New Screening Test Developed for the Blanching Resistance of Copper Alloys

NASA’s extensive efforts towards more efficient, safer, and more affordable space transportation include the development of new thrust-cell liner materials with improved capabilities and longer lives. For rocket engines fueled with liquid hydrogen, an important metric of liner performance is resistance to blanching, a phenomenon of localized wastage by cycles of oxidation-reduction due to local imbalance in the oxygen-fuel ratio. The current liner of the Space Shuttle Main Engine combustion chamber, a Cu-3Ag-0.5Zr alloy (NARloy-Z) is degraded in service by blanching. Heretofore, evaluating a liner material for blanching resistance involved elaborate and expensive hot-fire tests performed on rocket test stands. To simplify that evaluation, researchers at the NASA Glenn Research Center developed a screening test that uses simple, in situ oxidation-reduction cycling in a thermogravimetric analyzer (TGA). The principle behind this test is that resistance to oxidation or to the reduction of oxide, or both, implies resistance to blanching. Using this test as a preliminary tool to screen alloys for blanching resistance can improve reliability and save time and money.

In this test a small polished coupon is hung in a TGA furnace at the desired (service) temperature. Oxidizing and reducing gases are introduced cyclically, in programmed amounts. Cycle durations are chosen by calibration, such that all copper oxides formed by oxidation are fully reduced in the next reduction interval. The sample weight is continuously acquired by the TGA as usual.
Oxidation-reduction behavior of copper and its aerospace alloys. A horizontal trend (bottom four curves) suggests susceptibility to degradation by blanching, while a rising trend (top two curves) indicates resistance to blanching due to the growth of protective oxide.

The figure is a chart of sample weight change (vertical axis) versus the duration of oxidation-reduction exposure (horizontal axis). There are six plots in the chart. The four lowest plots—pure Cu, Cu-0.3Al, Cu-3Ag-0.5Zr (NARloy-Z), and Cu-0.1Zr (AmZirc)—are all horizontal, showing that, for these materials, all weight gained by oxidation was lost by reduction in each cycle. That indicates that all four materials are susceptible to blanching. The two top plots are for Cu-Cr-Nb alloys-Cu-4Cr-2Nb and Cu-8Cr-4Nb (GRCop-84). Both are rising curves, showing steady weight gain with time, an indication that a protective oxide grew throughout the exposure. Both materials should be resistant to blanching.

The graph shows the oxidation-reduction responses of two types of materials: One type (group I) is distinguished by a flat weight-change profile, whereas the other type (group II) exhibits a steady increase of weight with exposure time. (Only the trends are significant in this figure, not the relative heights: the plots have been spaced out vertically to avoid overlap.) Group I, at the bottom of the chart, includes pure Cu and three of its alloys. They all share one characteristic: upon oxidation, they form a nonprotective Cu₂O/CuO scale. The two Cu-Cr-Nb alloys at the top are in group II; they also form Cu₂O/CuO, but are further characterized by a compact layer of protective Cr-Nb oxides beneath the Cu₂O/CuO scale. In both groups, the Cu₂O/CuO scale formed during oxidation is removed during reduction in each cycle. That should result in zero weight change—and does for group I, but not for group II. For the latter, the additional layer of protective oxides is also resistant to reduction and its continuous growth leads to the monotonic weight increase seen in the figure. SEM examination after exposure reveals that the surfaces of group I samples are grooved and pitted with scars of incipient blanching attack, whereas group II samples are covered and protected by the Cr-Nb oxides. Cu-Cr coating compositions were observed to fall into group II, with a Cr₂O₃ subscale providing extra protection for blanching resistance.

The clear contrast in response between the two groups makes this test a reliable discriminant of blanching tendencies. These results indicate that Cu, NARloy-Z, and AmZirc should blanch (as they are known to do in service, ref. 1); in contrast, GRCop-84 should not—and hot-fire tests recently performed elsewhere indicate that GRCop-84 is resistant to blanching, as predicted by the graph. The simplicity of this test makes it a useful tool for screening. Results are read from weight-gain charts, rather than interpreted from visual signs of damage (as was done heretofore). Hence, with some precaution the test results can be used to rank alloys semiquantitatively on the basis of specific weight gains from a prescribed duration of oxidation-reduction cycling.

Reference

Author: Linus U. Thomas-Ogbuji
Headquarters program office: OAT
Programs/Projects: RLV, Gen 2