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IN-217-00
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MEMORANDUM

Nov. 22, 1995

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To: Charles Urbancic, Director
Sponsored Research Program

From: Dr. S.N. Tewari, Professor
Chemical Engineering Department

SN

Subject: Closing of NASA-Cooperative Agreement NCC-3-119(TWIR-6).

Enclosed is a Project Closing Report for the above project, "Creep of Refractory Fibers and Modeling of Metal and Ceramic Matrix Composite Creep Behavior". No patents were obtained under this grant. Following equipments were purchased on this grant. We would like to take possession of these equipments.

1. Pressure caster motion feedthrough, purchased on 3/24/93, Cost \$1695, Is part of the Pressure Infiltration Caster in H 470. (Requisition No. 186288)
2. Lap Top Computer, purchased on 10/15/93, Cost \$4673 (cost was shared with TWIR-13). (Requisition No. 189168)
3. Gateway 486 DX2-66 Computer, Purchased on 10/15/93, Cost \$4673 (Cost shared with TWIR-13). (Requisition No. 189168)

No invention and patent are to be filed on this grant.

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PROJECT CLOSING REPORT**"Creep of Refractory Fibers and Modeling of Metal and Ceramic Matrix Composite Creep Behavior" (NCC-3-119)**

The requirements for a advanced jet engine and space power systems, which may include a service life of 2 to 7 years at temperatures of 1300 to 1600 K, dictate the use of, 1) tungsten and/or molybdenum alloy fiber reinforced niobium alloy matrix composites, and, 2) alumina fiber reinforced nickel-base superalloy composites. In the continuous fiber reinforced metal matrix composites the fiber carries the vast majority of the applied load. Alumina based ceramic fibers and/or refractory metal alloy fibers (tungsten alloys and molybdenum alloys, such as tungsten lamp (218CS), tungsten + 1.0 a/o percent thoria (ST300) and tungsten+0.4 atom percent hafnium carbide (WHfC) fibers), have been typically chosen as the preferred fiber due to their high strength, stiffness and compatibility at temperatures greater than 1300 K.

In order to predict the service life of composites, it is necessary to evaluate the composite fiber component and develop a model which describes their high temperature deformation, especially the creep, behavior. In the following we will present a brief description of the research performed under this cooperative agreement, important results obtained in various research programs, and list the publications.

AREAS OF RESEARCH:

Our concentration during this research was on the following subprograms.

- (1) Ultra high vacuum creep tests on 218, ST300 and WHfC tungsten and MoHfC molybdenum alloy wires,
 - . temperature range from 1100 K to 1500 K
 - . creep time of 1 to 500 hours.
- (2) High temperature vacuum tensile tests on 218, ST300 and WHfC tungsten and MoHfC molybdenum alloy wires.
- (3) Air and vacuum tensile creep tests on polycrystalline and

single crystal alumina fibers, such as alumina-mullite Nextel fiber, yttrium aluminum garnet (YAG) and Saphikon,

- . temperature range from 1150 K to 1470 K
- . creep time of 2 to 200 hours.

(4) Microstructural evaluation of crept fibers,

- . TEM study on the crept metal wires.
- . SEM study on the fracture surface of ceramic fibers.

(5) Metal Matrix Composite creep models, based on the fiber creep properties and fiber-matrix interface zone formation.

IMPORTANT RESULTS OBTAINED:

Following is a brief description of the important results obtained in the major subprograms under this cooperative research program.

(1) TENSILE BEHAVIOR OF TUNGSTEN AND TUNGSTEN ALLOY FIBERS AT 1300 TO 1600 K:

The tensile behavior of 200 μm diameter tungsten and tungsten alloy fibers was studied at strain rates of $10^{-2}/\text{s}$ in the 1300K to 1600K temperature range. The fibers were tested in the as-drawn, electropolished and stress relieved conditions. Tensile behavior was correlated with the stability of the fibrous substructure and dispersed phases: potassium filled bubbles, thoria or hafnium carbide. The effectiveness of the dispersed phases in retarding the recrystallization was characterized. The superior strength and ductility at 1600K of the WHfC fiber appears to be due to its HfC particle stability which resists recrystallization.

