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The Aluminum-Bronze Conundrum: Slow-Motion Model Burn Ratios and Their Use[2]

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ABSTRACT: Materials used in oxidizers have experienced unintended fires, and a body of technology has been developed to understand and prevent these events. Such technology has been largely successful but there are behaviors that have not been fully understood. One such conundrum has been the fire nature of aluminum-copper alloys know as aluminum bronzes and of copper itself. Copper and aluminum bronze alloys (The ASM Manual lists 26 aluminum bronzes with from 2.6 to 15% aluminum) have many excellent properties. Those with low aluminum content have been known to be less combustible than is expected, while higher aluminum content (above ~10% Al) have been found to be more flammable than expected. This range is not rationalized in ASTM Standard G 94. Reconciliation of this conundrum and its bases is attempted using thermo-chemical equilibrium (TCE) concepts and a slow-motion combustion model with a secondary goal to illustrate once again why ASTM Committee G4 needs to incorporate TCE analysis into its collegium and body of work especially its G 94 document, something it has resisted doing since at least 2008.

KEY WORDS: copper, aluminum, aluminum bronze, oxygen, fire combustion, thermo-chemical equilibrium.

The writer has had an interest in combustion processes for decades in which he was involved with the evaluation of materials for safe use in oxidant atmospheres (mostly oxygen) but also before that, and since. Empirical test data are always important, a gold standard, to any such evaluation but it is also desirable to have a theoretical "feel", a context for how and why materials burn, because one can not test every empirical situation that arises. Often comparisons and extrapolations are required. So where do things stand today? As a charter member (1975) and past chair of ASTM Committee G-4 (1982-1985), he has seen how its standards have evolved, having prepared first drafts of several standards including ASTM G 94 on *Evaluating Metals for Oxygen Service* (1987) [*1*][2] evaluated and focused upon herein.

This is opinion that is self-published to address a long-term issue of concern. It has not been subjected to the ASTM Peer Review process that "certifies" and can improve the quality of discourse, but it therefore has also not been subject to that ASTM Peer Review

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Process that also censors unwelcome (politically incorrect?) materials. Both of which the writer has experienced. The reader must, *as the reader always should*, make an independent evaluation of the credibility of these discussions. Indeed, one of the most important public-service missions of Committee G4 is to provide tools with which to do that for everyone.

Fledgling G-4, started out much as an infant would with baby steps. Over time it assembled and refined available knowledge and tailored its application to oxidant systems and attempted to make it manageable to even, yet especially, those (like the writer, himself) without specialized post-graduate degrees or training. That led to Standard G94 in 1987 which back then and to a large extent today employs several often-employed insights to characterize and understand combustion. It includes both qualitative and empirical perspectives. Metals are ranked by "burn ratios (BRs)", oxide protection, heat of combustion, adiabatic combustion temperature, and a series of empirical test data. Among these, "burn ratios" provide one of the most important, but very limited tools in allowing speculation as to whether a metal will burn, will burn with ferocity, or if the prospect of combustion is probably excluded. Important in development of these tools is the following history.

In 1817, Humphry Davy was developing what may have been the first scientific perspectives on combustion, and in his *Some Researches on Flame* [*2*], he commented that for a material to burn:

> "The ratio of the combustibility of the different gaseous matters are likewise to a certain extent as the masses of heated matter required to inflame them."
>
> " ...flame...is extinguished.. only when the heat it produces is insufficient to keep up with the combustion, which appears to be when it is incapable of communicating visible ignition... ...as this is the temperature required for the inflammation ....."

This has often been "translated" from the original English to mean that a material (gas phase in Davy's case) can only burn if its heat of combustion is sufficient to raise the material to its ignition temperature. This is not to predict it *will* burn (sufficient heat *allows* but does not mandate combustion), but rather it can *suggest* the possibility of fire resistance if the condition is not met (insufficient heat precludes combustion). This perspective is known to be a watershed contribution from one of histories greatest scientists, but has nonetheless been found flawed and wanting in some ways.

In 1959, Irvin Glassman [*3*] applied similar thinking when he argued that for the rapid combustion of a metal powder as a propellant in a solid-fuel rocket engine, it would need to burn as a vapor (a gaseous diffusion flame in which the metal evaporates and sends a stream of gaseous fuel to burn in the ambient oxidant transferring, radiating, heat back to the metal to sustain evaporation and combustion) and *not* as a liquid or solid (with surface or interior combustion in which the oxidant must migrate to the metal surface potentially being obstructed by things like previously combusted metal slag accumulating there). He surmises that fast combustion would not be possible if a metal's combustion temperature (for example its boiling point or decomposition point) was lower than the metal's boiling point. This came to be known as Glassman's criteria and allowed *excluding* certain metals as prospective rocket fuels. Those excluded metals were of most interest to oxygen safety engineers whose goal, unlike Glassman's, was to avoid combustion. In Glassman's fledgling 1959 analyses,

Table 1 — Material Properties

Metal	ΔHc—cal/g	BR_{MP}	BR_{BP}
silver	35	0.40	-
nickel	980	3.70	-
Copper (Cu)	585	3.90*	-
5%AlCu	1100-1400	-	-
10%AlCu	1100-1400	-	-
Aluminum (Al)	7425	29.0	2.2

*From 1987 through at least 2021, the Burn Ratio of copper in ASTM G94 have been quoted as 2.00 a figure that is apparently in error.

some over-statement and misstatement of the theory occurred such as that where an oxide boiling point (but also meaning its vaporization or dissociation temperature) was greater than a metal's boiling (or vaporization) point expecting that vapor (gaseous diffusion) combustion *would*, rather than *could*, result. As with Davy's insight, this latter day scientific giant's argument, has also proven to be highly useful but also imperfect at times. He himself would remedy some of the exceptional cases within years but some issues would persist. Decades later his argument would be challenged for certain metals [*4*] and in part because many (including the writer at times) incorrectly assumed, that it predicted when vapor phase combustion *would* occur.

Shortly after the G-4 committee was launched [1975], the writer attended a Southern Research Institute (SRI) seminar in about 1977 when Munroe [*5*] proposed the concept of "burn ratios" which elaborated on Davy's and Glassman's thinking by arguing that if a metal does not have sufficient heat of combustion to (1) melt or (2) vaporize itself, then it can not (is *excluded* to) burn (1) as a liquid (slowly) or (2) as a vapor (quickly), respectively. The burn ratio idea appears to have been accepted as "intuitively obvious" rather than rigorously described. It has been very useful in giving perspective to coarse material evaluations for oxygen service and literally mathematically divides the heat of combustion by a simplified heat required to melt (sum of sensible and latent heats of) an elemental metal, calling the ratio the melting-point burn ratio (BR_{mp}), or the heat to boil (called the similar boiling-point burn ratio, BR_{bp}). These ratios are cited and tabulated in ASTM Standard G94 and selected values are shown in Table 1. They are based on elementary (indeed overly simplified) thermodynamic calculation. However, once again, as with Davy's and Glassman's insights, these burn ratios do not precisely reflect what actually happens when a metal burns and so they can be misleading. Might they be too conservative? For example we know pure copper is very fire resistant and yet its reported burn ratio is several times unity.

Furthermore, for nearly 50 years, calculation of burn ratios has been limited to elements that exhibit well-defined melting and boiling points, heat capacities and heats of combustion. Most metals used in oxygen service are alloys. This is unfortunate and tragic and even inexcusable for it has prevented a much better understanding of oxidant fire hazards like the copper and aluminum bronze conundrum to be focused on here.

The Copper and Aluminum Bronze Conundrum

Combustion tests of copper indicate it resists burning quite well even in pure high-pressure oxygen. It is a *very* fire-resistant material. In comparison, aluminum can burn as the burn ratio parameters predict it might in very pure oxygen and burns very rapidly (with at least a large vapor phase combustion portion) and it burns quite destructively.

Aluminum can be alloyed with copper to yield what are called aluminum bronzes. Fractions between 2.6% aluminum and 15% aluminum are cataloged. Although a minority fraction, the alloys at the upper end of this range, have been shown to burn aggressively and destructively as is confirmed by lab tests as well as oxygen hardware made with these high-aluminum bronzes that have exhibited incidents with extensive destruction. Experimental data for alloys from the middle of this range indicate much less flammability but the experience base appears quite small. The writer is not aware of test data nor experience with hardware at the low point of this range though the current body of "understanding" would suggest much less flammability if not the actual fire resistance of copper. So how should AlCu alloys be preferred or disdained for oxygen service and how does one make that decision?

Ideally, one might wonder if AlCu with 2.6% aluminum might have a low burn-ratio at the melting point suggesting fire resistance while AlCu with 15% or more Al, might have burn-ratios at the melting point or even at the boiling point of greater than unity, implying either kind of combustion is *not* excluded.

Table 1 shows the SRI burn ratios for several metals. In the case of copper, a BR_{mp} of 3.9 (apparently reported widely in error as 2.0) suggests combustion is not excluded. Indeed four times the heat needed to melt itself seems rather robust. So why does Cu resist combustion so well? Over the years, such things as protective oxide interfaces, kinetic reaction effects, and heat loss mechanisms have been considered but, to within the writer's knowledge, they were not indicted. Indeed, many of the putative alternative explanations for combustion-interference would not apply if the copper were to be tested in high surface-area-to-volume geometries. And yet, Cashdollar [*6*] reports that at least in air, copper dust clouds are also nonflammable. That just reinforces the conundrum.

This conundrum has persisted for more than the entire 35 years since G94 was published. As a result this opinion and analysis has again [*7*] examined the burn ratio approach with a goal to understanding and improving it. This is not the first such effort, in 2008 and 2014 formal appeals were made to G4 to launch a Thermo-Chemical Equilibrium (TCE) effort (Subcommittee or Task Force) citing the possibility of improved Burn Ratio formulations as one potent incentive. The committee has demurred. The SRI formulation is meaningful, but not the only one possible, and indeed the value SRI cited appears to have been in error for copper. So that error is corrected herein and two additional meaningful formulations of burn ratios are examined and appraised. The better of them employs thermo-chemical equilibrium perspectives that the writer has long-asserted are vital to ASTM Committee G4's primary objective.

Logic

First a clarification of the logical use of burn-ratio thinking. Burn ratios must be viewed in the perspective of logic. In logic the material implication [If A then B] is central. For current burn ratios this might be cited: IF [a material has a melting point burn ratio less than 1.0] THEN [the material can not burn as a liquid]. Logic then allows for the contra-positive formulation: IF [A metal can burn (can NOT not burn) as a liquid] THEN (its burn ratio must be equal to or greater [must NOT be less] than 1.0).

The inverse material implication: IF [a material has a melting point burn ratio greater than 1.0] THEN [the material can/will burn as a liquid] is a fallacy and so is its contrapositive.

As a result, the SRI melting point burn ratio says nothing about the flammability of metals with ratios at or above 1.0. It speaks only to the potential nonflammability of metals with ratios below 1.0. This is because some of the heat of combustion transferred from the metal to itself may not be effective at achieving phase change. Indeed some may be forced to do other things, and other inhibiting factors (like those previously cited) may intervene.

Thermo-Chemical Equilibrium

Since 2008, the writer has sought to incorporate into G4 standards, especially G94, thermo-chemical equilibrium analyses [*8*]. He has met with approximately zero success. It is admittedly a challenging topic to master and is not for the faint of heart nor those of scant motivation. Many a time it has humiliated the writer's best efforts to self-cope with it (fool me once, fool me twice, fool me often), and apparently even some of the G4 Committee's most astute members have had their problems.

However, it is the future and it has more than proven itself (in some cases for about a century in reconciling gas-phase combustion issues (another issue ASTM G4 has avoided) including the technology for automobile pollution and efficiency control. Furthermore, the onus of doing the massive daunting mathematics required is becoming practical (but by no means easy) even for anyone with a PC and a bull-dog-scale tenacity.

In 1992, TCE analysis was first introduced to the G4 collegium led by Steinberg, Wilson and Benz [*4*] reporting on a NASA WSTF study using NASA's own TCE software (Gordon-McBride Code), a very challenging command line algorithm at the time written in Fortran IV. By 1997 it appears Wilson, Steinberg and Stoltzfus [*9*] soured on its benefit and use when it appeared to be way too imprecise (sadly as a possible result of apparent misuse), and was spoken unkindly about in a paper or two, as well as, when Wilson, Steinbeg, and Benz became engaged in an unseemly dispute with Glassman over its proper use and meaning [4,*10,11*]. Perhaps a culture developed that disdained the enormity of its quest and value resulting in the loss of its many benefits. The writer's efforts to promote this theory and software has not enjoyed significant support from the ASTM G4 NASA-member community.

The writer believes that numerous errors were made in those early days including previously cited incorrect operation of the code [*8*], and has with no small degree of futility, pressed ASTM G4 to buy into its active use, both to exploit its potential results but also to tutor the committee and entire community as a vital yet unpleasant duty. When the apparent early errors are corrected some of the results it could have produced back then become far more reputable than how they were reported in the first papers. It has also been used in seeking to edify G4 on what the writer considers a gross dereliction of duty in its G 124 standard, an issue fought going back to the very first ballots of G 124 in the early 1990s (and perhaps another potent incentive to disdain its use).

Since then the writer has struggled to master both later improved but still challenging NASA versions in Windows software now titled CEA (Chemical Equilibrium for Applications) and a second early similar version algorithm from Outokumpu titled "HSC" Chemistry [*12*]. The results of both correspond well with each other and are impressive. Furthermore, the writer believes that G4's mission has suffered substantially for not seeking to exploit this technology as this paper will seek to demonstrate but also including the previously cited major flaw in its current G 124 standard based on a misunderstanding of metal ignition processes that might have been avoided with better TCE chops in the committee.

The early HSC Version was chosen here to seek an explanation (and not for the first time) for the aluminum-bronze conundrum, and a plausible if incomplete result may have finally been achieved in this humble opinion and is proposed to the oxygen safety community for whatever use it may allow, but also to bolster the case for deploying TCE methods and results.

New, Better Burn-Ratio Formulations

Burn Ratios, their formulation and their significance have been an issue the writer has struggled with before. Burn ratios are to some extent like low hanging fruit, easy to buy into. However, the past ability to simply calculate burn ratios but only for elements among metals has made the evaluation and ranking of alloys difficult. TCE theory can eliminate this barrier and perhaps open other useful tools and parameters as will be explored herein.

