



Oxidation-Reduction Resistance of Advanced Copper Alloys

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Abstract

Resistance to oxidation and blanching is a key issue for advanced copper alloys under development for NASA's next-generation of reusable launch vehicles. Candidate alloys, including dispersion-strengthened Cu-Cr-Nb, solution-strengthened Cu-Ag-Zr, and ODS Cu-Al₂O₃, are being evaluated for oxidation resistance by static TGA exposures in low-p(O₂) and cyclic oxidation in air, and by cyclic oxidation-reduction exposures (using air for oxidation and CO/CO₂ or H₂/Ar for reduction) to simulate expected service environments. The test protocol and results are presented.

Introduction

Due to their high thermal conductivity, copper alloys make excellent liners for the hot sections of high-heat-flux engines, such as combustion chambers of rocket engines for launching space payloads. However, in that aggressive service environment Cu alloys are prone to degradation by oxidation-related phenomena. In a combustor there are always issues of static and cyclic oxidation; in a hydrogen-fueled ("LH₂-LOX") rocket engine there is the additional issue of blanching, which causes the most serious oxidation-related damage to the liners [1–4]. Blanching is caused by spatial and temporal variations in oxidant-to-fuel (O/F) ratio, which change the local ambient from oxidizing to reducing and back [3]. Oxide film formed in the fuel-lean cycle is reduced and removed in the fuel-rich cycle, thus exposing the metal to further attack. Therefore, blanching is somewhat analogous to cyclic oxidation, except that the duration of an oxidation-reduction cycle may be in microseconds, rather than the minutes or hours that characterize cyclic oxidation. The "blanched" (i.e., bleached) spots indicate accelerated degradation, which has serious consequences for the impairment of cooling systems beneath the liner. Thus, evaluation of copper alloys for oxidative degradation involves tests for static oxidation, cyclic oxidation, and oxidation-reduction resistance.

Advanced copper alloys of interest to aerospace engine makers (as liners for thrust cell combustion chambers and nozzle ramps) are under study at NASA and in industry. They include: Cu-8Cr-4Nb, developed by the NASA Glenn Research Center in conjunction with Case Western Reserve University (designated "GRCop-84"); Cu-3Ag-0.1Zr ("NARloy-Z", which is the current Space Shuttle Main Engine liner material); and Cu-0.1Zr ("Amzirc"). Cu-8Cr-4Nb is a dispersion-strengthened alloy, comprised of a Cu matrix with a 14 vol% dispersion of insoluble Cr₂Nb precipitates [5]; the other two are solution-strengthened alloys. All are of interest to thrust-cell designers because of their very good thermal and mechanical properties, especially at

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elevated temperatures. These alloys, along with Cu-Al₂O₃ (“Glidcop”, an ODS alloy) have been evaluated for resistance to oxidative degradation, as part of NASA’s program for next-generation launch technology (NGLT). The ODS alloy has a nano-scale dispersion of Al₂O₃ in Cu; there are three versions, with 15, 25, and 60 wt% Al (0.3, 0.5, and 1.1 wt% Al₂O₃, respectively), designated Glidcop “AL-15,” “AL-25,” and “AL-60,” respectively. The evaluation performed in this study included static oxidation by TGA in various oxygen partial pressures dictated by the thermodynamics of a LOX/LH₂ engine, cyclic oxidation in air, and oxidation-reduction experiments conducted by in-situ switching between oxidant and reductant gases for various programmed durations.

Experimental Details

The materials were powder metallurgy (PM) alloys, extruded and rolled to develop optimum mechanical properties. Samples for oxidation testing were cut into rectangular or circular coupons 1 mm thick, with 19 mm as their largest dimensions, and polished to 1000-grit finish; those for oxidation-reduction were cut into mini-disks 5 to 7 mm in diameter and polished wafer-thin to a mirror finish.

