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review

OF RECENT DEVELOPMENTS

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Refractory Metals

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COLUMBIUM ALLOYS

Westinghouse Astronuclear has concluded a program aimed at the development of a fabricable, moderately oxidation-resistant alloy for potential application as a protective cladding as backup for primary protective coatings for high-strength columbium-alloy turbine blades.⁽¹⁾ One feature of this program was the development of a model to predict the maximum surface recession allowable in a cladding alloy while still providing adequate protection to the core alloy for target times up to 50 hours at temperatures to 2200 F. Based on this analysis, maximum oxidation-rate constants for the cladding-alloy candidate at 2000 and 2200 F were set at values of 5.6 and 4.0 mils/hour^{1/2}, respectively.

Of numerous alloys investigated, best oxidation resistance was demonstrated for Cb-15Ti-10Ta-10W-2Hf-3Al alloy, designated as B-1, which showed surface recession-rate constants of roughly 2.5 and 1.5 mils/hour^{1/2} at 2200 and 2000 F, respectively. The surface oxide formed on exposing the B-1 alloy in flowing air at temperatures through 2400 F was quite adherent, although some spalling occurred on cooling below 1500 F. Some further improvements in the alloy's oxidation resistance at 2000 and 2200 F was afforded through the use of a 1-hour, 2400 F oxidation exposure either prior to or during a 40-hour exposure period. A brief comparative evaluation indicated that the weight-gain behavior of the B-1 alloy at 2200 F for times to 64 hours was approximately equivalent to that shown by several experimental variations of Wah Chang's new, oxidation-resistant WC-3015 alloy.

A single B-1 alloy ingot, containing 3.2 to 3.6 percent aluminum, was fabricated to sheet product for mechanical-property evaluations. The recrystallized material was brittle at room temperature and displayed a 2T ductile-to-brittle transition temperature between 175 and 200 F. Tensile properties for the recrystallized sheet were as follows:

| | Temperature, F | | |
|--------------------------------|----------------|--------|--------|
| | 1800 F | 2000 F | 2200 F |
| Ultimate Tensile Strength, ksi | 39.2 | 30.1 | 12.0 |
| Yield Strength, ksi | 34.7 | 29.5 | 12.0 |
| Elongation, percent | 27 | 94 | 146 |
| Reduction in Area, percent | 26.5 | 100 | 100 |

Lowering the aluminum content of this alloy to about 2.5 percent was expected to improve its low-temperature ductility and fabricability without adversely affecting its oxidation behavior.

The results of several studies concerned with the effects of thermal-mechanical variables on the creep properties of high-strength columbium alloys also was reported by Westinghouse Astronuclear.⁽²⁾ One phase of this program involved a property comparison of the Cb-1 (Cb-30W-1Zr-0.06C-0.04N) and B-88 (Cb-28W-2Hf-0.067C) alloys to reconcile reported variations in the mechanical properties of the two compositions. Both materials were characterized with regard to recrystallization, grain growth, and response to thermal-mechanical processing. The alloys were quite similar in their response to thermal treatment with the exception that Cb-1 showed an aging response in the 1830 to 2190 F range which was attributed to the precipitation of a zirconium nitride or carbonitride. The 2400 F creep-rupture properties of both alloys were found to be quite similar when compared in equivalent structural conditions. For example, the stress levels required to cause rupture in 10 hours for both materials fell within the ranges given below:

| Test Conditions | 10-Hour Rupture Strength, ksi |
|-----------------------------------|-------------------------------|
| Stress relieved, 1 hour at 2500 F | 25 to 30 |
| Recrystallized, 1 hour at 3090 F | 31 to 34 |

Tensile properties were also determined for both alloys in these same test conditions at temperatures from -110 to 600 F. In general, these tests showed that, condition for condition, the Cb-1 alloy maintained higher strengths at low temperature than the B-88 composition. However, room-temperature ductility in the Cb-1 composition was only marginal, and ductile-to-brittle transition temperatures for this alloy were 80 to 100 F higher than for the B-88 alloy. Recrystallization treatments increased the transition temperatures of both alloys by 50 to 100 F.

In another phase of this program, the effects of work hardening and recovery on the yield strengths of creep-resistant alloys at temperatures of 1200 to 1600 F were investigated.⁽²⁾ By prestraining a Cb-22W-2Hf-0.06C alloy (designated as B-99) 9 percent at 300 F, the 1400 F yield strength of the alloy

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was able to be increased from 50 ksi to 95 ksi. Creep-rupture properties for the B-99 alloy in a fully recrystallized condition also were determined. These are compared with values for the B-88 alloy in a similar structural condition as follows: (2)

| Temperature, F | 100-Hour Rupture Strength, ksi | |
|-------------------|--------------------------------|------|
| | B-88 | B-99 |
| 2000 | 56 | 45 |
| 2200 | 36 | 28 |
| 2400 | 25.5 | 21 |

As expected, the B-88 alloy showed superior properties by virtue of its higher tungsten content.