The elementary earlier described insights of Davy, Glassman and Munroe, were based on the idea that a material must properly exploit its own heat of combustion to sustain any fire. Hence, in keeping with the thinking, during propagation, incremental heat of combustion must be used to heat, melt or vaporize incremental metal that may then burn. This will examine one prospect for that process.

This is not to argue that solids can not burn. Indeed, the classic example is the charcoal fire which is so hard to start burning, largely due to the negligible vapor pressure of atmospheric-pressure carbon which neither melts nor boils during combustion at atmospheric pressure. Yet even here, a key factor to combustion is in heating the entire carbon bed to a point where its in-situ heat of combustion is capable of supporting surface combustion, which is, as expected, typically very slow combustion. However, a more sophisticated perspective will be attempted later. Note that while "burn ratios" can not be reported for such carbon, due to the "melting and boiling" problem, TCE methods do allow similar understanding. An earlier commentary suggest that the carbon burn ratio at the sublimation point (BR_{sp}) is much smaller than unity [*12*] perhaps precluding gaseous diffusion combustion.

Hence, with common metals in the adiabatic case, there must be sufficient heat (as predicted by the BR_{mp} and/or BR_{bp}) to melt (or vaporize) the metal. This led to the first clas-

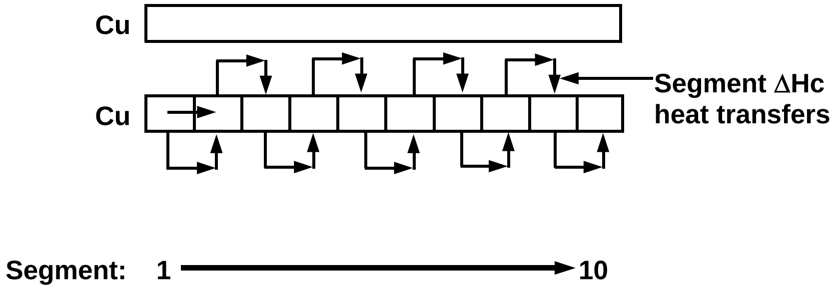

FIG. 1—*Hypothetical divided, insulated copper specimen.*

sic formulation for SRI Burn Ratios (call it BR1 here) cited in G94 [*1*] of :

$$BR1_{mp} = \Delta H_{combustion} / (\Delta H_{rt\text{-}mp} + \Delta H_{fusion})$$

$$BR1_{bp} = \Delta H_{combustion} / (\Delta H_{rt\text{-}mp} + \Delta H_{fusion} + \Delta H_{mp\text{-}bp} + \Delta H_{vap})$$

Where: $\Delta H_{combustion}$ = heat of combustion
$\Delta H_{rt\text{-}mp}$ = heat to warm metal room temperature to melting point
ΔH_{fusion} = latent heat of fusion
$\Delta H_{mp\text{-}bp}$ = heat to warm metal from meting point to boiling point
ΔH_{vap} = latent heat of vaporization

Hence from Table 1, since silver's heat of combustion is just 35 cal/g and that is just 0.4 times the amount needed to fully melt it, it seems unlikely to be able to burn. Whereas aluminum has a heat of combustion of 7425 cal/g which is 29 times the amount needed to melt aluminum so that burning as a liquid is clearly not excluded on this basis. Note that exclusion from burning as a solid also implies exclusion from burning as a liquid, exclusion from burning as a liquid also implies exclusion from burning as a vapor.

However, the oxidant safety community has not focused to date on all the details of delivering the heat. Hence when copper has a $BR1_{mp}$ of 3.9 (or even the 2.00 as has been previously reported in apparent error), clearly a heat greater than that required to melt itself, the community has resorted to explanations for its resistance to combustion such as that protective oxide can inhibit delivery, reaction kinetic effects can slow delivery, and heat loss mechanisms can fritter the heat away. However, other factors may play a role including TCE factors like those used in earlier commentary to examine minimum burn lengths to define self-sustaining combustion [*13*,*14*].

Consider the hypothetical perfectly-adiabatic case of copper as depicted in Fig. 1. Next imagine a slow-motion or stop-action chemical-reaction of this copper: increment-by-increment. More sophisticated countercurrent heat exchanger models (that may or may not be realistic in the real world) can and have been speculated upon earlier [*7*]. Also assume the copper might be capable of burning as a liquid. Imagine it being divided into ten segments (increments) that can be independently controlled and insulated perfectly. Each segment is to be reacted with a stoichiometric amount of oxygen to allow formation of CuO, the

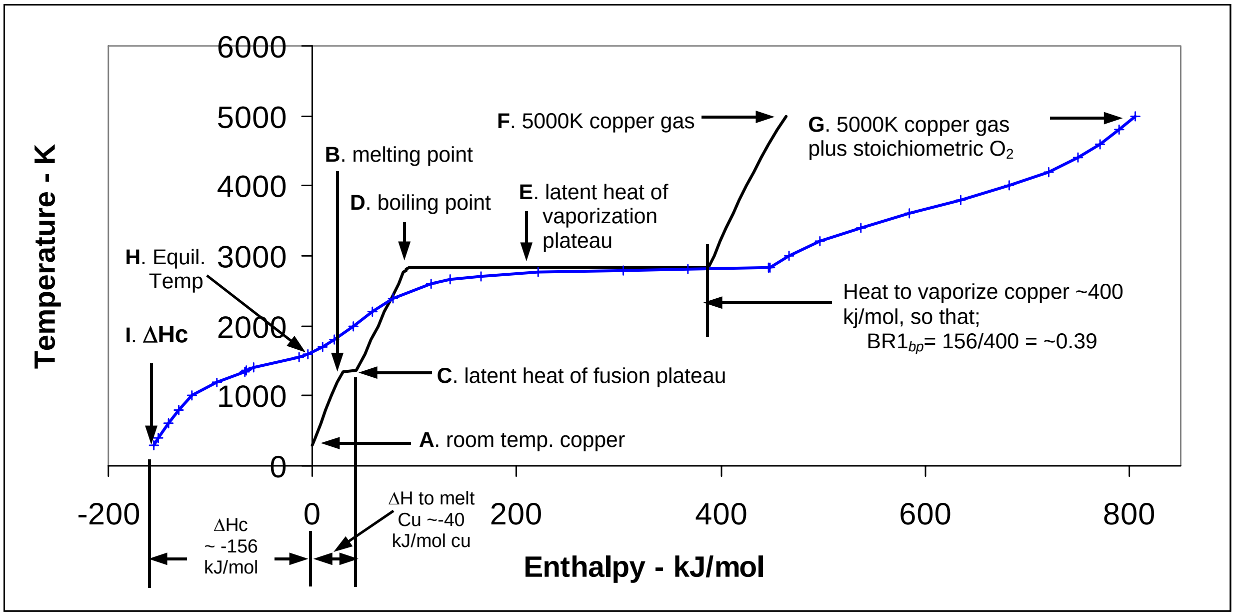

FIG. 2 —*Copper thermodynamics and thermo-chemical equilibrium per HSC.*

most stable copper oxide (as apparently typically happens in combustion). Imagine the first segment to be perfectly insulated and achieving its equilibrium with oxygen as predicted by both TCE software codes. This might happen quickly if burning and melting were to happen, but could also result from normal corrosion processes though it might take millions of years for that equilibrium to obtain. FIG. 2 displays the equilibrium temperature, heat transfers at a few points including final equilibrium at point "I" using the Outokumpu HSC software for one mol of copper.

Room temperature copper starts at point "A" and is heated to point "B", the melting point. Further heating melts the copper along the latent heat of fusion plateau shown as point "C". The liquid copper is then heated to its boiling point at point "D "and then a huge amount of heat is added to vaporize the copper through its latent heat of vaporization plateau (shown as point "E"). Finally the copper gas is shown heated to 5000K at point "F".

When the heat to form 5000K stoichiometric oxygen gas is added, the curve jumps to point "G" where it produces approximately the same conditions that result for unmixed copper and oxygen as for chemical equilibrium of a mixture as shown, because at this temperature little reaction is possible, indeed diatomic oxygen is taken as being dissociated into individual oxygen atoms. No copper oxide can survive at sufficiently high temperature. As an equilibrium mixture cools from point "G", various compounds and phases form, each of them adding or subtracting heat. At the point "H" all added heat is retrieved and so point "H" is the equilibrium condition point that the copper and oxygen would produce upon millennia of slow adiabatic corrosion, or perhaps rapid combustion...if the rapid process of combustion were possible. In other words, if combustion were to occur the state of the adiabatic copper would jump from point "A" to point "H".

Notice that at equilibrium, the temperature (also called the adiabatic combustion temperature whether combustion is possible or not) predicted is about 1630 K. If that were allowed to cool to room temperature at point "I", the heat that would flow from it would be about -156,000 J (also known as both the Heat of Formation and Heat of Combustion when combustion is possible). Notice that the curve for copper alone dictates that to fully melt copper requires the addition of about 40 kJ of heat. Therefore the SRI $BR1_{mp}$ is roughly 156/40 or about 3.9 (formerly reported as 2.0 in presumed error)[3]. This $BR1_{mp}$ suggests the burning of copper as a liquid can not be excluded thermodynamically. We can examine the validity of this BR1 estimate or we can be resourceful to rationalize copper's burn resistance.

So let's attempt to examine a slow motion, stop action, fictitious model to burn the segments in the enlarged Fig. 3, Part 1. We have retrieved –156 kJ/mol of heat of combustion from segment one at room temperature. If we can add 25% of this heat to Segment 2, then at point "A", we will have fully melted the copper segment and it might burn as a liquid. If it does burn, its status will shift to the equilibrium curve at Point "B" at about 2000K. If we now allow it to cool to point "C", we can extract the exact supplemental heat added and return it to Segment 1. At this point Segment 2 would have the same equilibrium that Segment 1 had following its combustion and further cooling will allow it to transfer another –156,000 J/mol. This incremental heating can now be used to similarly promote combustion of Segment 3 and so forth.

This result from this model would not be changed even if $BR1_{mp}$ was somewhat less than 3.9, and as small as 1.0. Notice that the same description of this BR1 model applies for all values of BR1 down to 1.0 for which *all* the heat of combustion of any Segment x would be used to melt all of Segment (x+1). But what about $BR1_{mp}$ values below 1.0?

Suppose $BR1_{mp}<1.0$. Down to say a carefully chosen 0.92. So if combustion proceeded like this visualization (not alleging it does this in reality), this does not say that 0.92 of Segment 2 could be melted even with all of the heat of combustion transferred from Segment 1. Note on Figure 3, Part 2, that the latent heat of fusion of copper is about 30% of the total to fully melt copper. Hence a BR1 of 0.92 indicates that after segment 2 was heated to its melting point, only about 66% of it (at point D) could be melted. Combustion of that portion at point E, and cooling it to point F and ultimately to room temperature would transfer only 66% of the heat needed to fully melt the next segment. This is a decaying sequence that helps understand while some metals when ignited burn with a decaying fire and then extinguish.

Indeed. if the $BR1_{mp}= 0.7$ and Segment one were to combust, then no more than 70% of the heat need to fully melt segment 2 might transfer and would not produce any melting at all. Hence the lower values of $BR1_{mp}$ especially when less then unity are good indicators of fire resistance.

Of course if Segment 2 had an ignition temperature less than its melting point, it might ignite as a solid and burn with its own preheated heat of combustion. Some metals, iron for example with a $BR1_{mp}$ of 5.1, will ignite while solid and burn as a liquid if raised to its ignition temperature which is less than its melting point. This contingency is examined in an earlier analysis [*14*] and more sophisticated models might yield a different conclusion. However in the case of copper this possibility does not apply.

Hence for some metals, another key parameter might be the ratio of the heat of combustion to the heat required to achieve ignition temperature. However, in the case of copper,

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[3] It appears SRI based the calculation upon the formation of Cu_2O with half the heat of formation of CuO and which TCE predicts will not form.

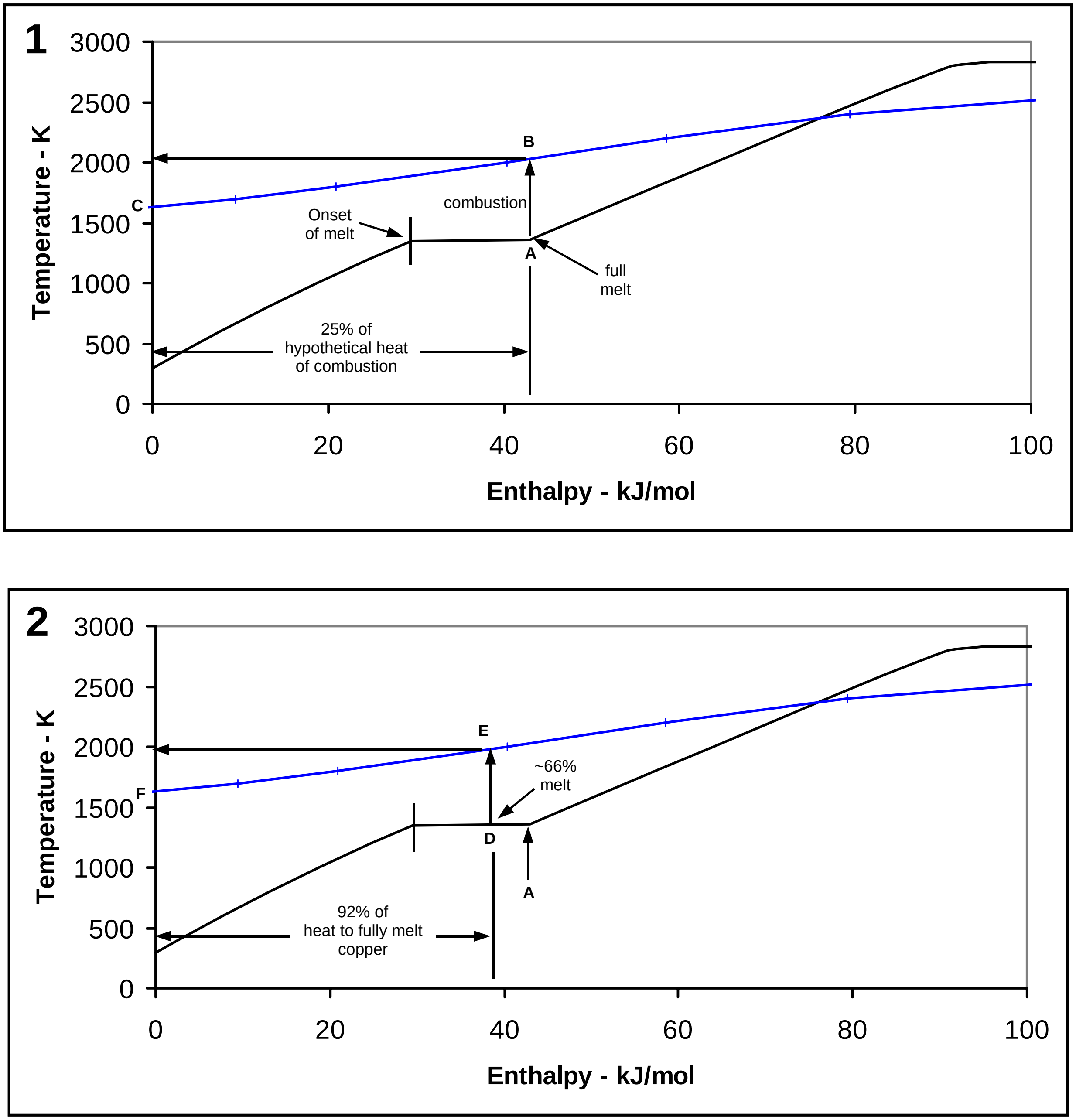

FIG. 3 —Magnified c*opper thermodynamics and thermo-chemical equilibrium per HSC.*

ignition has not been observed below (or for that matter above) its melting point.