Static TGA oxidation was conducted in oxygen diluted with argon to desired O₂ concentrations ranging from 0.033 vol% to 100% O₂, at temperatures of 550 to 850 °C; oxidation durations were 10 to 50 hr. Cyclic oxidation was done in air at 500 to 700 °C, each run consisting of twenty half-hour cycles (for total exposure times of 10 hr) with the samples weighed on every cycle. For blanching simulation the mini-disks were cycled at 800 °C between air and reducing gas. This reductant was initially 90% CO/10% CO₂, later 5% H₂ in Ar (5% being the maximum hydrogen concentration permitted by safety considerations). All gases were of ultra-high-purity grade. The oxidation-reduction schedule was: 0.5 hr to heat to 800 °C in H₂/Ar, ~3 hr of oxidation-reduction cycling, and 1 hr of cooling to room temperature in H₂/Ar.

One oxidation-reduction cycle consisted of exposure for t_O minutes in air followed by t_R minutes in H₂/Ar. Switching between the two environments was done in-situ. The values of t_O and t_R were optimized to satisfy two criteria: (1) that a detectable quantity of oxide be observed to grow in the oxidation half-cycle and then to be fully consumed in the reduction half-cycle thereby exposing the substrate for further reaction; and (2) that a large number of cycles be accommodated in a 5 hr experiment, for maximum cumulative effect. In practice this amounted to fixing t_O at a low value and increasing t_R until both criteria were satisfied. The values of t_O and t_R , respectively, that gave satisfactory results are 0.5 and 5 minutes for reduction in CO/CO₂; for reduction in 5%H₂/Ar they were 0.1 and 5 minutes. This need to amplify the oxidation and reduction effects also necessitated doing the test at the rather high temperature of ~800 °C, rather than the wall temperature of ~600 to 700 °C expected in service.

Results and Discussion

Static Oxidation

TGA results for the Cu alloys are compared in Fig. 1 for a representative set of conditions. Note that: (1) 700 °C is in the upper reaches of expected service temperatures, and oxidation rates and mechanisms were found to be independent of $p(O_2)$ in the range of 0.25 to 100% O₂ [6]. (2) Cu and the two solution-strengthened alloys are in one class, with very similar oxidation rates;