MOLYBDENUM ALLOYS

The results of a study at NASA Lewis have been reported on the thermo-mechanical processing of a series of arc-melted and extruded molybdenum-hafnium-carbon alloys. (3) The hafnium and carbon levels explored varied from 0.47 to 1.09 and 0.29 to 1.19 percent, respectively (all compositions in atomic percent).

One type of processing schedule involved different annealing treatments (e.g., solution treating at 3800 to 4000 F and/or aging at 2800 to 3500 F, both treatments terminated by helium quenching) prior to final swaging. These treatments, in general, produced an overaged HfC precipitate within a strain-hardened matrix. Also, the elevated-temperature tensile strengths of these alloys over the range of 2200 to 3000 F were comparable to those achieved with the Mo-Cb-TZM and Mo-TZC alloys tested in the stress-relieved condition.

The most outstanding mechanical properties were achieved in a series of metastable molybdenum-hafnium-carbon alloys which were swaged under conditions where the HfC precipitation occurred during deformation. This metastability occurs with Hf/C ratios between 1 and 1.5. One such alloy, Mo-0.6Hf-0.5C, had an ultimate tensile strength greater than 100 ksi at temperatures up to 2700 F and maintained a 30 to 50-ksi strength advantage over the Mo-Cb-TZM and Mo-TZC alloys at temperatures from 2200 to 3000 F. The same Mo-0.6Hf-0.5C alloy also showed superior resistance to stress rupture at 2400 F with exposure times to 100 hours.

REFRACTORY-METAL COMPOSITES

Solar's program for the Navy to reinforce weak, but oxidation-resistant, columbium alloys with tungsten wire has shown some promising results. (4) Preliminary screening identified a Cb-40Ti-10Cr-5Al alloy as having an attractive combination of oxidation resistance and fabricability. Results of cursory oxidation tests are as follows:

| Oxidation Temperature, F | Specific Weight Change in 16 Hours, (a) mg/cm ² | Thickness of Oxide and Continuous Subscale After 16 Hours, mils |
|--------------------------|--|---|
| 1600 | 6.2 | 0.6 |
| 1800 | 4.9 | 1.0 |
| 2000 | 5.6 | 3.0 |
| 2200 | 3.6 | --- |
| 2400 | -19.8 ^(b) | 3.0 ^(b) |

(a) Excluding any spalled oxide.

(b) All oxide spalled.

The degree of oxidation resistance indicated above, although not sufficient to eliminate the need for protective coating, is attractive from the fail-safe standpoint of providing substantial time after primary coating failure without gross loss of structural capability. This alloy also looked good in a brief evaluation of resistance to sulfidation. Annealing of a W-3Re-filament/columbium-alloy composite for time and temperature conditions up to 100 hours at 2400 F indicated excellent retention of integrity and structure in the 10-mil-diameter embedded W-3Re wires. (By comparison, nickel-, cobalt-, or iron-base matrices show gross reaction with tungsten filaments.)

Oxidation tests (16 hours at 1400 to 2400 F) of composite specimens indicated no substantial degradation of either the embedded W-3Re wire or of the inherent oxidation behavior of the columbium-alloy matrix, although some matrix hardening occurred as a result of oxygen contamination. Tensile tests on composite specimens (at a 27 percent reinforcement level) showed excellent agreement with the rule of mixtures at room and elevated (to 2300 F) temperatures. Similarly, the rule-of-mixtures relationship also appears to apply to the stress-rupture properties of composite specimens containing 13 to 24 percent reinforcement at temperatures from 1750 to 2000 F. These data have been summarized graphically in the March 20 Review of Recent Developments on Fiber-Reinforced Metals.

In another phase of the Solar program, good compatibility of the Bendix Chrome 90 alloy (Cr-3MgO-2.75V-0.5Si) with W-3Re filaments also was demonstrated for exposures through 100 hours at 2200 F. (4)

TUNGSTEN ALLOYS

Various procedures for fabricating sheet of the WT-38 alloy (tungsten containing 3.8 volume percent of ThO₂) were explored on a recently completed Westinghouse program. (5) Specifically, both isostatically pressed and hot-pressed billets were extruded, using conventional or Dynapak extrusion techniques, to sheet bars on the order of 1/2 inch thick by 1-1/2 inches wide. These were then either directly rolled to sheet or annealed, forged, re-annealed, and rolled to sheet. Numerous sheet samples of good quality, in sizes up to 3 by 10 inches at gages of 0.025 to 0.050 inch, were obtained. The 2200 C (3990 F) tensile properties of these various sheets, after annealing for 1/2 hour at 2400 C (4350 F), varied within the limits given as follows:

| | Alloy Sheet Material | Alloy Tested as Swaged Rod (6) |
|--------------------------|----------------------|--------------------------------|
| Ultimate Strength, ksi | 8.7 - 16.6 | 17.0 |
| 0.2% Yield Strength, ksi | 7.0 - 13.6 | 13.2 |
| Elongation, % | 10 - 21 | 17 |
| Reduction in Area, % | 5 - 23 | 21 |

As noted above, some of the sheet materials showed 2200 C tensile properties equivalent to those obtained on rod material of the same composition in an earlier program. (6) Also, the ductile-to-brittle bend transition temperature of the sheet material (200 to 300 C or 390 to 570 F) compared favorably with the tensile transition temperature of the rod.