Obviously this interpretation is quite simplified and a more sophisticated analysis may be better. Hence the BR1 formulation could be improved, but nonetheless has been very useful for understanding some coarse things about metals.

Formulation 2 — BR2

Notice that each segment of a specimen that completely burns must react with a constant amount of oxygen gas. Even in an adiabatic case, as each segment heats it must also heat the oxygen. On Figure 2, Points “F’ and “G”, illustrated how the amount of heat required to warm stoichiometric oxygen to the 5000K temperature (the gap between Points “F” and “G”), is nearly as great as the heat required to heat the copper specimen to 5000 K.

If 5000 K copper were heat-exchanged with room temperature oxygen the combined temperature would plunge. Hence perhaps one should also include the heat to warm the oxygen to the melting point in an alternative second Burn Ratio formula.

Therefore, a second, BR2, formulation estimate might be:

$$BR2_{mp} = \Delta H_{combustion} / (\Delta H_{Cu\ (rt\text{-}mp)} + \Delta H_{fusion} + \Delta H_{O_2\ (rt\text{-}mp)})$$

$$BR2_{bp} = \Delta H_{combustion} / (\Delta H_{Cu\ (rt\text{-}mp)} + \Delta H_{fusion} + \Delta H_{Cu(mp\text{-}bp)} + \Delta H_{vap} + \Delta H_{O_2\ (rt\text{-}bp)})$$

Where: $\Delta H_{combustion}$ = heat of metal combustion
$\Delta H_{rt\text{-}mp}$ = heat to warm metal room temperature to melting point
ΔH_{fusion} = latent heat of metal fusion
$\Delta H_{mp\text{-}bp}$ = heat to warm metal from melting point to boiling point
ΔH_{vap} = latent heat of metal vaporization
$\Delta H_{O_2\ (rt\text{-}mp)}$ = heat to warm oxygen to melting point
$\Delta H_{O_2\ (rt\text{-}bp)}$ = heat to warm oxygen to boiling point

In this case, the fraction of the heat of combustion that is needed to melt or boil the next segment is increased and so a smaller burn ratio would be calculated. Fig 4 is another thermal profile generated with HSC of the kind used to estimate these changes and that the writer feels should be generated and published within a G4 standard for all metals commonly used with the full range of oxidants.

Shown on Figure 4 is the same curve to heat then melt then boil copper metal as in Figure 2. Also exhibited using HSC results is the heat to warm stoichiometric (to form CuO) oxygen gas. These two curve’s heats are added (laterally) to represent the sum of the separate (unmixed) heats assuming no interactions. The curves are again extended to 5,000 K at which point the copper gas has expanded and the diatomic oxygen gas, O_2, has broken into monomolecular, O, oxygen. If the copper and oxygen were to be mixed at the 5,000 K point one would expect little if any reactive heating or cooling (Note that a small amount of *cooling* is indicated in this analysis). The fourth curve (with “+” markers) is the same thermochemical equilibrium calculation from HSC for the copper and oxygen mixture and is the same as the corresponding curve in Figure 2. Notice at 5,000 K it is virtually exactly the same value as for the sum of the unmixed components. Upon cooling from 5,000K this curve again shows how thermo-equilibrium temperature varies as various chemical compounds and phases form and passes through the ~1630 K adiabatic combustion temperature at the zero enthalpy point.

Ultimately upon cooling the same -156 kJ heat of combustion is recorded. However, in this case the heat to warm the combined copper and oxygen is about 55 kJ/mol. Therefore the $BR2_{mp}$ formulation is roughly 156/55 is about 2.8. This is significantly less than the 3.9 estimate from $BR1_{mp}$, and therefore more reflective (well! less contradictory) of the fire resistance copper exhibits in tests and real-world experience.

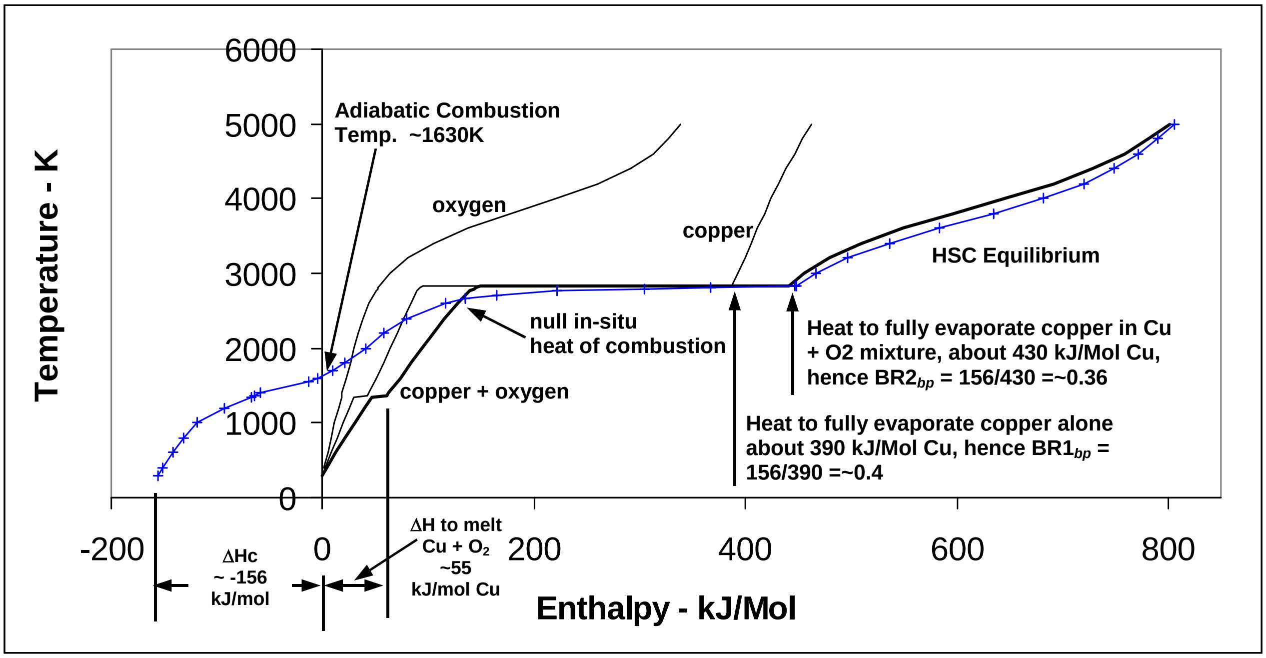

FIG. 4 —*Copper plus oxygen thermodynamics and thermo-chemical equilibrium per HSC.*

Notice the point on FIG. 4, designated as the “null in-situ heat of combustion” point. Recall from FIG 2, if room temperature copper at point “A” were to combust, its state would shift vertically to point “H” and after cooling back to room temperature at point “I” would transfer its heat of combustion of 156,000 J/mol. Similarly if copper were to be warmed to an elevated ambient temperature and combusted its state would shift up to the equilibrium curve and upon cooling back to its ambient state would release a different “in-situ” heat of combustion (call it in-situ heat of formation if combustion is not possible). However, at the point on FIG 4 designated “null in-situ heat of combustion” the preheated copper state is the same as the equilibrium curves and so combustion would not release any heat. Furthermore, at ambient temperatures above this, where the preheated copper curve lies above the equilibrium curve, when copper is combined with oxygen, a “negative combustion” is predicted: the products cool instead of warming. The reaction is endothermic. Hence copper is precluded from “burning” as a gas. This might be equivalent or identical to restating Glassman’s criteria as: metals that have as in-situ heat of combustion temperature less then their boiling/vaporization temperature cannot burn as a vapor.

This second more realistic and meaningful burn ratio formulation that TCE allows calculation of helps explain why copper is less likely to burn as a liquid but does not exclude combustion (still being about 2.8) and again requiring resort to things like mechanistic arguments to understand copper’s combustion resistance is needed.

Formulation 3 — BR3

Burn ratios in a truer spirit of these insights can also be formulated yet a third way (and perhaps still others). Recall the Second Law of Thermodynamics (SLT), to wit, this short version:

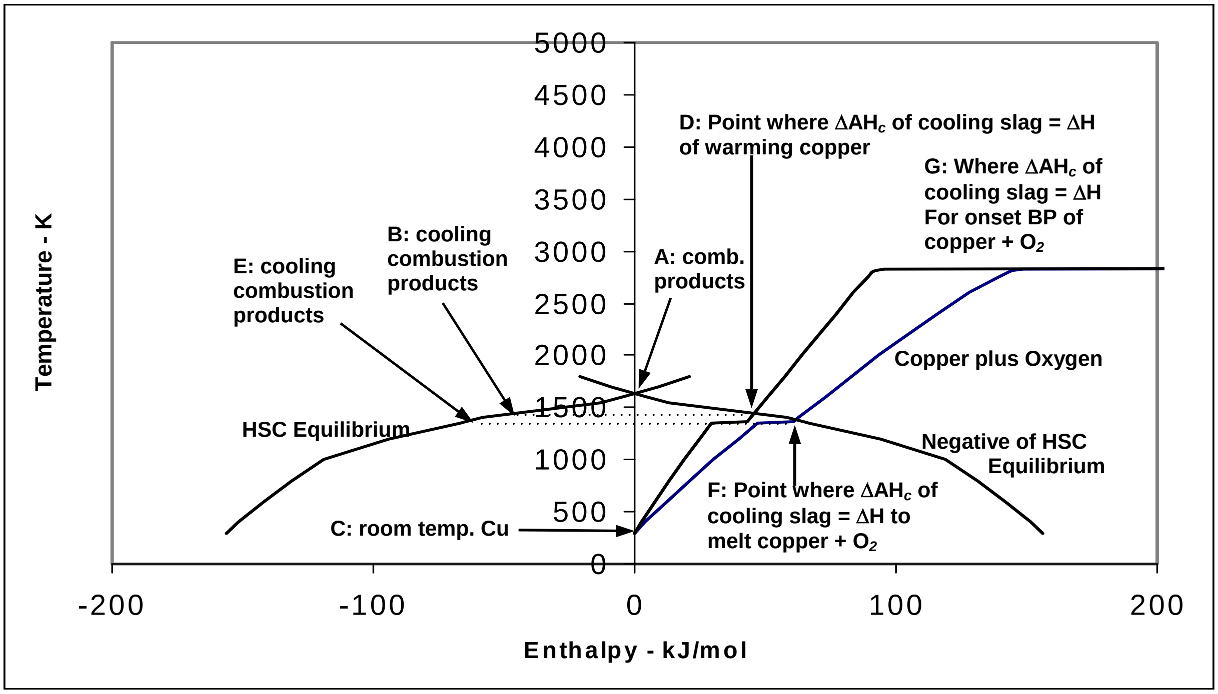

FIG. 5 —*Comparison of* ΔAH_c to heats to melt Cu and Cu plus O_2.

SLT: Heat flows from a higher temperature to a lower temperature not vice versa.

Hence just as it is obvious (easy to buy into the idea) that a material must release enough heat of combustion to melt itself (yielding the entire body of melting point burn-ratio insight in G94), so too a metal must develop a temperature in its products of combustion above those that it wishes to melt namely meaning in the simplest cases above its melting temperature. After all, one can not do certain kinds of brazing using a torch that does not get hot enough, regardless of how long the low temperature torch is used and how much heat it transfers (this is “obvious” to anyone who has tried to silver braze with a propane/air torch).

Instead of using the entire heat of combustion, in the calculation one may be limited to an “Available Heat of Combustion (ΔAH_c)”. If one considers segment one combustion in Fig 1, and then places it in thermal contact with cool segment 2 at room temperature, the entire heat of combustion can not be transferred to the metal and oxygen of segment 2. As the temperature of segment one falls and causes the temperature of segment 2 to rise, the SLT tells us that heat flow ceases when they are equal. Nor can one simply split the difference, take half the heat of combustion, and assign it to each segment for the heat/temperature curves for the pre- and post-combustion segments are different in properties.

Fig 5 duplicates and magnifies the key data of Fig 4 and shows how this works, thanks to TCE software. Notice as the combustion products at point “A” cool to point “B”, the maximum heat that can be transferred to heat the copper alone (no O_2) is from point “C” to point “D”, which is just slightly more than needed to melt the copper. The negative of the cool-down curve is shown to indicate the intersection where equality occurs at point “D”. If the combustion products cool further, to point “E”, they intersect the curve for heating of the copper plus stoichiometric oxygen at a lower temperature with a larger heat transfer at point “F” where the intersection with the negative of the cool-down curve shows they are nearly exactly the amount need to melt the copper.