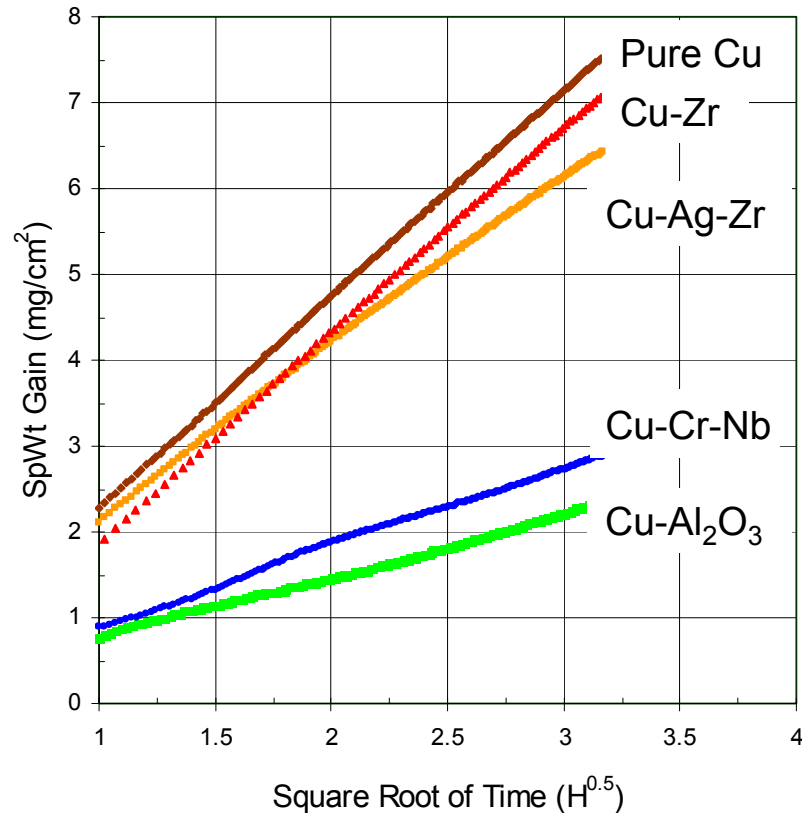


Fig. 1. Oxidation kinetics in 2.2% O₂ at 700 °C, illustrating parabolic behavior for Cu and the alloys at all temperatures investigated and in 0.25 vol% to 100% O₂

and the dispersion-strengthened alloys (Cu-8Cr-4Nb and Cu-Al₂O₃) in another class with much lower oxidation rates. (3) The kinetics are parabolic for all the alloys (and stayed so for temperatures and in all ambients with 0.25% and higher O₂ concentrations).

The uniformly parabolic kinetics are consistent with the fact that the major event occurring in each case is oxidation of Cu to its usual duplex oxide (Cu₂O/CuO), which is controlled by diffusion of Cu through the oxide. In Cu and the solution-strengthened alloys, this conversion of Cu to Cu₂O/CuO remains the sole oxidation process involved. In the dispersion-strengthened alloys, on the other hand, the overall rate is controlled by processes no doubt involving the dispersoids. For Cu-8Cr-4Nb that process is a modified reservoir effect resulting from oxidation of Cr₂Nb [6]; the sub-layer of Cr-Nb oxides is indicated in Fig. 2, and beneath it is a characteristic precipitate-free zone in the substrate. For Cu-Al₂O₃ it appears that the slow oxidation kinetics must relate to the presence of nano-dispersed Al₂O₃, but the exact details remain as yet unidentified. Fuller accounts of these observations appear elsewhere [6].

Temperature Cycling

Figure 3(a) shows cyclic-oxidation weight changes for several Cu alloys. The disparity among the three Cu-Al₂O₃ compositions (ODS-15, 25, and 60), which differ in only their Al₂O₃ contents, is unexplained. Apart from that disparity, and the insignificant weight change of pure