Attempts to correlate the 2200 C tensile properties of the sheet specimens with hardness or

microstructure, as viewed optically, were not successful. Thus, all sheet material showed essentially the same thoria distribution (i.e., a mean particle diameter and interplanar spacing of about 450 Å and 3000 Å, respectively) regardless of processing history. However, transmission electron microscopy revealed that the highest strength material had retained a fine-grained (i.e., about 2 microns in diameter) subgrain structure which was lacking in the other sheet material. This subgrain structure was developed by direct rolling of Dynapak-extruded material. The optimum processing schedule was given as follows:

- (1) Isostatically press compacts at 30 ksi and room temperature
- (2) Presinter for 1 hour at 1600 C (2910 F) in hydrogen
- (3) Clad with unalloyed molybdenum and Dynapak extrude to sheet bar through a 4:1 reduction at 1750 C (3180 F)
- (4) Remove cladding and condition, as required
- (5) Cross roll from a preheating temperature of 1650 C (3000 F) using 15 percent reductions per pass.

Two reports describing the performance of tungsten-alloy inserts in rocket-motor applications were also received. One of these was an analytical Rocketdyne study to design an optimum zinc-infiltrated, self-cooled insert for a hybrid propellant motor utilizing a solid binder plus 45 percent aluminum fuel and nitrogen tetroxide oxidizer.⁽⁷⁾ A computer-programmed, heat-transfer analysis was used to study the duration of thermal protection of various self-cooled composite designs of different matrix porosities for the anticipated conditions of 6855 F maximum flame temperature and maximum combined film and radiative heat-transfer coefficient of 2300 Btu/ft²-hr-F. This study indicated that a bilayer composite containing 50 percent porosity in a volume beneath a 20 percent porous throat surface layer would give a 30 to 40 percent improvement over a tungsten heat-sink-type nozzle. However, a single test performed on a zinc-infiltrated nozzle having these graded structural characteristics resulted in premature failure due to throat erosion. This was ascribed to rocket-motor operating conditions not anticipated in the theoretical nozzle performance analysis.

In the second of these reports, Philco-Ford has described stop-start firing tests on six silver-infiltrated tungsten-nozzle inserts prepared for the Air Force by other subcontractors.⁽⁸⁾ The firing tests were conducted on a 5000-pound-thrust solid-propellant simulator using a simulated ANB-3066 propellant having a 5750 F flame temperature and containing 18 percent aluminized solid propellant. The six nozzle assemblies were divided into three groups of two each, which were subjected to a total of three hot-gas test pulses, extending up to 60 seconds each. While all six nozzles survived the tests, three developed surface cracks within the restart mode of each test duty cycle. In all six tests, extensive erosion occurred in the entrance and exit portions of the ATJ graphite which was used to support the infiltrated nozzle inserts.

Five of the six inserts also exhibited some shrinkage in throat diameter as a result of the firings. All six inserts have been returned to the original subcontractors for follow-up post-test analyses.

REFRACTORY MATERIALS, GENERAL

Four reports have been issued by ManLabs on a very comprehensive program aimed at characterizing the stability of a wide variety of refractory materials under high-velocity conditions. Specifically, the oxidation behavior of refractory metals (coated and uncoated), refractory borides, graphites and JT composites, hypereutectic carbide-graphite composites, metal-oxide composites, and iridium-coated graphites are being investigated over the spectrum of conditions encountered during reentry or high-velocity atmospheric flight as well as those employed in conventional furnace tests. A principal goal of this program, which includes support from numerous subcontractors, is elucidation of the relationship between hot gas/cold wall (HG/CW) and cold gas/hot wall (CG/HW) surface effects in terms of heat- and mass-transfer rates at high temperatures.

Three of these four reports deal with CG/HW studies. Thus, Reference 9 describes the facilities and techniques employed in performing CG/HW testing and References 10 and 11, respectively, give the results of low- and high-velocity tests on these materials. In brief, the techniques include low-velocity tests in resistance-heated tube furnaces and low- and high-velocity tests of inductively heated specimens. Oxidation exposures spanned the temperature range between 1000 and 4200 F at flow rates between 0.2 and 300 ft/sec. The uncoated refractory metals under evaluation include Hf-20Ta-2Mo and selected iridium-base alloys. Coated refractory metals system under study include WSi₂/W and Sn-Al/Ta-10W.

The fourth ManLabs report describes the facilities and techniques to be used in HG/CW testing.⁽¹²⁾ The facilities include the Model 509, ROVERS, and Ten Megawatt Arc installations at Avco and the Wave Superheater Hypersonic Tunnel at Cornell Aeronautical Laboratory. The range of basic parameters being explored in these evaluations is as follows:

| | |
|---------------------|---------------------------------------|
| Stagnation Pressure | 0.002 to 4 atmospheres |
| Stagnation Enthalpy | 2000 to 16,000 Btu/lb |
| Coldwall Heat Flux | 100 to 15,000 Btu/ft ² sec |
| Exposure Times | 20 to 23,000 seconds. |

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