Hence the following Formulation 3 for the burn ratio, $BR3_{mp}$, can be proposed

$$BR3_{mp} = \Delta HA_{combustion} / (\Delta H_{Cu\ (rt\text{-}mp)} + \Delta H_{fusion} + \Delta H_{O_2\ (rt\text{-}mp)})$$

$$BR3_{bp} = \Delta HA_{combustion} / (\Delta H_{Cu\ (rt\text{-}mp)} + \Delta H_{fusion} + \Delta H_{Cu(mp\text{-}bp)} + \Delta H_{vap} + \Delta H_{O_2\ (rt\text{-}bp)})$$

Where: $\Delta HA_{combustion}$ = heat of combustion available for transfer
$\Delta H_{rt\text{-}mp}$ = heat to warm metal room temperature to melting point
ΔH_{fusion} = latent heat of fusion
$\Delta H_{mp\text{-}bp}$ = heat to warm metal from melting point to boiling point
ΔH_{vap} = latent heat of vaporization
$\Delta H_{O_2\ (rt\text{-}mp)}$ = heat to warm oxygen to melting point
$\Delta H_{O_2\ (rt\text{-}bp)}$ = heat to warm oxygen to boiling point

Using formulation 3, the $BR3_{mp}$ as shown on Figure 5 is about 1.0, a value that argues copper is borderline for combustion even in a perfectly adiabatic case, and its resistance should be greater in a real case where additional heat losses and other inhibiting obstacles to combustion are present. In real combustion, any heat losses at all would reduce the $BR3_{mp}$ below the threshold requirement. Notice also that the available heat of combustion to boil copper is zero, therefore $BR3_{bp} = 0$, for again in much like Glassman's insight, the adiabatic combustion temperature is less than the boiling-point temperature.

This perspective suggests that were the copper and oxygen to be initially heated to an elevated level that a threshold might be exceeded and combustion might be possible. FIG 6 repeats FIG 5 and indicates how an ambient 1000K temperature would affect the BR3 parameter for copper with warmed oxygen. The cool-down curve is flipped to show that the $BR3_{mp}$ with a 1000K ambient increases to about 1.2. Although there are test data for copper at room temperature and elevated pressure, there do not appear to be test data for elevated ambient temperature. Further useful data in this regard may be possible to achieve without bankrupting research budgets and will be examined in a still-later section.

Consequences

This in effect argues dual (or an even greater number of) criteria must be met to enable combustion. This is not a new or curious possibility. Indeed, it is well established that for a flammable material to burn, it must meet dual criteria: (1) an ignition temperature some amount greater then the minimum, and (2) an ignition energy some amount greater then the its respective minimum. One can provide extreme temperature at less than the minimum ignition energy (for example a spark to ignite cold metals) or one can provide extreme ignition heat short of the minimum ignition temperature and combustion does *not* occur.

This suggests, as has been known, copper combustion is excluded even in oxygen and that is good to verify. Unless proven invalid, this perspective provides a very nice resolution to the conundrum of copper's too-high $BR1_{mp}$. Therefore, this kind of analysis is ideal for citation in the ASTM G94 standard. Thanks to TCE software G94 can cite theoretical: Burn Ratios, adiabatic combustion temperatures, and perhaps other parameters, not only for

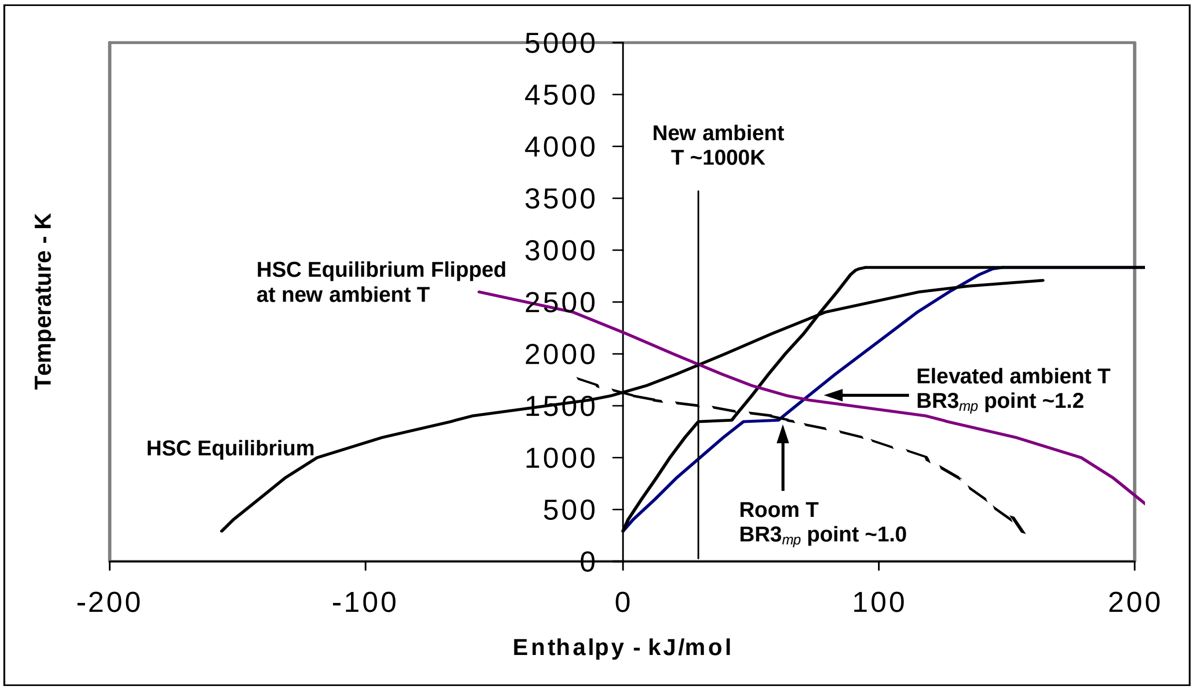

FIG. 6 —*Effect of elevated ambient temperature.*

a small number of elements, but for a vast range of metals and alloys. Its absence 35 years after first publication raises questions as to whether G4's ability or intention to serve its prime objectives has been misplaced.

Liquid Versus Vapor Burning

So far, we have examined a material, copper, that does not burn in oxygen despite a curiously high $BR1_{mp}$. We have seen that even if some liquid were to form from prior segment combustion or from added ignition heat, that any combustion would "coast" down and extinguish. Any supplemental heat would be depleted in portions needed to bring each segment up to its melting temperature. Hence it seems all of the BR_{mp} formulations must be based on heat to melt the entire segment. Is this the case also with burning as a vapor? Must BR_{bp} formulations be based upon the heat needed to boil the *entire* segment? In other words can a metal with a $BR_{bp}<1$ burn partially as a vapor? This is an issue off-point for the goal of this commentary, but is worthy of separate examination. However, the key factors previously examined might still apply. For example, as has been shown before, if a specimen's heat of combustion has 70% of the heat required to fully vaporize another segment a disproportionate amount of that 70% might be required to heat the segment to it boiling point and so less than 70% of the segment could be actually vaporized, and this is a harbinger of a decaying combustion. However, in this case, one might also find that the transient combustion and fractional combustion during that coast-down might be significantly destructive.

Nonetheless, FIG. 4 also shows the $BR1_{bp}$, and $BR2_{bp}$ values for copper of roughly 0.4 and 0.36. Note on FIG. 4 that since the adiabatic combustion temperature of the copper plus oxygen is just 1630K that no heat transfer above the boiling point of copper (about 2835K) is possible and the $BR3_{bp}$ is 0/430 = 0. Perhaps more sophisticated models will al-

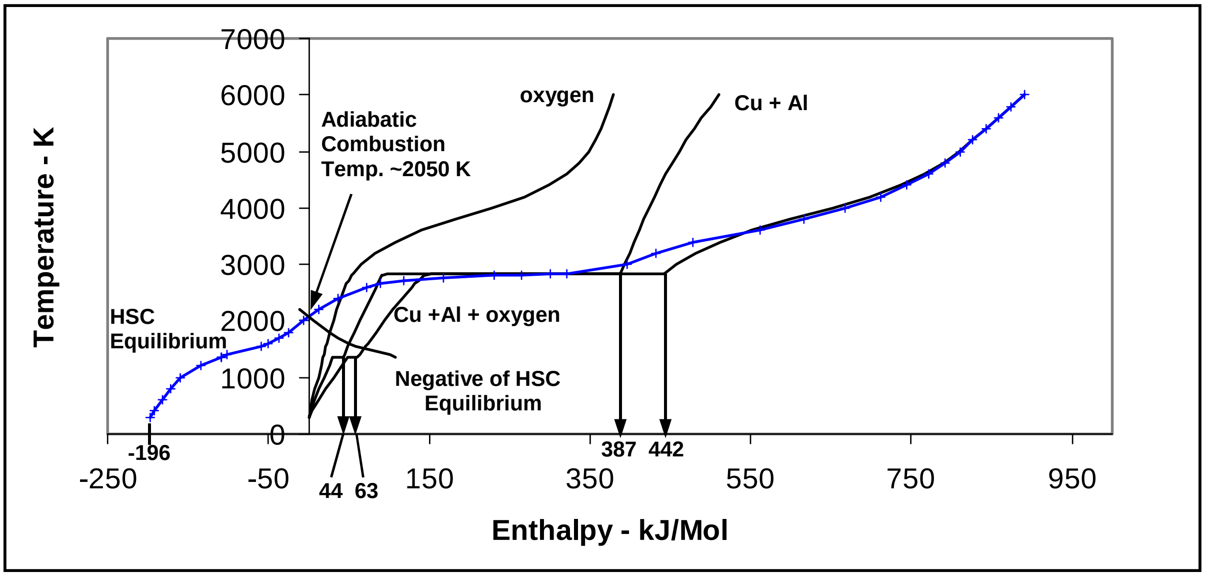

FIG. 7 —*Fig. 4 analog for 2.6% aluminum/copper.*

low refinement, but this suggests copper has little chance of burning even partially as a vapor.

A Tale of Two Bronzes

As noted earlier, aluminum can be alloyed with copper to yield what are called aluminum bronzes. We have seen there are about 26 alloys cited in the ASM handbook with aluminum weight fractions between 2.6% aluminum and 15% aluminum. Although aluminum is a minority weight fraction, the alloys at the upper end of this range (>10% Al [*15*]), have been shown to burn aggressively and destructively as is confirmed by oxygen hardware made with these high-aluminum bronzes that have exhibited incidents with extensive destruction. Experimental data for alloys from the middle of this range (~7% Al [*1*]) indicate much less flammability but this is a small experimental base and the experience base also appears quite small or is undocumented. There do not appear to be test data nor a lot of experience with hardware at the low point of this range though the current body of "understanding" would suggest much less flammability if not the actual fire resistance of copper. So should AlCu alloys be preferred or disdained for oxygen service? To see what perspective HSC software can provide to this "burning" issue, Figures analogous to Figures 4 and 5 will be provided for the entire range of possible Al and Cu mixtures, 0-100%. These will allow $BR3_{mp}$ *and* $BR3_{bp}$ (as well as other) parameters to be estimated. The extreme limits of the alloy family (2.6% to 15% by weight) will be covered. Pure copper has already been addressed.

2.6% Aluminum/Copper

Figures 7 and 8 are analogous to Figures 4 and 5, respectively, but exhibit the heats to warm 2.6% aluminum, 97.4% copper (by weight) with stoichiometric oxygen to form CuO and Al_2O_3. Also shown is the sum of the unmixed materials and the HSC curve for the

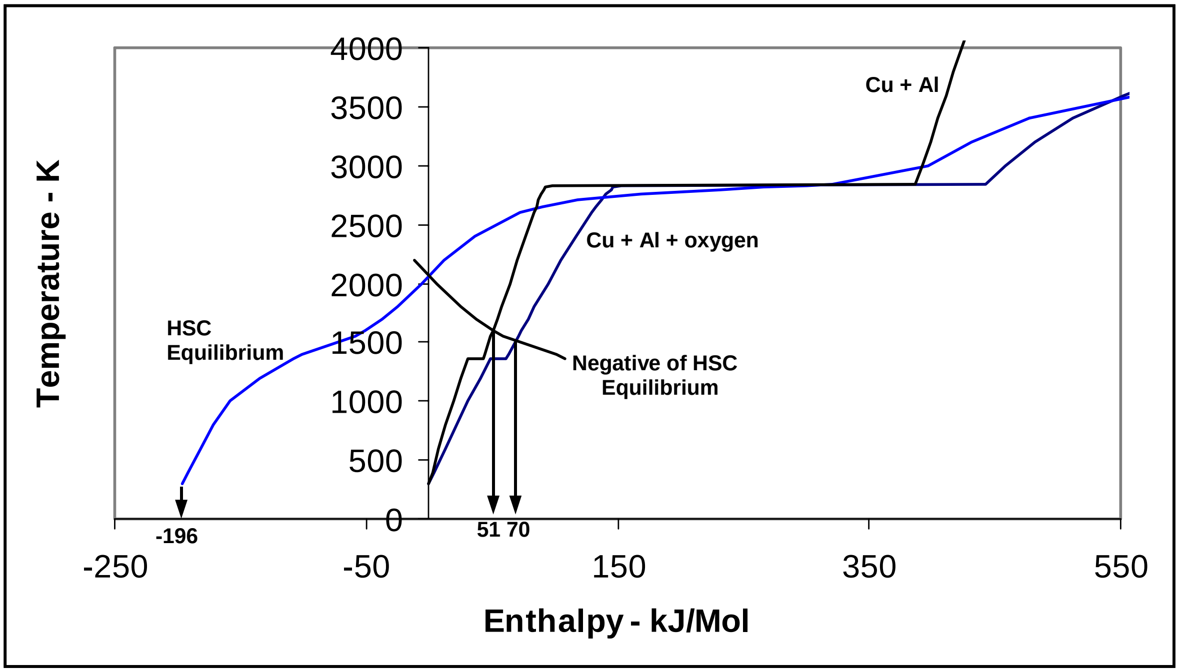

FIG. 8 —*Fig. 5 analog for 2.6% aluminum/copper.*

equilibrium combined materials. The Appendix provides more details on the conditions used for those who might wish to replicate, fine-tune, or critique this example.