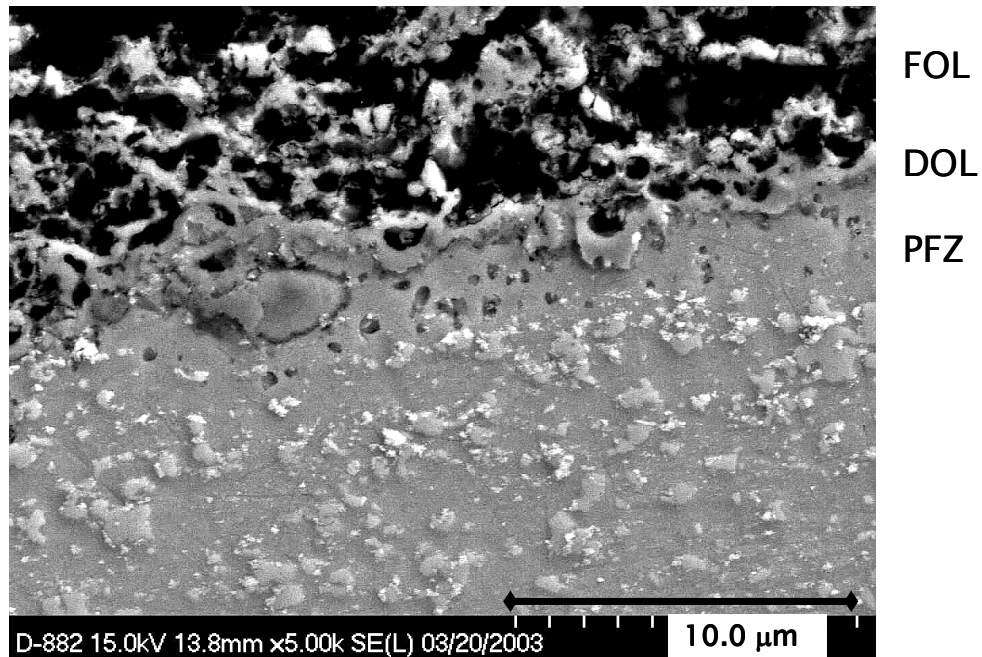


Fig. 2. SEM cross-section of Cu-8Cr-4Nb oxidized in air at 700 °C, showing oxide/substrate boundary: FOL (friable oxide layer) is inner layer of Cu_2O ; DOL (dense oxide layer) is a layer of Cr-Nb oxides; PFZ is a precipitate-free zone induced in the matrix by oxidation.

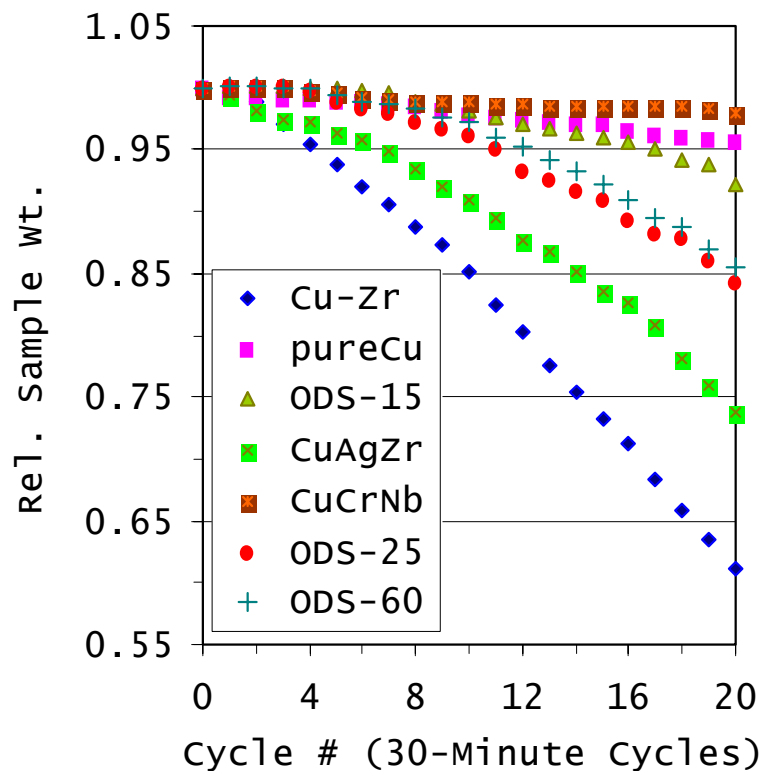


Fig. 3a. Cyclic-oxidation weight changes in air at 600 °C.