(2) TENSILE AND CREEP-RUPTURE BEHAVIOR OF MOLYBDENUM ALLOY WIRES IN THE 1200 K TO 1600 K TEMPERATURE RANGE:

The tensile and creep-rupture behavior of 380 μm diameter molybdenum alloy wires was studied in the 1200 K to 1600 K temperature range. The wires were tested in the as-drawn, electropolished and stress relieved conditions. Tensile and creep rupture behavior were correlated with the stability of the fibrous substructure, hafnium carbide dispersed phases, and, alloying element of tungsten. The effectiveness of the carbide

dispersoid phase in retarding recrystallization was characterized. The superior strength and ductility of the MoHfC + 45 w/o W alloy fiber appears to be due to the more stable HfC particle with tungsten element which resists recrystallization.

(3) PRELIMINARY EVALUATION OF TENSILE AND STRESS-RUPTURE BEHAVIOR OF W + 24 A/O Re + 0.4 A/O HfC WIRE:

The tensile properties of hafnium carbide dispersed tungsten-rhenium alloy wire, W + 24a/o Re + 0.4a/o HfC (W24ReHfC) were studied from liquid nitrogen temperature (LN_2) to 1750 K and its stress-rupture behavior determined from 1144 K to 1500 K. These results were compared to previous data on W + 4a/o Re + 0.4a/o HfC (W4ReHfC) and W + 0.4a/o HfC (WHfC) wire (Petrasek 1972).

The room temperature (RT) tensile strength of the W24ReHfC wire was about 3250 MPa. It is higher than that of the W4ReHfC (3160 MPa) and WHfC (2250 MPa) wires. The RT ductility of the W24ReHfC wire was quite high with a 50 % reduction of area, as compared with the room temperature ductilities of 28 % and 2 %, respectively for W4ReHfC wire and the WHfC wire. At temperatures of 1144 to 1366 K, the W24ReHfC wire had tensile strengths, which favorably compare to the W4ReHfC and WHfC wire. However, above 1366 K, the W4ReHfC wire had both a greater tensile strength and stress-rupture strength than the W24ReHfC wire. These properties suggested that the W24ReHfC wires hold promise as potential fiber reinforcements in composites from room temperature to about 1350 K.

(4) EFFECT OF COMPOSITION AND MICROSTRUCTURE ON THE CREEP AND STRESS RUPTURE BEHAVIOR OF TUNGSTEN ALLOY WIRES AT 1366 K TO 1500 K:

The stress-rupture behavior of tungsten and tungsten alloy wires (200 to 380 μ m in diameter) was studied from 1366 to 1500 K. The investigated wires were: lamp (218), W + 1.0 at % thoria (ST300), W + 0.4 at % hafnium carbide (WHfC), W - Re (24 at % Re) + 0.4 at % hafnium carbide, (W24ReHfC), and Mo - W (34 at % W) + 0.1 at % hafnium carbide (MoWHfC). The rupture strength of ST300 wires

(310 MPa) was slightly higher than that of the 218 wires (290 MPa) at 1500 K for 200 hr, but substantially lower than that of the WHfC and W24ReHfC wires (510 and 400 MPa, respectively). Creep behaviors of the 218, ST300, and WHfC wires were studied from 1400 to 1500 K. The steady-state creep rate of the ST300 wires was lower than that of the 218 wires, but higher than that of the WHfC wires. The WHfC had the lowest steady-state creep constant in the stress range of 200 to 500 MPa at 1500 K. The superior creep and stress-rupture strength of the WHfC wires over the 218 wires were due to their microstructural stability as determined by SEM and TEM evaluations. Stability of the fibrous microstructure was mainly due to the fine hafnium carbide dispersoids (35 nm average particle diameter). For similar thermal exposures the fibrous subgrain width of the WHfC wires remained nearly unchanged at approximately 0.35 μm , whereas significant grain broadening (increasing from 0.3 to $\sim 1.5 \mu\text{m}$) was observed in the 218 and ST300 wires.