From these figures, we see that the heat of combustion increases from about 156 kJ/mol to about 196 kJ/mol (+33%), $BR1_{mp}$ from 3.9 to 4.5, $BR1_{bp}$ from 0.4 to 0.51, $BR2_{mp}$ from 2.8 to 3.1, $BR2_{bp}$ from 0.36 to 0.44, $BR3_{mp}$ from 1.0 to 1.1, $BR3_{bp}$ remains at zero. Again the $BR3_{bp} = 0$, because the adiabatic combustion temperature (about 2050 K) is well below the 2835K boiling point temperature of copper.

8% Aluminum/Copper

Figures 9 and 10 are also analogous to Figures 4 and 5, respectively, but exhibit the heats to warm 8% aluminum, 92% copper (by weight) with stoichiometric oxygen to form CuO and Al_2O_3. Also shown is the sum of the unmixed materials and the HSC curve for the equilibrium combined materials. The Appendix provides more details on the conditions used for those who might wish to replicate, fine-tune, or critique this example.

From these figures, we see that the heat of combustion increases from about 156 kJ/mol to about 272 kJ/mol, $BR1_{mp}$ becomes 4.5, $BR1_{bp}$ becomes 0.70, $BR2_{mp}$ becomes 4.25, $BR2_{bp}$ becomes 0.60, $BR3_{mp}$ becomes 1.48, and $BR3_{bp}$ remains at zero. Again the $BR3_{bp} = 0$, because the adiabatic combustion temperature (about 2650K) is still below the 2835K boiling point temperature of copper.

16% Aluminum/Copper

Figures 11 and 12 (page 19) are also analogous to Figures 4 and 5, respectively, but exhibit the heats to warm 16% aluminum, 84% copper (by weight) with stoichiometric oxy-

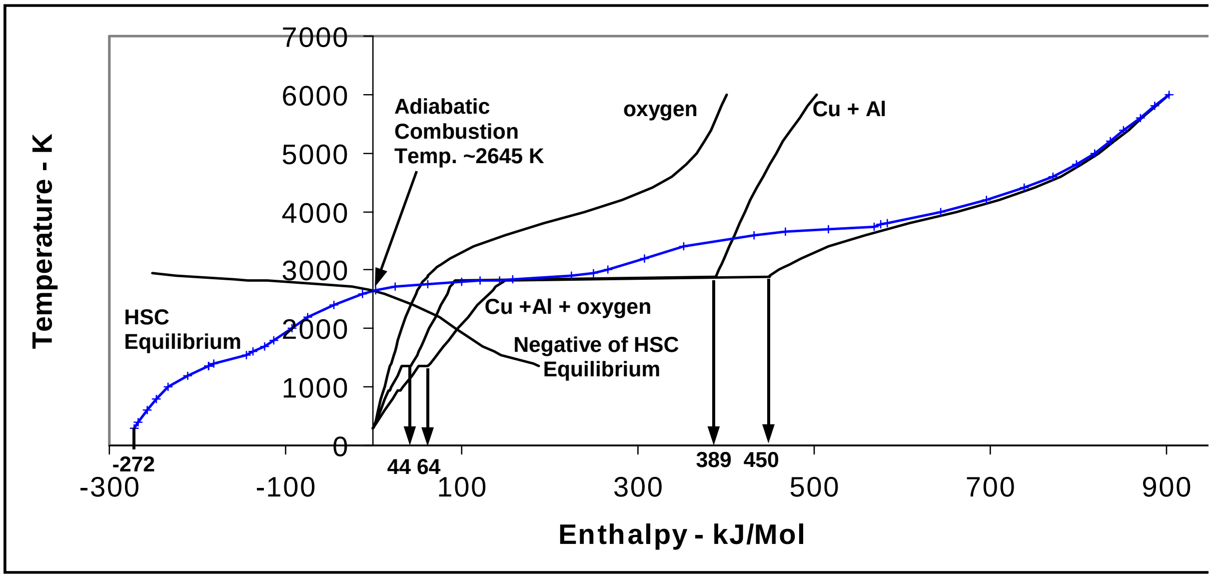

FIG. 9 —*Fig. 4 analog for 8% aluminum/copper.*

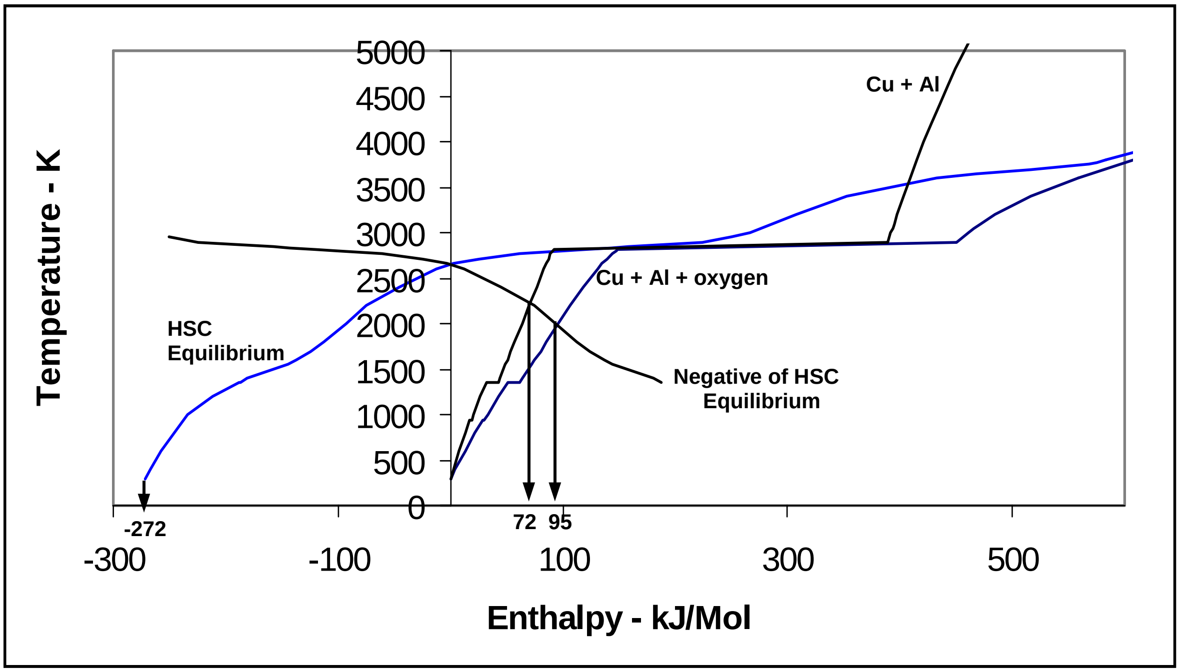

FIG. 10 —*Fig. 5 analog for 8% aluminum/copper.*

gen to form CuO and Al_2O_3. Also shown is the sum of the unmixed materials and the HSC curve for the equilibrium combined materials. The Appendix provides more details on the conditions used for those who might wish to replicate, fine-tune, or critique this example.

From these figures, we see that the heat of combustion increases from about 156 kJ/mol to about 360 kJ/mol, $BR1_{mp}$ becomes 8.18, $BR1_{bp}$ becomes 0.93, $BR2_{mp}$ becomes 5.54, $BR2_{bp}$ becomes 0.80, $BR3_{mp}$ becomes 2.09, and $BR3_{bp}$ remains at about zero. Again the $BR3_{bp} \sim 0$, because the adiabatic combustion temperature (about 2840K) is about equal to

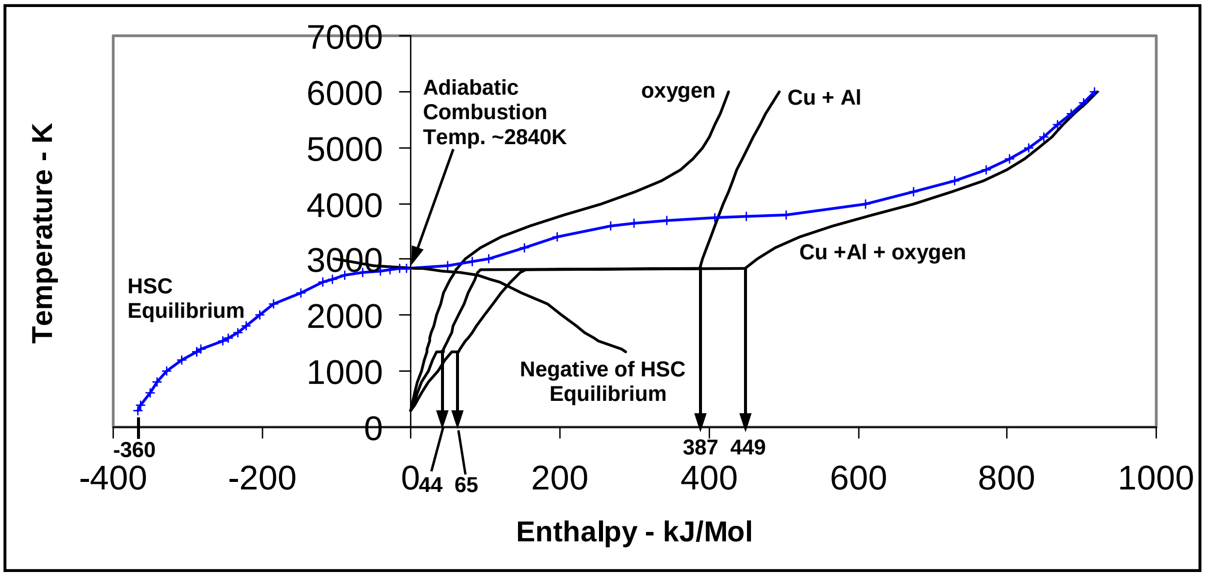

FIG. 11 —*Fig. 4 analog for 16% aluminum/copper.*

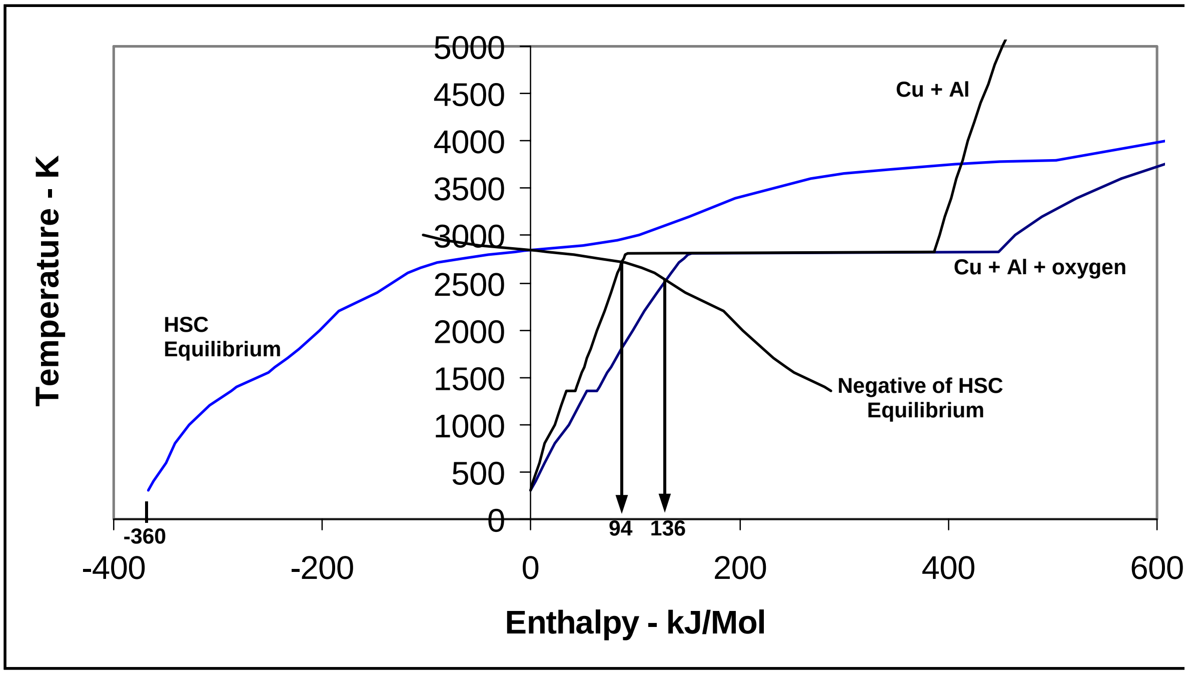

FIG. 12 —*Fig. 5 analog for 16% aluminum/copper.*

the (2835K) boiling point temperature of copper.