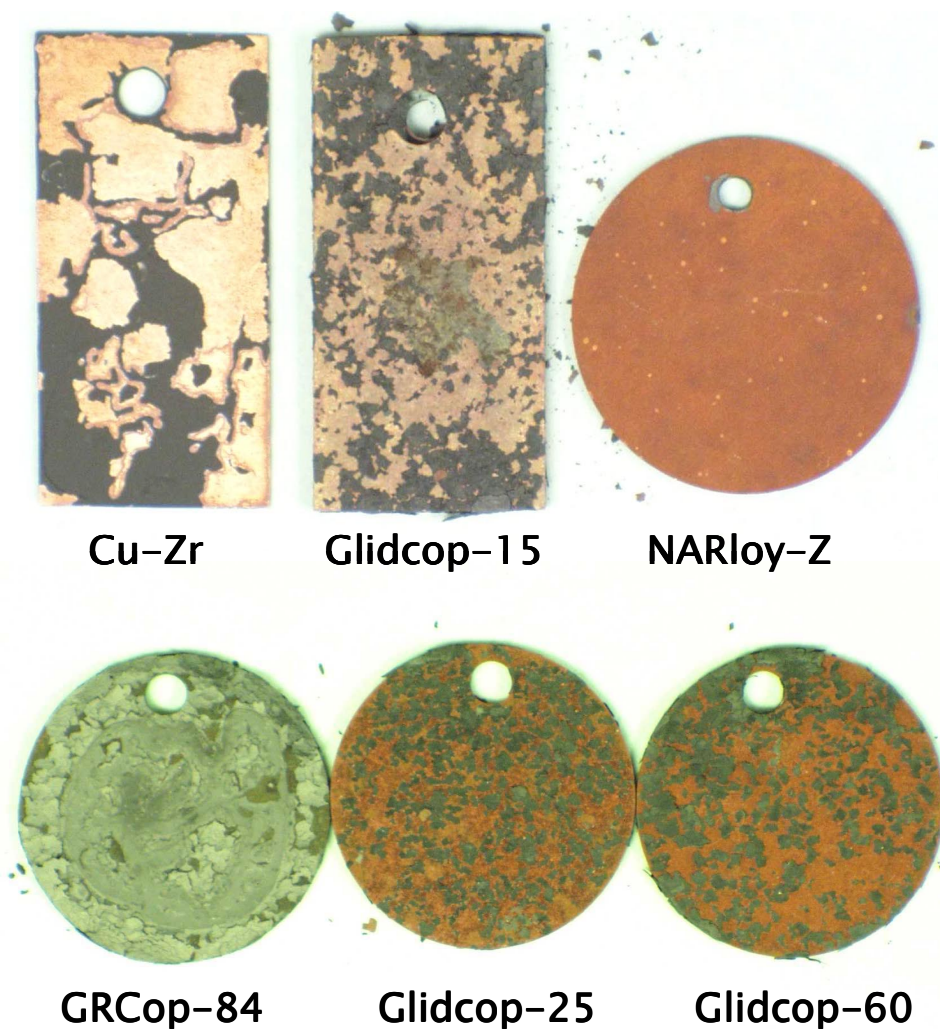


Fig. 3(b). Cu alloys after 10 hr of cyclic oxidation in air at 600 °C. Cu-8Cr-4Nb, which had the lowest weight change in Fig. 3(a), also shows the fullest oxide cover in Fig. 3(b).

These 600 °C cyclic-oxidation results are representative of the results obtained at the other temperatures: the dispersion-strengthened alloys resisted cyclic oxidation (i.e., exhibited the least weight changes) better than the solution-strengthened alloys, and good performance in this regard correlated with retention of oxide scale through the cycles.

Oxidation-Reduction Cycling

Figure 4 shows the weight-change responses of Cu-8Cr-4Nb and Cu-3Ag-0.5Zr (which is known to undergo blanching) during oxidation-reduction. The oxidation was performed in air and the reduction in CO/CO₂ or H₂/Ar as indicated in the figure. The responses are qualitatively the same for the two different reductants. Cu-3Ag-0.5Zr, which is prone to blanching, is characterized by a flat weight-gain response (after the ~20 minutes it took to attain exposure