(5) TENSILE CREEP AND STRESS-RUPTURE BEHAVIOR OF SMALL DIAMETER POLYCRYSTALLINE ALUMINA FIBERS AT 1100 TO 1350 K:

Tensile creep studies were conducted on polycrystalline Nextel 610 and Fiber FP alumina fibers with grain sizes of 100 and 300 nm, respectively. Test conditions were: temperatures from 1073 to 1323 K and tensile stresses from 60 to 1000 MPa. For both fibers, only a small primary creep portion occurred followed by steady-state creep. The stress exponents for steady-state creep of Nextel 610 and Fiber FP were found to be about 3 and 1, respectively. At lower temperatures, below 1273 K, the finer grained Nextel 610 had a much higher 0.2 % creep strength for 100 hours than the Fiber FP; while at higher temperatures, Nextel 610 had a comparable creep strength to the Fiber FP. The stress and grain size dependencies suggest Nextel 610 and Fiber FP creep rates are due to grain boundary sliding controlled by interface reaction and Nabarro-Herring mechanisms, respectively.

(6) TENSILE AND STRESS-RUPTURE BEHAVIOR OF HAFNIUM CARBIDE DISPERSED MOLYBDENUM AND TUNGSTEN BASE ALLOY WIRES:

The tensile strain rate sensitivity and the stress-rupture strength of Mo-base and W-base alloy wires, 380 μm in diameter, were determined over the temperature range from 1200 K to 1600 K. Three molybdenum alloy wires; Mo + 1.1w/o hafnium carbide (MoHfC), Mo + 25w/o W + 1.1w/o hafnium carbide (MoHfC+25W) and Mo + 45w/o W + 1.1w/o hafnium carbide (MoHfC+45W), and a W + 0.4w/o hafnium carbide (WHfC) tungsten alloy wire were evaluated. The tensile strength of all wires studied was found to have a positive strain rate sensitivity. The hafnium carbide dispersed W-base and Mo-base alloys have superior tensile and stress-rupture properties than those without HfC. On a density compensated basis the MoHfC wires exhibited superior tensile and stress-rupture strengths to the WHfC wires up to approximately 1400 K.

(7) ASSESSMENT OF FIBER COATING INTERFACE SHEAR STRENGTH:

For structural composites with interface coatings, adequate load transfer will be required at both coating-matrix and coating-fiber interface. To understand the interaction between the fiber and fiber coatings, a variety of simple tests were performed on stand-alone coated fibers to possibly quantify the fiber-coating interfacial shear strength. These tests included, (1) fiber pull-out from embedded lengths in epoxy or other appropriate matrix material that bond well to the coating (so far the epoxy matrix has been observed to be most suitable for this fiber pull-out experiment without breaking or slipping), (2) SEM measurements of crack spacing in the coating after tensile straining of the coated fiber, and (3) SEM observation of the fiber pull-out from the coating after fiber fracture. These studies also shed light on the intrinsic fracture strain of the coating and the effects of temperature and environment on various interface properties. The fiber pull-out experiment was carried out on the various oxide and refractory metal coated sapphire. It was found that the ZrO₂ coated sapphire has the highest interfacial debonding

strength of 30 MPa.

(8) TENSILE STRAIN RATE SENSITIVITY OF TUNGSTEN/NIOBIUM COMPOSITES AT 1300 TO 1600 K:

The tensile strain rate sensitivity of continuous tungsten fiber reinforced niobium composites, fabricated by an arc-spray process was studied. The strain rate sensitivity of the composites was controlled, mainly, by the tungsten fiber component, even though the sensitivity of the composite tensile strength was higher than the free fibers. Using the rule of mixture, the measured composite tensile strength was evaluated, it was found that the deviation is dependent on the reinforcing tungsten alloy fiber chemistry, i.e., positive deviation for ST300/Nb and negative deviation for 218CS/Nb.

(9) CREEP MODEL AND CREEP MECHANISM OF TUNGSTEN/NIOBIUM COMPOSITES AT 1400 AND 1500 K:

With the assumption of the no-interaction between fiber and the matrix several possible creep models were examined. The candidate creep models were;

- . viscoelastic model,
- . elastic fiber model,
- . transient creep model and
- . creeping fiber model.

