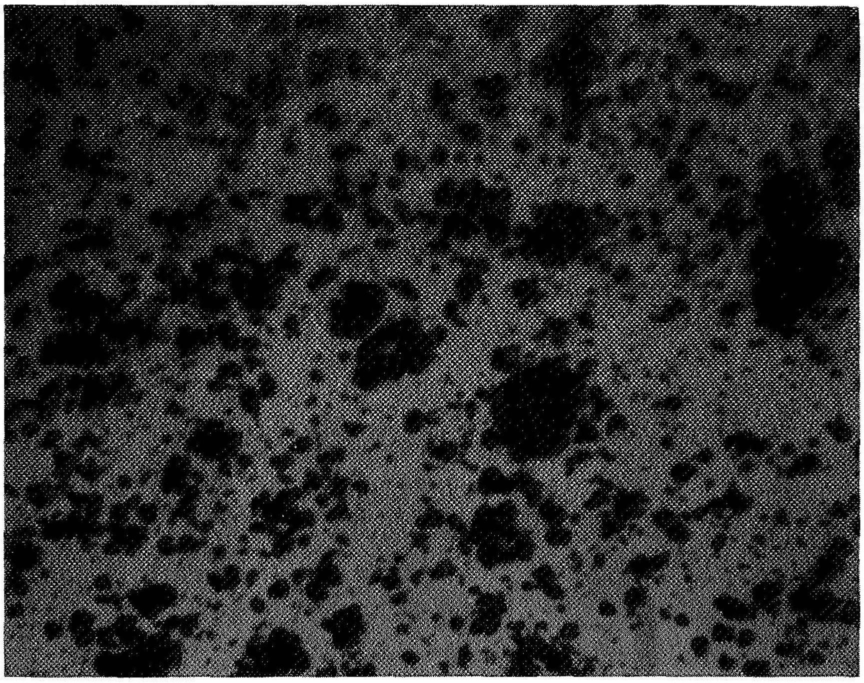

FIGURE 4: NS-4 SINTERED AT 1240°C FOR 68 HOURS
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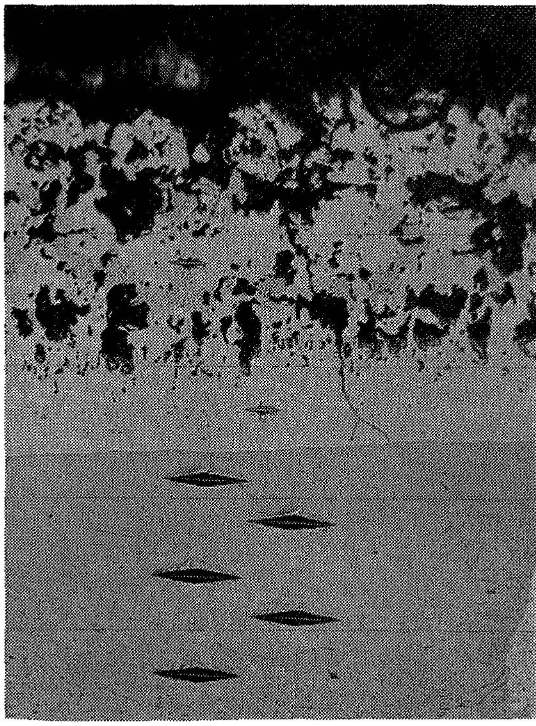
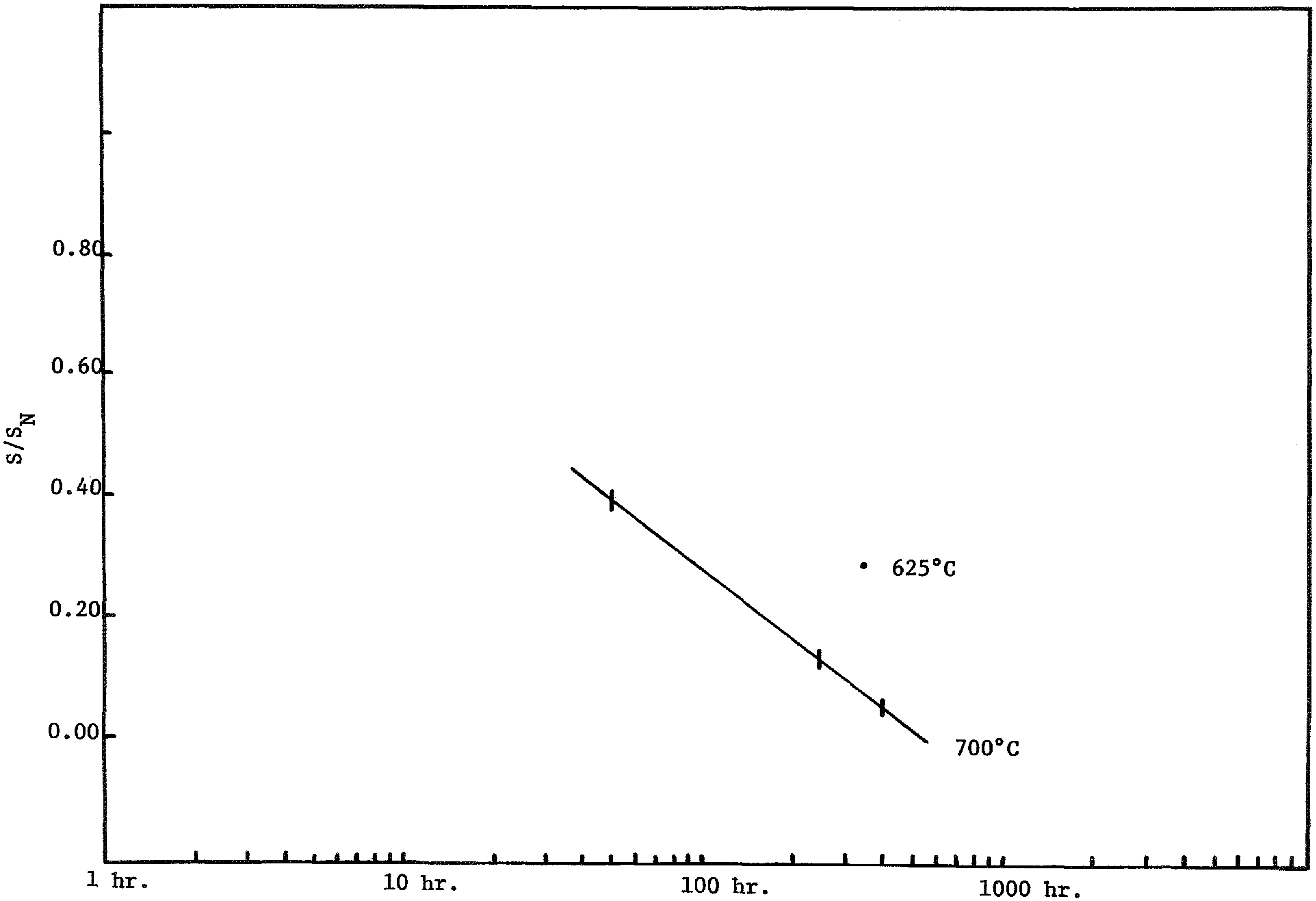
KHN
(50-gram load)




| | |
|---|---|
| **Experiment Number:** | $T_2$-187 |
| **Coating:** | TNV-7 (15Ti-35W-15V-35Mo) |
| **Substrate:** | T222 |
| **Sintered:** | 15 Hours at 2760 F (55 mg/cm$^2$ gain) |
| **Silicided:** | 7 Hours at 2150 F (40 mg/cm$^2$ gain) |
| **Etchant:** | 60% Lactic Acid (85% solution)<br>20% Concentrated HF<br>20% Concentrated $HNO_3$ |

**Magnification: 250X**

FIGURE 5: AS-SILICIDED MICROSTRUCTURE OF TNV-7 COATING


0.80
0.60
0.40
0.20
0.00
$S/S_N$
625°C
700°C
1 hr.
10 hr.
100 hr.
1000 hr.

The absence of pest at elevated temperatures with $MoSi_2$ was ascribed to the onset of plastic deformation in the matrix, acting to relieve the stress in the neighborhood of surface flaws, and therefore to reduce the effect of preferential oxidation. Pest in $CbAl_3$ has not been investigated nearly as extensively as pest in $MoSi_2$. The pest range for $CbAl_3$ has been reported as 540-850°C. Presumably, failure is most rapid towards the middle of this range. We investigated the deformation characteristics of polycrystalline $CbAl_3$ at 525°C and 725°C in compression. At the lower temperature, no deformation was observed, and the samples fractured at a stress of 36,300 psi. At 725°C, about 1/2% deformation was put into the sample at a compressive stress of 28,100 psi. We expect, therefore, that the time to pest failure at a given stress level will start to increase at temperatures above 725°C, and will check this point in the next quarter.