40% Aluminum/Copper

Figures 13 and 14 are analogous to Figures 4 and 5, respectively, but exhibit the heats to warm 40% aluminum, 60% copper (by weight) with stoichiometric oxygen to form CuO and Al_2O_3. Also shown is the sum of the unmixed materials and the HSC curve for the

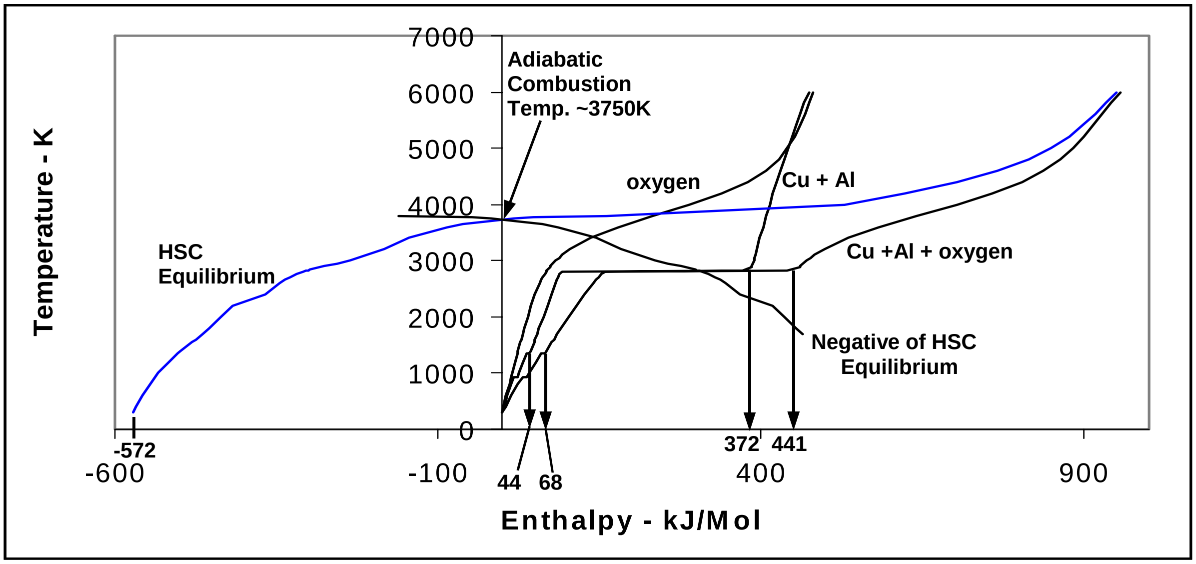

FIG. 13 —*Fig. 4 analog for 40% aluminum/copper.*

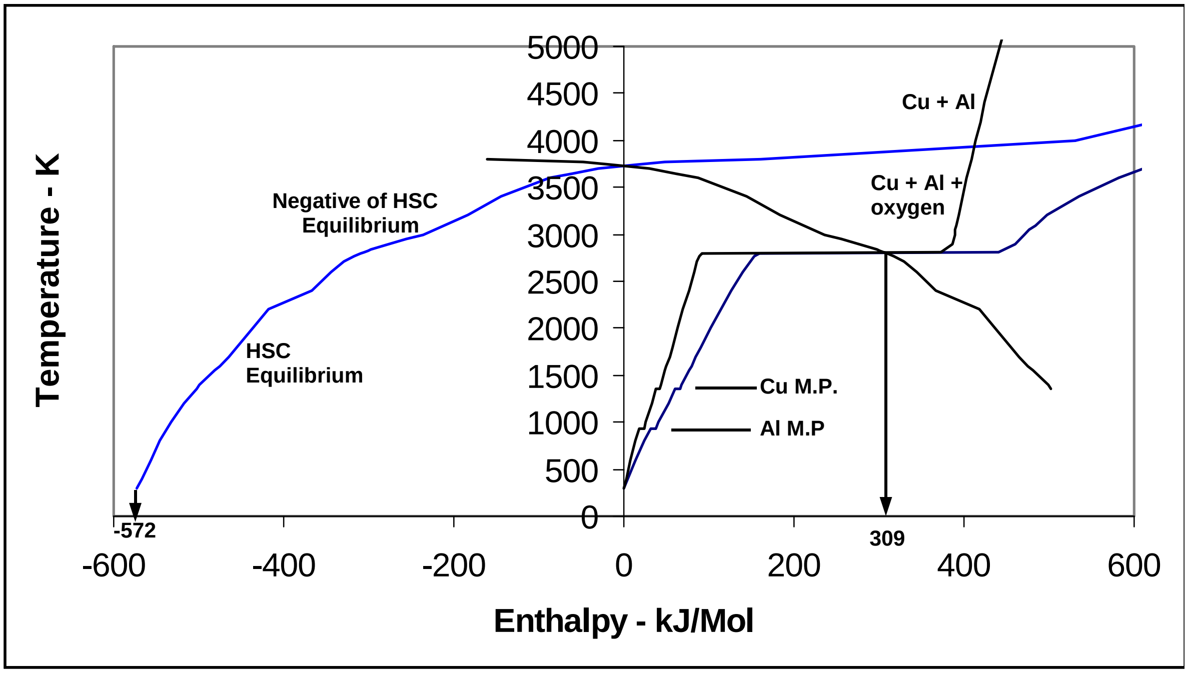

FIG. 14 —*Fig. 5 analog for 40% aluminum/copper.*

equilibrium combined materials. The Appendix provides more details on the conditions used for those who might wish to replicate, fine-tune, or critique this example.

From these figures, we see that the heat of combustion increases from about 156 kJ/mol to about 572 kJ/mol, $BR1_{mp}$ becomes 13.0, $BR1_{bp}$ becomes 1.5, $BR2_{mp}$ becomes 8.41, $BR2_{bp}$ becomes 1.29, $BR3_{mp}$ becomes 4.5, and $BR3_{bp}$ becomes 0.70 because the adiabatic combustion temperature (3750K) now exceeds the (2835K) boiling point temperature of copper.

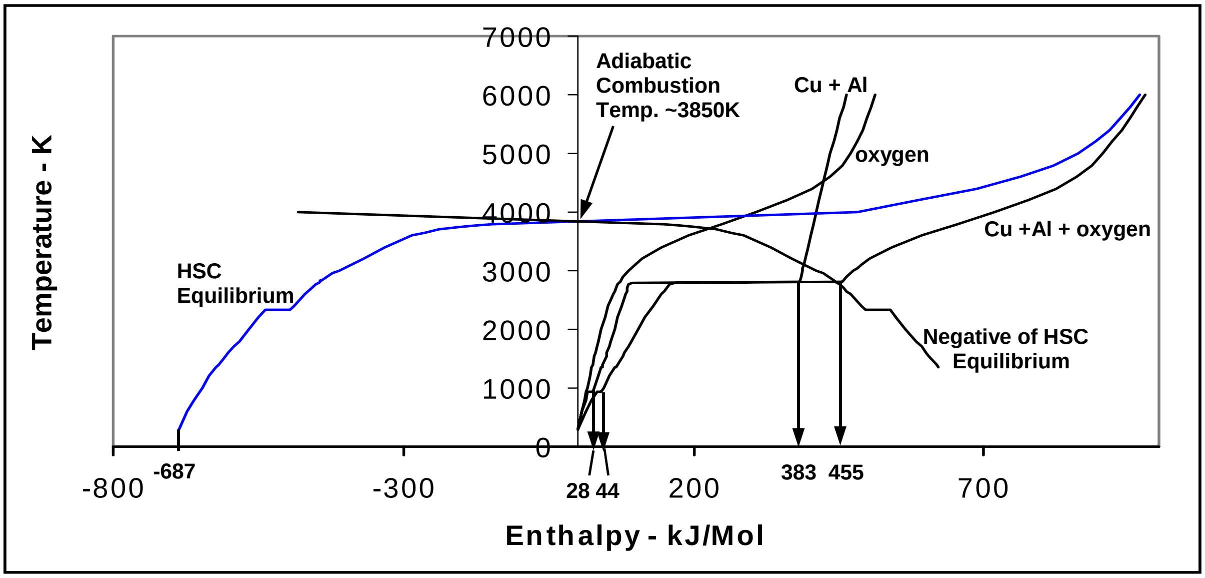

FIG. 15 —*Fig. 4 analog for 60% aluminum/copper.*

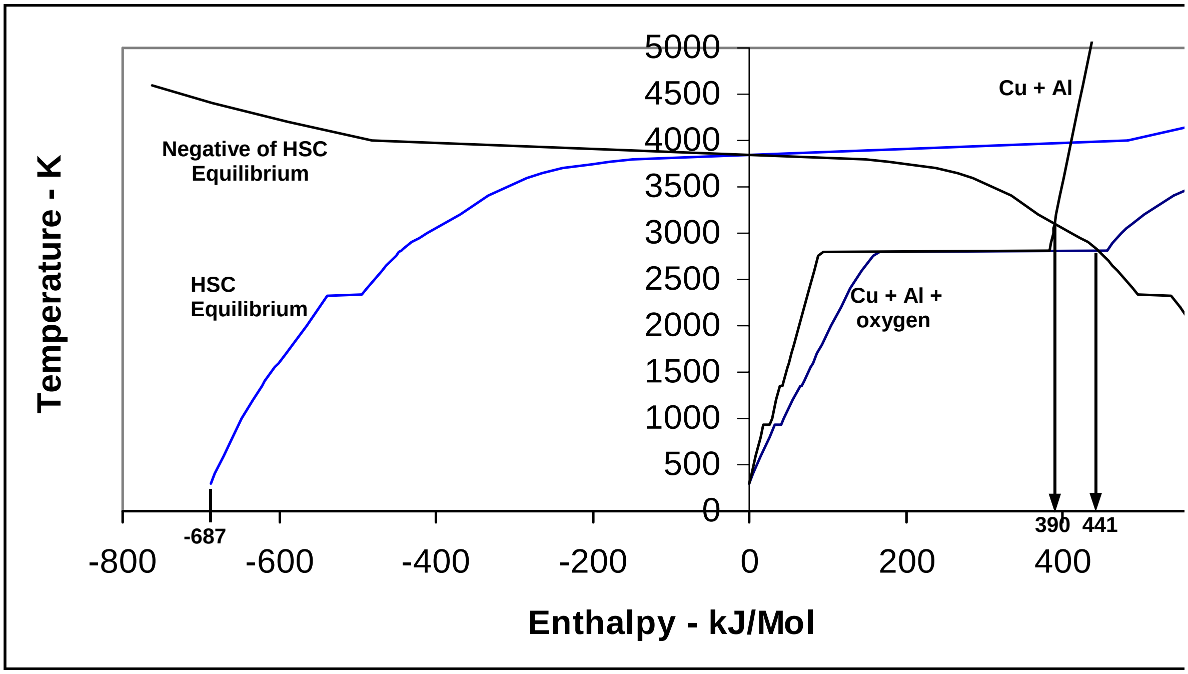

FIG. 16 —*Fig. 5 analog for 60% aluminum/copper.*

60% Aluminum/Copper

Figures 15 and 16 are also analogous to Figures 4 and 5, respectively, but exhibit the heats to warm 60% aluminum, 40% copper (by weight) with stoichiometric oxygen to form CuO and Al_2O_3. Also shown is the sum of the unmixed materials and the HSC curve for the equilibrium combined materials. The Appendix provides more details on the conditions

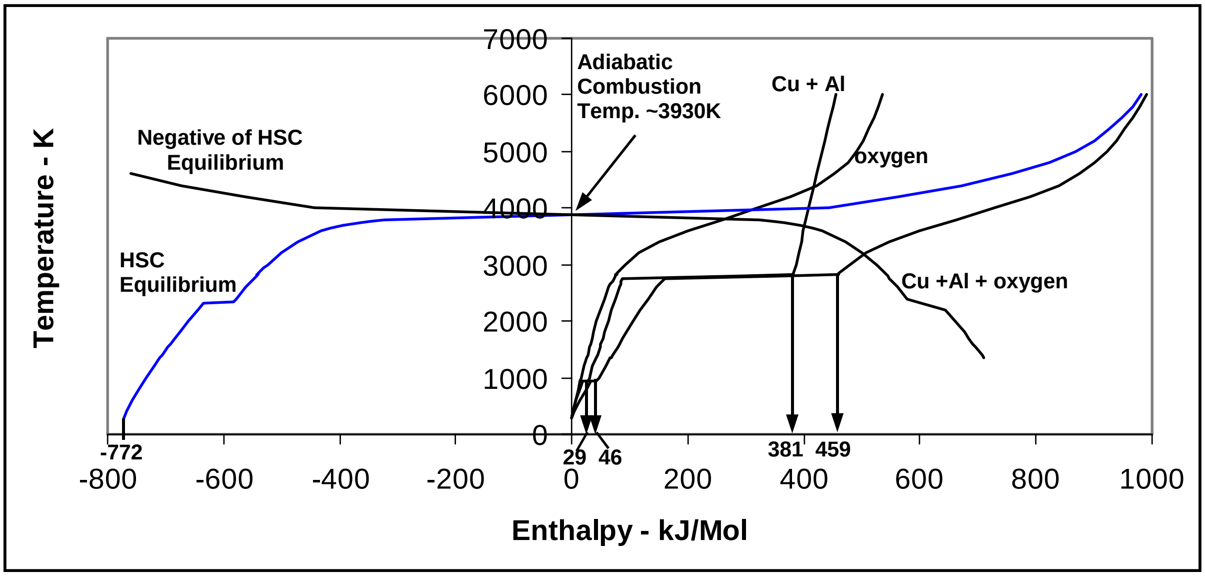

FIG. 17 —*Fig. 4 analog for 80% aluminum/copper.*

used for those who might wish to replicate, fine-tune, or critique this example.

From these figures, we see that the heat of combustion increases from about 156 kJ/mol to about 687 kJ/mol, $BR1_{mp}$ becomes 24.5, $BR1_{bp}$ becomes 1.70, $BR2_{mp}$ becomes 15.6, $BR2_{bp}$ becomes 1.51, $BR3_{mp}$ becomes 10.0, and $BR3_{bp}$ becomes 0.97 again in part due to the adiabatic combustion temperature (about 3850 K) is well above the (2835K) boiling point temperature of copper.

80% Aluminum/Copper

Figures 17 and 18 are also analogous to Figures 4 and 5, respectively, but exhibit the heats to warm 80% aluminum, 20% copper (by weight) with stoichiometric oxygen to form CuO and Al_2O_3. Also shown is the sum of the unmixed materials and the HSC curve for the equilibrium combined materials. The Appendix provides more details on the conditions used for those who might wish to replicate, fine-tune, or critique this example.

From these figures, we see that the heat of combustion increases from about 156 kJ/mol to about 772 kJ/mol, $BR1_{mp}$ becomes 26.6, $BR1_{bp}$ becomes 2.02, $BR2_{mp}$ becomes 16.8, $BR2_{bp}$ becomes 1.68, $BR3_{mp}$ becomes 10.9 and, $BR3_{bp}$ becomes 1.09, again in part due to the adiabatic combustion temperature (about 3930K) is well above the (2835K) boiling point temperature of copper.

100% Aluminum

Figures 19 and 20 (page 23) are also analogous to Figures 4 and 5, respectively, but exhibit the heats to warm pure aluminum with stoichiometric oxygen to form Al_2O_3. Also shown is the sum of the unmixed materials and the HSC curve for the equilibrium combined materials. The Appendix provides more details on the conditions used for those who might wish to replicate, fine-tune, or critique this example.