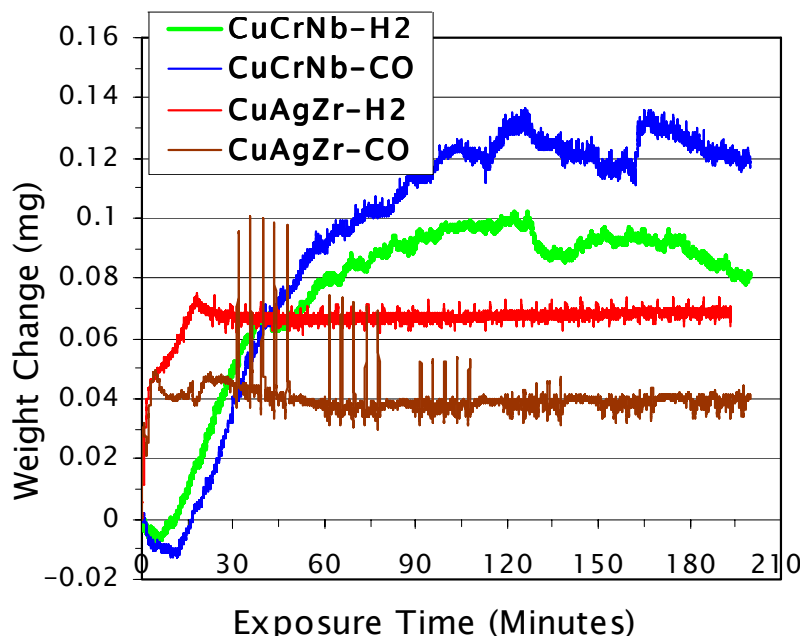


Fig. 4. Weight-change profiles for Cu-3Ag-0.5Zr and Cu-8Cr-4Nb during oxidation-reduction exposures at 800 °C. In each case air was the oxidant and CO or H2 the active reductant, as indicated.

temperature). Thus, for this material, weight gained during the oxidation stage of a cycle was completely lost during the reducing stage. In contrast, Cu-8Cr-4Nb is characterized by continuous weight gain, reaching saturation after ~2 hr.

The appearance of the samples after oxidation-reduction also correlated with the above weight-gain profiles: Cu-3Ag-0.5Zr coupons emerged with a clean, metallic luster while Cu-8Cr-4Nb coupons came out dark.

Shown in Fig. 5 are SEM images of the sample surfaces: Cu-3Ag-0.5Zr was deeply pitted and scarred, while Cu-8Cr-4Nb was fully covered in a mat identified by EDS as oxides of Cr and Nb, as detailed elsewhere [7]. It seems these Cr-Nb-O phases resist reduction and hence protect the substrate from further degradation. In other words, to the extent that oxidation-reduction is a key factor in blanching attack, this alloy should resist blanching at the temperatures where Cr-Nb oxides grow [7].

Summary and Conclusion

In an effort to assess, by laboratory means, the blanching resistance of an advanced Cu alloy, Cu-8Cr-4Nb, this material was subjected to 40 to 50 in-situ cycles of oxidation-reduction. The same treatment was given to Cu-3Ag-0.5Zr, an alloy that is known to undergo blanching degradation in service as a rocket engine liner. Cu-3Ag-0.5Zr, which usually forms a $\text{Cu}_2\text{O}/\text{CuO}$ scale, registered zero net weight gain during the exposure; the sample emerged without oxide cover, its surface deeply sculpted in a manner consistent with blanching features usually observed