With the help of the experimentally determined stress component and composite properties for the tungsten/niobium system, the proposed model was evaluated. The creeping fiber model was fit best with the experimental data at 1400K and 1500K. With increasing temperature the interaction between niobium and tungsten was significant, and thus a modified and improved composite creep model had to be established.

The creep behavior of a high temperature refractory metal alloy composite fabricated by an arc-spray process was evaluated using three models: an elastic-fiber model, a primary creeping-fiber model and a steady-state creeping-fiber model. Creep properties of the continuous tungsten fiber (ST300 and 218), the Nb-1Zr matrix and the composite (ST300/Nb-1Zr, ST300/Nb

and 218/Nb) were determined and compared with the models. Comparison of the calculated and the measured composite creep properties indicated that the steady-state creeping-fiber model fitted better than the elastic-fiber or the primary creeping-fiber model. The steady-state creeping-fiber model calculated creep strength agreed well with the measured values. In addition, the creep strength of the ST300/Nb-1Zr and ST300/Nb composites was higher than that of the 218/Nb composites. The main reason for this was the higher creep strength of ST300 than that of the 218 fiber with a thin interface zone.

PUBLICATIONS AND PRESENTATIONS

1. H.M.Yun and R.H.Titran: presented at the TMS Fall Meeting, Indianapolis, Indiana, Oct. 02-05, 1989, and published at Metallurgical Transactions 23A, 1992, 3121-33, "Tensile Strain Rate Sensitivity of Tungsten/Niobium Composites at 1300K to 1600K".
2. T.L.Grobstein and H.M.Yun: Presented at the MRS Meeting, Boston, Nov. 27-Dec. 2, 1989, "The Interface in Tungsten Fiber Reinforced Niobium Metal Matrix Composites".
3. H.M.Yun and R.H.Titran: presented at the ASM AeroMat'90 Meeting, Long Beach, May 21-24, 1990, "High Temperature Stress-Rupture Behavior of the Advanced Mo 0.4HfC fibers".
4. T.L.Grobstein and H.M.Yun: presented at the 8th Symposium on Space Nuclear Power Systems, New Mexico, Jan. 6-10, 1991, "The Role of Interface in Refractory Metal Matrix Composites".
5. H.M.Yun: presented at the TMS Annual Meeting, New Orleans, Feb. 17-21, 1991, and published at Metallurgical Transactions 24A, 1993, 209-14, "Preliminary Evaluation of the W - 24Re - 0.4HfC Fibers".
6. H.M.Yun and R.H.Titran: presented at the TMS Annual Meeting, New Orleans, Feb. 17-21, 1991, and published at Journal of Materials Science and Engineering A165, 1993, 65-74, "Effect of Composition and Microstructure on the Creep and Stress-Rupture Behavior of Tungsten Alloy Wires at 1366 - 1500 K".

7. H.M.Yun and R.H.Titran: presented at the TMS Fall Meeting, Cincinnati, Ohio, Oct. 02-05, 1991, "Modeling of the 1400 to 1500 K Creep Behavior of W/Nb-1Zr Refractory Metal Alloy Composites".
8. H.M.Yun and J.C.Goldby: presented at the 17th Annual Conference on Composites and Advanced Ceramics, Cocoa Beach, FL, Jan. 10-15, 1993, "Tensile Creep Behavior of Polycrystalline Alumina Fibers at 1000 to 1300 K", NASA Technical Memorandum No. 106269.
9. H.M.Yun and R.H.Titran: Presented at the MRS Meeting, Boston, Nov. 27-Dec. 2, 1993, and submitted to Metallurgical Transactions A, "Tensile and Stress-Rupture Behavior of Hafnium Carbide Dispersed Molybdenum and Tungsten Base Alloy Wires".
10. H.M.Yun, J.C.Goldby and J.A.DiCarlo: presented at the 95th Annual Meeting and Exposition of the American Ceramic Society, Cincinnati, OH, Apr. 18-23, 1993, "Stress-Rupture Behavior of Small Diameter Polycrystalline Alumina Fibers", NASA Technical Memorandum No. 106256.
11. J.C.Goldby, J.A.DiCarlo, H.M.Yun and G.N.Morscher: presented at the 6th Annual HITEMP Review, Cleveland, OH, Oct. 25-27, 1993,
12. Thermomechanical Properties of Advanced Polycrystalline Oxide Fibers", published at NASA Conference Publication 19117, 85-1-85-11.
13. H.M.Yun, J.C.Goldby and J.A.DiCarlo: presented at the 18th Annual Conference on Composites and Advanced Ceramics, Cocoa Beach, FL, Jan. 09-14, 1994, "Time - Temperature Effects of the Rupture and Creep Strength of Oxide Fibers".
14. J.C.Goldsby, H.M.Yun and J.A.DiCarlo: presented at the 18th Annual Conference on Composites and Advanced Ceramics, Cocoa Beach, FL, Jan. 09-14, 1994, "Pre-Annealing Effects on Creep and Rupture of Nextel 610 Polycrystalline Alumina Fibers".
15. J.Hurst, H.M.Yun, D.Gorican and J.A.DiCarlo: presented at the 18th Annual Conference on Composites and Advanced Ceramics, Cocoa Beach, FL, Jan. 09-14, 1994, "Creep Stress - Rupture Behavior of Sintered SiC Fibers". J.C.Goldsby.
16. H.M.Yun and J.A.DiCarlo: presented at the 96th Annual Meeting and Exposition of the American Ceramic Society, Indianapolis, IN,