From these figures, we see that the heat of combustion increases from about 156 kJ/

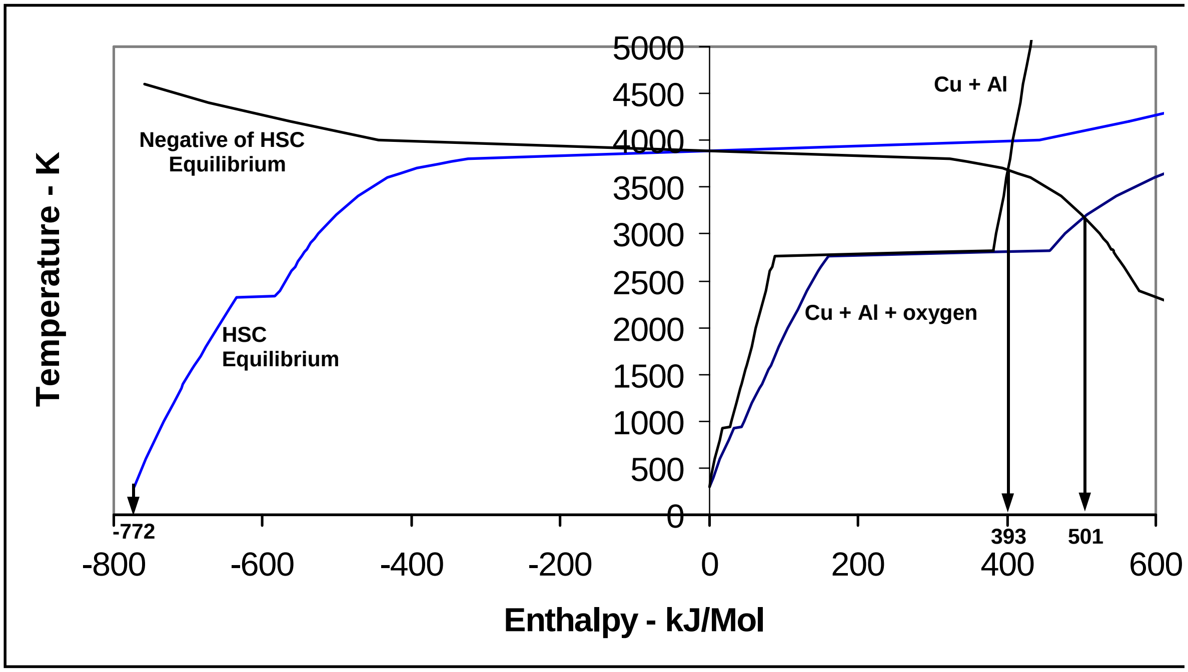

FIG. 18 —*Fig. 5 analog for 80% aluminum/copper.*

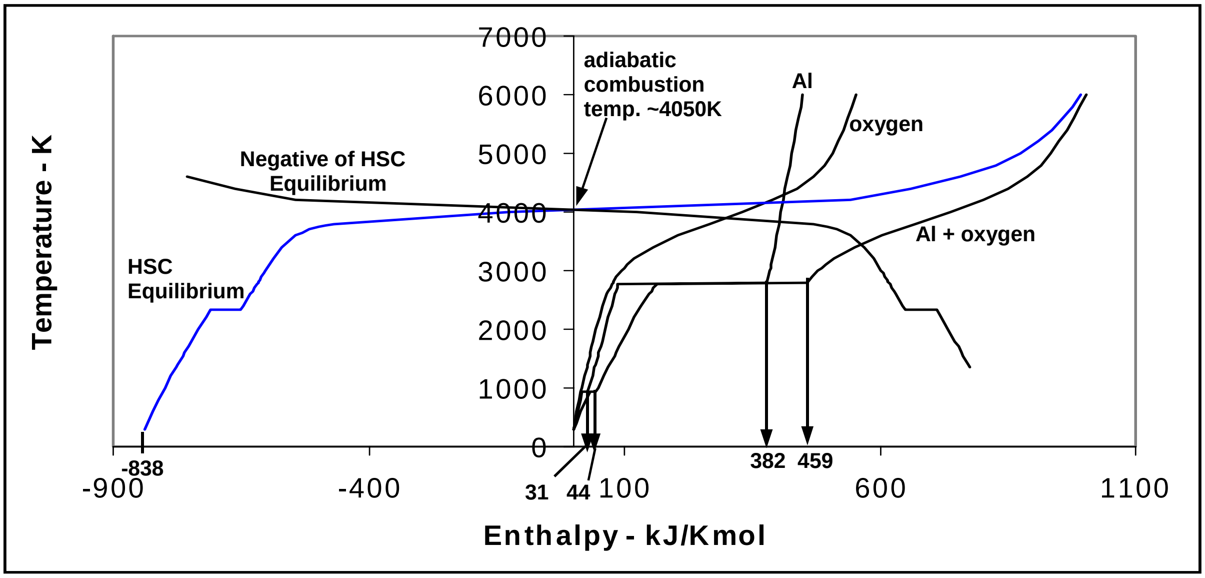

FIG. 19 —*Fig. 4 analog for 100% aluminum .*

mol to about 838 kJ/mol, $BR1_{mp}$ becomes 28.3, $BR1_{bp}$ becomes 2.19, $BR2_{mp}$ becomes 19.0, $BR2_{bp}$ becomes 1.83, $BR3_{mp}$ becomes 12.9 and $BR3_{bp}$ becomes 1.24 in part due to adiabatic combustion temperature (about 4050 K) is well above the (2743K) boiling point temperature of aluminum.

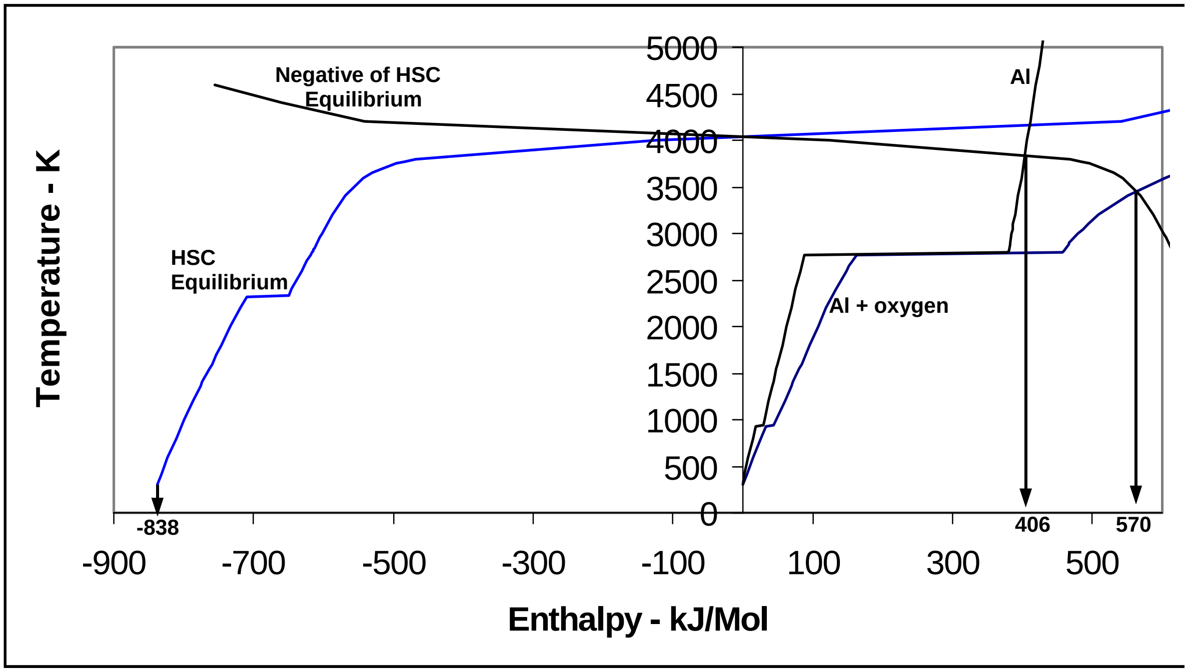

FIG. 20 —*Fig. 5 analog for 100% aluminum .*

The Big Picture

Notwithstanding flaws that may be found in this treatment, once again, this treatment argues that TCE thermal profiles, challenging as they are to prepare (and read) correctly, even for highly credentialed commentators, need to be generated and published as perhaps the only way to gain a more thorough and realistic perspective on oxygen compatibility of the full range of metals and alloys that might be considered for *any* oxidant service. This much-improved base of theoretical data is possible and has been possible for decades. The reluctance of ASTM Committee G4 to take on this effort, after 35 years, notwithstanding the dire pressures faced in today's world is difficult to fathom.

Currently ASTM G4's G94 standard contains a table listing heats of combustion for just 31 metals from scattered sources. TCE software would allow this table to be expanded to almost any degree desired and those with software chops can estimate heats for virtually any mixture of elements at any ambient temperature and pressure. Figure 21 exhibits how heat of combustion varies using an equilibrium rather than linear combination calculation for the copper and/or aluminum mixtures in this commentary. Note that the ΔH_c increases faster than linearly with the aluminum concentration (by weight) initially.

G94 contains a table citing 23 adiabatic flame temperatures from two references (at least some probably calculated rather than measured) and this table too could be expanded to whatever was desirable rather than what has been published. Figure 22 exhibits how equilibrium adiabatic combustion temperatures (ACTs) are estimated with HSC software. As for heats of combustion, the ACT increases faster than linearly with the aluminum concentration (by weight) initially.

G94 contains tables listing 27 BR1 melting-point burn ratios for metal elements and just eight boiling point-burn ratios for metal elements. These too can be expanded to virtu-

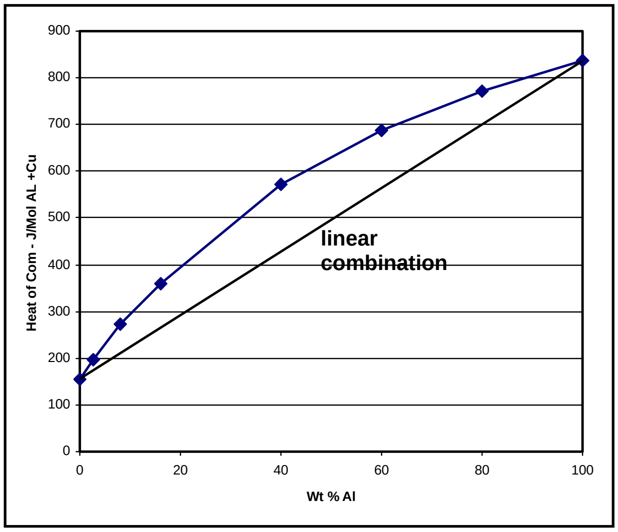

FIG. 21 —*Effect of Aluminum weight fraction on Heat of Combustion .*

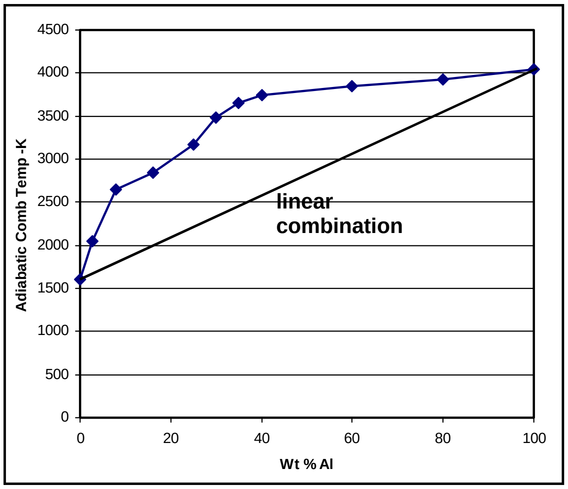

FIG. 22 —*Effect of Aluminum weight fraction on Adiabatic Combustion Temperature .*

ally any desired number of metals and alloys for the three burn ratio formulations examined herein using TCE software. Figs 23 (melting point) and Fig. 24 (boiling point) exhibit these data for the copper/aluminum burn ratio possibilities examined herein.

ASTM G4 is a public service Committee whose charter is to focus on far more than the present cognoscente are willing to support and instead are doubtless avoiding. Not only would a catalog of whole thermal profiles provide a valuable user asset (without the onus of creating the profiles) but they could guide new and novel experimental efforts, an example to be suggested below. All of these kinds of data and still others would have been of outstanding value during the writer’s active years.

Many years ago following an ambitious effort under the leadership of Frank Benz, NASA WSTF undertook to re-examine their methods of appraising oxygen fire hazards and played a major role that led to the development of several standards within G4 (most notably G 124). There was even ambitious talk at one point of WSTF setting up a melt shop to pro-