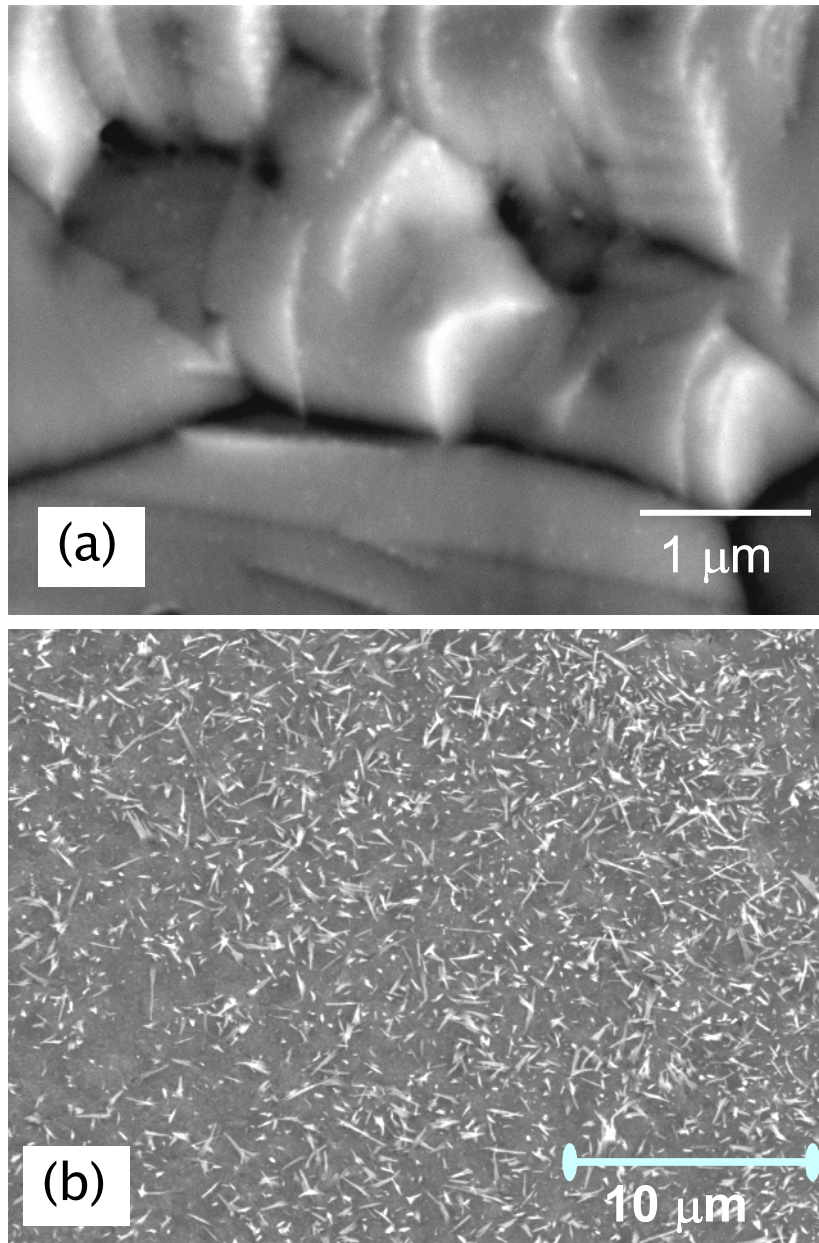


Fig. 5. SEM images of (a) Cu-3Ag-0.5Zr and (b) Cu-8Cr-4Nb surfaces after oxidation-reduction cycling: The former is bare, with deep fissures (shown at higher magnification) indicative of extensive attack, while the later is covered by protective oxide.

in service. In contrast, Cu-8Cr-4Nb (which usually forms an additional subscale of Cr-Nb oxides) registered continuous weight gain, and the sample emerged with a protective cover of Cr-Nb oxides which are resistant to reduction.

Cu-8Cr-4Nb is very likely to resist blanching degradation in service since it has been shown in this study to resist oxidation-reduction, and also shown (elsewhere) to resist static and cyclic oxidation much better than Cu-3Ag-0.5Cr).

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For efficient dissipation of the extreme thermal loads, copper alloys are preferred as liner materials for combustion chambers in rocket engines; but they have poor oxidation resistance, and are prone to blanching degradation from cyclic oxidation and reduction in service. Therefore, resistance to oxidation and blanching is a key issue in choosing and developing advanced Cu alloys for NASA's next generation of reusable launch vehicles. A few alloys under consideration, including "GRCop-84" (a dispersion-strengthened Cu-Cr-Nb), "NARloy-Z" (a solution-strengthened Cu-Ag-Zr), and "GlidCop" (an ODS Cu-Al₂O₃), have been evaluated by static TGA in low-p(O₂) ambients and by cyclic oxidizing-reducing exposures (air-CO/CO₂ as well as air-H₂/Ar) to approximate service conditions. The dispersion-strengthened alloys exhibited by far the highest resistance to static oxidation, and GRCop-84 also showed the most resistance to degradation by oxidation-reduction cycling. The test protocol and results will be discussed.