Apr. 24-28, 1994, "The Effect of Temperature and Time on the Tensile Strength of an Advanced CVD SiC Ceramic Fiber".

16. A.Sayir, R.M.Dickerson and H.M.Yun: presented at the 96th Annual Meeting and Exposition of the American Ceramic Society, Indianapolis, IN, Apr. 24-28, 1994, "High Temperature Mechanical Properties of Directionally Solidified Al₂O₃/Y₃Al₅O₁₂(YAG) Eutectic Fibers".

17. H.M.Yun, J.C.Goldby and J.A.DiCarlo: presented at the 96th Annual Meeting and Exposition of the American Ceramic Society, Indianapolis, IN, Apr. 24-28, 1994, published at NASA TM 106692 and will be published in "High Temperature Ceramic Matrix Composites, 1994"., and also,

"Stress-Rupture Behavior of As-Produced and Coated Polymer Derived SiC Fibers".

18. G.N.Morscher, H.M. Yun and J.C.Goldsby: presented at the "1994 Utah Gordon Conference on High Temperature Plasticity", sponsored by the American Ceramic Society, Snowbird, Utah, Aug. 7-11, 1994, will be published in the conference proceedings, "Viscoelastic Analysis of Bend Stress Relaxation and Tensile Primary Creep of a Polycrystalline SiC Fiber".

19. J.A.DiCarlo and H.M. Yun: presented at the "1994 Utah Gordon Conference on High Temperature Plasticity", sponsored by the American Ceramic Society, Snowbird, Utah, Aug. 7-11, 1994, will be published in the conference proceedings, "Issues for Creep and Rupture Evaluation of Ceramic Fibers".

20. J.A.DiCarlo, H.M.Yun, G.N.Morscher, and J.C.Goldsby: presented at the 7th HiTEMP Conference, sponsored by NASA, Westlake, OH, Oct.24-26, 1994, published in the conference proceedings, vol. III, p76-1 76-10 "Tensile Creep-Rupture Modeling of SiC Fibers".

21. A.Sayir, H.M.Yun, P.O.Dickerson, and L.E.Matson: presented at the 7th HiTEMP Conference, sponsored by NASA, Westlake, OH, Oct.24-26, 1994, published in the conference proceedings, vol. III, p74-1 74-12, "High Temperature Mechanical Properties of Directionally Solidified Al₂O₃/Y₃Al₅O₁₂(YAG) Eutectic Fibers".

22. S.C.Farmer, A.Sayir, P.O.Dickerson, and H.M.Yun: presented at the "1994 MRS Fall Meeting", sponsored by Materials Research Society, Boston, MA, Nov.28-Dec.2, 1994, will be published in "Ceramic Matrix Composites, Advanced High Temperature Structural Materials", "High Temperature Mechanical Properties of Al₂O₃/ZrO₂(Y₂O₃) Fibers".