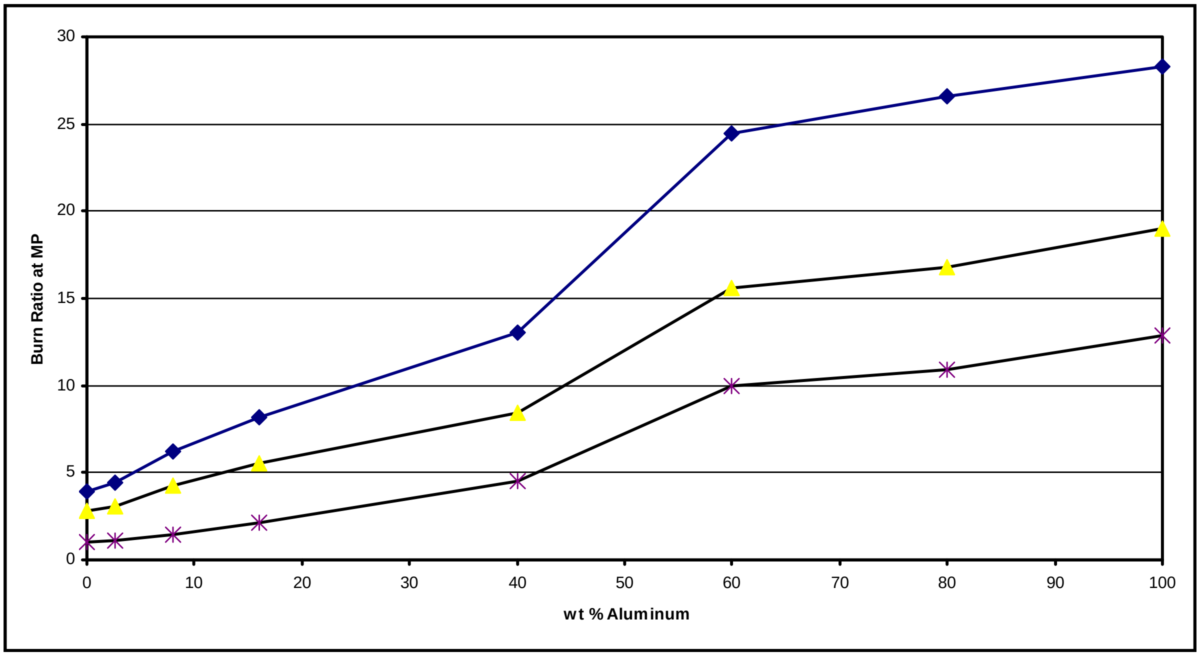

FIG. 23 —*Effect of Aluminum weight fraction on Melting Point Burn Ratio.*

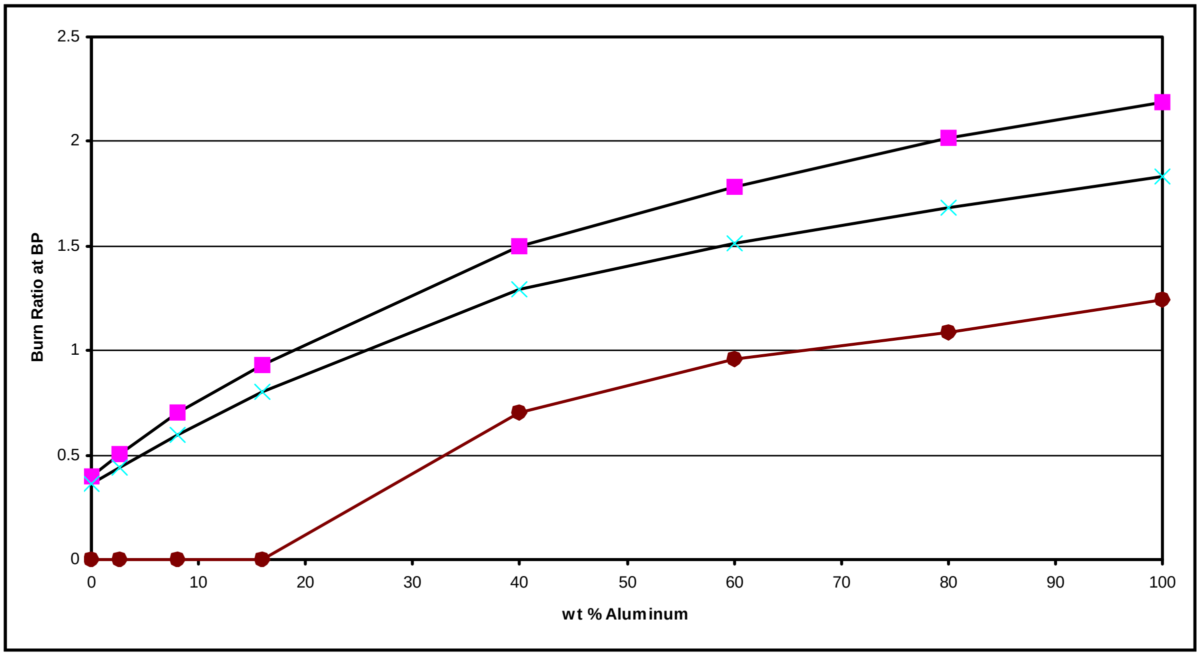

FIG. 24 —*Effect of Aluminum weight fraction on Boiling Point Burn Ratio.*

duce small quantities of existing and new alloys for testing. Indeed, as a result, the old NASA NHB 8060.1 manual was replaced with a new material evaluation protocol.

That very ambitious melt shop approach does not appear to have been realized, and perhaps for good reason. A melt-shop approach is a brute force, highly expensive effort at best.

And yet industry needs a way to appraise the full range of possibilities, and the body of data available was and still appears to be quite limited.

The writer was involved in obtaining specimens for a mid-1980s Industry Sponsored Program at WSTF that are now cited in, and literally made the G 94 and to some extent G 124 standards possible. Several resulting tables have been the backbone of G 94 for 35 years. Years before that the writer was involved in obtaining specimens to support John Zabreski's much earlier precursor testing [*15*] that in many ways was the harbinger for metal fire limit testing that led to the NASA work reported in G 94 [*1*]. Finding the alloy in the size you need and knowing its composition to the precision you would like is neigh onto an impossible quest (the reason why sometimes curious metals have sometimes been tested as the closest alloy available to a very desired choice. This writer once spent an afternoon feverishly machining 1.125 inch diameter cast iron bars down to 1/4 inch diameter rods to produce such specimens. He repeated this vain exercise in seeking specimens for the G4 ISP.

The cataloged aluminum bronze alloys previously discussed are examples of metals highly *un*likely to be available in order to test and generate curves like those of FIGs. 21-24. And if they could be obtained variations in the composition might make a well-behaved curve impossible to achieve. These figures are highly valuable resources in this codger's opinion. And yet it would be incredibly valuable to experimentally confirm the nature of all or at bare least some of these curves.

There is a way that might just be possible. A promising possibility that may be worthy of another Industry Sponsored Program much like that first test program proposed by Robert Lowrie (a past G4 chair) and led by his coworker John Cronk (another past G4 Chair) both of the no-longer operating Airco Corp.

A New Test Program and Standardization Opportunity

The practical production of specimens in a melt shop to test by G 124, or other ASTM Standards may be impractical and not just because of cost. However, high purity powders of all the elements found in all of the alloys of interest to oxidant service are readily available and affordable. They can be mixed with superb precision using standard laboratory balances to the exact nominal specs for alloys….easily. It is melting them down and forming them into precise homogeneous alloy rods that is so insurmountable.

However, as powders they are high-surface-area-to-volume which tends to imply maximum flammability. Perhaps, they should be tested as powders. It is reported that copper is non-flammable when dispersed and tested in air as a powder [*6*], replicating what we know about copper in tests of rods. Aluminum is very flammable replicating what we know about the extreme fire nature of aluminum. Indeed the internet contains advertising for numerous vendors that will test powders and dusts similarly to the way Cashdollar using ASTM Standards (from Committee E-27) did it. Testing in oxygen or at pressure is not a trivial change but neither is it as challenging as using G4 standards like G 124.

The testing should be relatively economic (a shocking claim to make these days). The results should be worst case, near adiabatic and might just yield well-behaved validation for curves for the full range of alloy compositions that would suddenly become available. Multiple spark plug igniters could yield similar benefit to statistical numbers of negative tests either with multiple spark locations scattered about in the dust cloud or at a origin to establish a propagating combustion. It might even allow exploration of composite variations and their effects on compatibility.

This would require ASTM G4 to gain some nuanced facility with gas phase flammability, something it has resisted with passion since 2000 on the basis gases are not structural therefore not of interest to oxygen compatibility. However, powdered solids used in structural components combust like gases in clouds if the mean diameters approach the Sauter dimension.

High transparency and a large pubic database of test and theoretical data like these may not benefit everyone, but are a superb basis for ASTM G4's existence.

Conclusion

The materials covered in this commentary are not new, but they may be esoteric. These are very challenging to assemble and the chances for error are significant. Many have erred before and many will err after. The writer is prepared to be embarrassed, but nonetheless, errors not withstanding, the promise and the merit and need for these data are manifest. This is an effort that could have (*should have*) been undertaken in the early 1990s. The fact that it is not common practice in oxygen compatibility today is in the writer's opinion shameful.

As a retired now voluntary worker, whose efforts have been fully disdained by ASTM G4, one must note ASTM Committee G4 is the only game in town. One can not input to CGA, EIGA, IOMA, NFPA. Only ASTM supposedly drew it strength (or at least did at one time) from a *full consensus* structure, badly degraded in recent decades.

Oxygen safety technology is not settled. Incidents continue to happen including on rather spectacular scale and all hurt the entire industry even if not as much as they hurt those who experience the specific damage. Also historic incidents remain that are unexplained. Yet efforts to advance the technology seem stagnant and moribund. The writer's own efforts have been rather wide reaching, yet for twenty years have all been declined, deferred, ignored or just blown off with at times lame excuses.

To be sure, for Generation 2 and now Generation 3 of ASTM G4, these have been a challenging two decades. International competition has forced efficiency efforts, 9/11 has messed things up royally, ditto the housing bubble, and two pandemics one of which persists as of this writing. No wonder G4 has retrenched to as it once asserted its four most basic duties: Minimum standards maintenance, its symposium series, its seminar series, and its education program.

And yet, while that may have been a valid triage at one time, it can become a "operational equilibrium" nightmare forever. Nor has it been followed scrupulously, and some of the deviations from this professed minimalism, have been less than admirable and misdirected in the writer's judgment. Cosmetic changes to standards often appear more to be marking territory than improving product, weakening of the collegiality and transparency serve authoritarianism more than consensus and progress.

G4 may not be able to undertake bold new initiatives as a group, but it does not have to freeze progress by censoring and discouraging those gains that are possible.

As a result, this commentary is intended for a Dissent website to revisit the numerous proposals this writer has pitched to G4 since his retirement in 1999. The voluntary oxygen safety community should not be shielded from potentially useful material (what anyone believes *should* be in G4 standards along with rationales) even if they have to assess its merit by themselves and lose the currently diluted “consensus” imprimatur. Anyone is free to read whatever they wish (including “as is” and “use at your own risk” opinion) and G4 is free to incorporate them into its standards and give them consensus standing at any time.

The writer is someone who at one time struggled to address more than one nasty incident. In some every putative cause known was examined and tested and yet none could be cited as the cause. Literally unrecognized causes were being sought so they could be evaluated and even tested. Since then the writer has suggested the possibility that things like random radioactive decay of tramp or low radio-activity materials and/or cosmic rays might play a role (and formally documented it and presented it to G4 at a regular meeting). Although it sounds bizarre on first blush, the possibility is not insanity and it has not been ruled in ...but it has not been ruled out either. Like TCE efforts it has been ignored.

In the case of TCE incorporation into oxygen safety practices, this is the writers sixth formal effort. Alas, G4 has found no way to incorporate this even as speculation into any of its standards. Its standards have been changed on several occasions that the writer takes as motion masquerading as accomplishment while real progress appears rather stagnant. But that is just this opinion.

This commentary has placed burn ratio and other data into a new context and that context gives new insight into the aluminum bronze conundrum and ways to evaluate these and other alloys. It will be combined with other analyses and made available to any, including future G4 generations should they wish to consider or even factor renegade opinions like this into their oxygen safety decisions.

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Appendix

Species Used for HSC Software Data Extractions (1.0 mol total metal reactant case)

Copper /Oxygen Data (each with trace argon gas)

Copper versus Enthalpy
1.0 mol Cu, 0.0005 mol Ar(g), Cu(g), Cu_2(g),

Oxygen versus Enthalpy
0.5 mol O_2(g), 0.0005 mol Ar(g), O(g), O_3(g),

Copper/Oxygen Equilibrium versus Enthalpy
1.0 mol Cu, 0.5 mol O_2(g), 0.0005 mol Ar(g), O(g), O_3(g), Cu(g), Cu_2(g), CuO, Cu_2O

Copper/Aluminum/Oxygen Data (each with trace argon gas)

Copper/Aluminum versus Enthalpy
2.6%Al: 0.05950 mol Al, 0.94085 mol Cu, 0.0005 Ar(g), plus below.
8.0% Al: 0.16999 mol Al, 0.83001 mol Cu, 0.0005 Ar(g), plus below.
16%Al: 0.30968 mol Al, 0.69032 mol Cu, 0.0005 Ar(g), plus below.
40% Al: 0.61091mol Al, 0.38909 mol Cu, 0.0005 Ar(g), plus below.
60%Al: 0.77938 mol Al, 0.22062 mol Cu, 0.0005 Ar(g), plus below.
80%Al: 0.90404 mol Al, 0.095963 mol Cu, 0.0005 Ar(g), plus below.

Remainder for all % Cases: Cu(g), Cu_2(g), Al(g), Al_2(g),

Oxygen versus Enthalpy
2.6%Al: 0.51479 mol O_2(g), 0.0005 mol Ar(g), O(g), O_3(g).
8% Al: 0.54250 mol O_2(g), 0.0005 Ar(g), O(g), O_3(g).
16%Al: 0.57742 mol O_2(g), 0.0005 Ar(g), O(g), O_3(g).
40% Al: 0.65273 mol O_2(g), 0.0005 mol Ar(g), O(g), O_3(g)
60%Al: 0.69485 mol Al, 0.38909 mol Cu, 0.65273 mol O_2(g), 0.0005 Ar(g), O(g), O_3(g).
80%Al: 0.72601 mol O_2(g), 0.0005 Ar(g), O(g), O_3(g).

Copper/Aluminum/Oxygen Equilibrium versus Enthalpy
2.6%Al: 0.059150 mol Al, 0.94085 mol Cu, 0.51479 mol O_2(g), 0.0005 Ar(g), plus below.
8% Al: 0.16999 mol Al, 0.83001 mol Cu, 0.54250 mol O_2(g), 0.0005 Ar(g), plus below.
16%Al: 0.30968 mol Al, 0.69032 mol Cu, 0.57742 mol O_2(g), 0.0005 Ar(g), plus below.
40% Al: 0.61091mol Al, 0.38909 mol Cu, 0.65273 mol O_2(g), 0.0005 Ar(g), plus below.
60%Al: 0.77938 mol Al, 0.22062 mol Cu, 0.69485 mol O_2(g), 0.0005 Ar(g), plus below.
80%Al: 0.90404 mol Al, 0.095963 mol Cu, 0.726004 mol O_2(g), 0.0005 Ar(g), plus below.

Remainder for all % Cases: O(g), O_3(g), Cu(g), CuO(g), Cu_2(g), Al(g), AlO (g), Al_2O_2(g), Al_2O(g), Al_2(g), AlO, Al_2O_3, CuO, Cu2O, AlO, Al_2O_3, CuO*Al_2O_3, Cu_2O*Al_2O_3

Appendix
Continued

Species Used for HSC Software Data Extractions

Aluminum/Oxygen Data (each with trace argon gas)

Aluminum versus Enthalpy

1.0 mol Al, 0.00005 mol Ar(g), Al(g), AL_2(g)

Oxygen versus Enthalpy

0.75 mol O_2(g), 0.0005 mol Ar(g), O(g), O_3(g)

Aluminum/Oxygen Equilibrium versus Enthalpy

1.0 mol Al, 0.75 mol O_2(g), 0.00005 mol Ar(g), O(g), O_3(g), Al(g), AlO (g), Al_2O_2(g), Al_2O(g), AL_2(g), AlO, Al_2O_3

Software: HSC Chemistry for Windows, Version 3.02, Outokumpu Research Oy, Finland.