Creep in Practical Coating Formulations

Since plastic deformation seems to play an important role in alleviating pest failure, we surmised that practical pest-resistant coating formulations may deform at a lower temperature than pure $MoSi_2$. Creep tests were performed on rectangular bar specimens cut from the sintered NS-1 and NS-4 formulations described earlier.

The creep test results are given in Table I. The Instron cross head was moved at a speed of 0.002 cm/min. No deformation was evidenced at 325°C, but plastic deformation was introduced at temperatures of 515°C and above. Pure polycrystalline $MoSi_2$ was shown previously to deform at 600°C. Since pest failure in $MoSi_2$ is most rapid near 500°C, introduction of plastic deformation at this temperature could be very effective in prolonging the lifetime of a silicide-based coating. It should be emphasized that the empirical formulations only retard pest failure. They do not eliminate it.

## PLANS FOR THE NEXT QUARTER

The delayed failure experiments on polycrystalline $CbAl_3$ will be completed. Additional measurements will be made at 625°C, and a delayed failure curve will be obtained above 725°C, where we have observed plastic

TABLE I

CREEP TEST ON SINTERED SPECIMENS

| Spec. Number | Composition | b | d | $h_1$ | $h_2$ | w (kg) | σ (psi) | T (°C) |
|---|---|---|---|---|---|---|---|---|
| 1 | NS-1-68 | .1195 | .1020 | .2413 | -- | 270 | 48,600 | 325 broke |
| 2 | NS-1-36 | .1227 | .1164 | .1618 | -- | 35 | 5,400 | 325 broke |
| 3 | NS-4-36 | .1075 | .1160 | .2428 | -- | 132 | 24,900 | 325 broke |
| 4 | NS-4-68 | .12 | .11 | -- | -- | 350 | 58,000 | 330 broke |
| | | | | | | no deformation evident | | |
| 1 | NS-1-68 | .1158 | .1012 | .2270 | .2250 | 197 | 37,100 | 518 |
| 2 | NS-1-36 | .1170 | .1040 | .2190 | -- | 55 | 9,950 | 511 broke |
| 3 | NS-4-36 | .1118 | .1159 | .2662 | .2410 | 288 | 49,000 | 516 |
| 4 | NS-4-68 | .1365 | .1250 | .2842 | .0105 | 312 | 40,250 | 515 |
| 1 | NS-1-68 | .1048 | .1154 | .2685 | .2680 | 86 | 15,600 | 660 |
| 2 | NS-1-36 | .1075 | .1140 | .2038 | -- | 27 | 4,840 | 659 broke |
| 3 | NS-4-36 | .1358 | .1070 | .2450 | .2440 | 173 | 26,400 | 652 |
| 4 | NS-4-68 | .1242 | .1200 | .2928 | .2920 | 104 | 15,400 | 658 |
| 1 | NS-1-68 | .1190 | .1120 | .2764 | .2755 | 84 | 13,900 | 775 |
| 2 | NS-1-36 | .1218 | .1147 | .2098 | -- | -- | -- | 775 broke on htg. |
| 3 | NS-1-36 | .1172 | .1250 | .2272 | -- | 103 | -- | 775 broke |
| 4 | NS-1-68 | .1210 | .1200 | .2914 | -- | 225 | -- | 775 broke |

deformation. If single crystals of $CbAl_3$ can be grown, an attempt will be made to induce pest-like failure by application of tensile stress in air at a temperature near 700°C. The deformation behavior of the single crystals would then be investigated at high temperatures outside of the pest range.

The NS-1 and NS-4 formulations may be sintered for longer times to develop more fully dense structures for creep test.

REFERENCES

(1) J. B. Berkowitz-Mattuck, M. Rossetti, and D. W. Lee, "Enhanced Oxidation of Molybdenum Disilicide Under Tensile Stress: Relation to Pest Mechanisms," AIME Trans., 1970, Vol. 1, p. 479.

(2) R. T. Wimber and A. R. Stetson, "Development of Coatings for Tantalum Alloy Nozzle Vanes," NASA Report No. CR-54529, prepared under Contract No. NAS3-7276, July, 1967.