Oxidation Resistance and Critical Sulfur Content of Single-Crystal Superalloys

The high-temperature components of a jet turbine engine are made from nickel-base superalloys. These components must be able to withstand high stresses, fatigue, and corrosive reactions with high-temperature gases. Such oxidation resistance is associated with slow-growing $\text{Al}_2\text{O}_3$ scales that remain adherent to superalloy components after many thermal cycles. Historically, good oxidation resistance has been obtained by coating these components with Ni-Cr-Al-Y coatings, where small additions of yttrium (Y) were necessary for scale adhesion. Subsequently, it was found that the Y aids scale adhesion by preventing sulfur from segregating to the scale metal interface and thus preventing the sulfur from weakening the oxide-metal bonds. Y is a difficult element to incorporate in single-crystal superalloy castings, but it was shown in early work at the NASA Lewis Research Center that good adhesion could be obtained for low-sulfur, uncoated, single-crystal superalloys, without Y additions (ref. 1).

Low sulfur contents for these uncoated superalloys were achieved in the laboratory by a high-temperature hydrogen annealing process. This process allows segregation and surface cleaning of sulfur monolayers in a reducing environment. (Annealing in air or oxygen simply traps the sulfur at the oxide-metal interface). Although this process has been pursued by industry (ref. 2), another approach is to remove sulfur from the alloy in the melting process. Both processes involve extra effort and costs that must be balanced against improved performance. The present study was designed to establish a guideline for the minimum level of desulfurization needed to achieve maximum performance (ref. 3).

Coupons of various thicknesses of the superalloy PWA 1480 were hydrogen annealed at various times (8 to 100 hr) and temperatures (1000 to 1300 °C), resulting in coupons with sulfur contents ranging from about 0.05 to 5 ppm. This variation occurs because sulfur removal is approximately controlled by diffusion and the parameter $(D t/L^2)$, where $D$ is the diffusion coefficient of sulfur, $t$ is diffusion time, and $L$ is the sample thickness.

Cyclic oxidation tests at 1100 °C were then used to assess adhesion and spalling. The weight change of one set of 20-mil (0.5-mm) samples, annealed for 20 hr at 1000, 1100, 1200, and 1300 °C, is shown in the following figure. Clearly, the effect of the annealing temperature is quite dramatic in that the higher temperatures produced scales that spalled very little, whereas the lower temperatures resulted in severe weight losses comparable to those for the as-received, unannealed sample.
Effect of hydrogen annealing temperature on the 1100 °C cyclic oxidation weight change behavior of 0.5-mm (20 mil) PWA 1480 superalloy coupons annealed for 20 hr.

Similar effects were observed as a function of annealing time or sample thickness, because these parameters determine the final sulfur content from the hydrogen annealing process. Thus, spalling behavior can be related to a single parameter: sulfur content. This relationship is shown in the next figure, where the weight change after 500 1-hr cycles for the 20-mil samples is plotted against the sulfur content, as measured by glow discharge mass spectrometry. (Individual points are identified by the annealing temperature and time.) There is a steep reduction in the degree of spallation as the sulfur content is reduced below the as-received value of ~6 ppmw (parts per million by weight). Furthermore, there is very little spallation for samples having less than 1 ppmw sulfur, with no further benefit for samples having less than about 0.3 ppmw sulfur. These values translate to 1 to 2 monolayers of total sulfur segregation possible for a given sample geometry and sulfur level. A similar analysis of results, summarized from many published studies, produced the same sulfur dependencies for PWA 1484, René N5, René N6, René 142, and CMSX 4 superalloys (ref. 3).

Correlation between sulfur content and cyclic oxidation performance for PWA 1480.
Minimal scale spallation (weight loss) is shown for sulfur levels below 0.3 ppmw.

Thus, for typical airfoil dimensions in advanced aeroengines, 0.5 ppmw sulfur would be a commendable target level and should result in excellent scale adhesion. Most advanced turbine blades are also thermal barrier coated with an insulating layer of plasma-sprayed
ZrO$_2$ The integrity of this coating will also depend on good Al$_2$O$_3$ scale adhesion, since the scale grows beneath the ZrO$_2$. These low-sulfur alloys will improve scale adhesion and, thus, should improve ZrO$_2$ coating lives, even when NiCrAlY bond coats are employed.

References


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