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Background

In light of the discovery of the activated zinc 65 in the TEF process piping, a discussion of potential sources and mechanisms for the production of this species has been initiated. A suspected source is the presence of Cu as a contaminant in many of the alloy components that comprise the TPBARs and the presence of Zn as a contaminant in the aluminide coating. These two sources are expected to produce metallic transmutation products that could be mobile and be extracted from the metallic components of the TPBARs. Another potential source is the presence of ZnO that is present as part of the crud on the external surfaces of the TPBARs. In addition, it is conceivable to have ZnO within the TPBARs from transmutation products and subsequent oxidation reactions with water.

This memo does not attempt to address all of the possible sources, nor does it derive the most likely scenarios as to how Zn or ZnO may be present in the TPBARs it merely posits that it is present as a transmutation product and if present, elementally, it may be mobile under high vacuum conditions at high temperatures as indicated by the pressure temperature curve shown in Fig. 1. Further, this document shows that it is thermodynamically feasible to reduce ZnO to Zn by solid state reactions of the ZnO with other metallic components in the TPBARs. However, for these reactions to occur, the ZnO must be in contact with the more active metal so that the chemical reactions can occur.

The proposed reactions are based on equilibrium thermodynamics. For simplicity, they do not take into account the quantities of the various materials, the compositions, the effect of alloying, or other technical issues, they are intended only to provide feasibility for the reduction reactions. A more complete thermodynamic model can be developed, but it will require actual contents and be much more complicated with little value added.

Vaporization and Diffusion

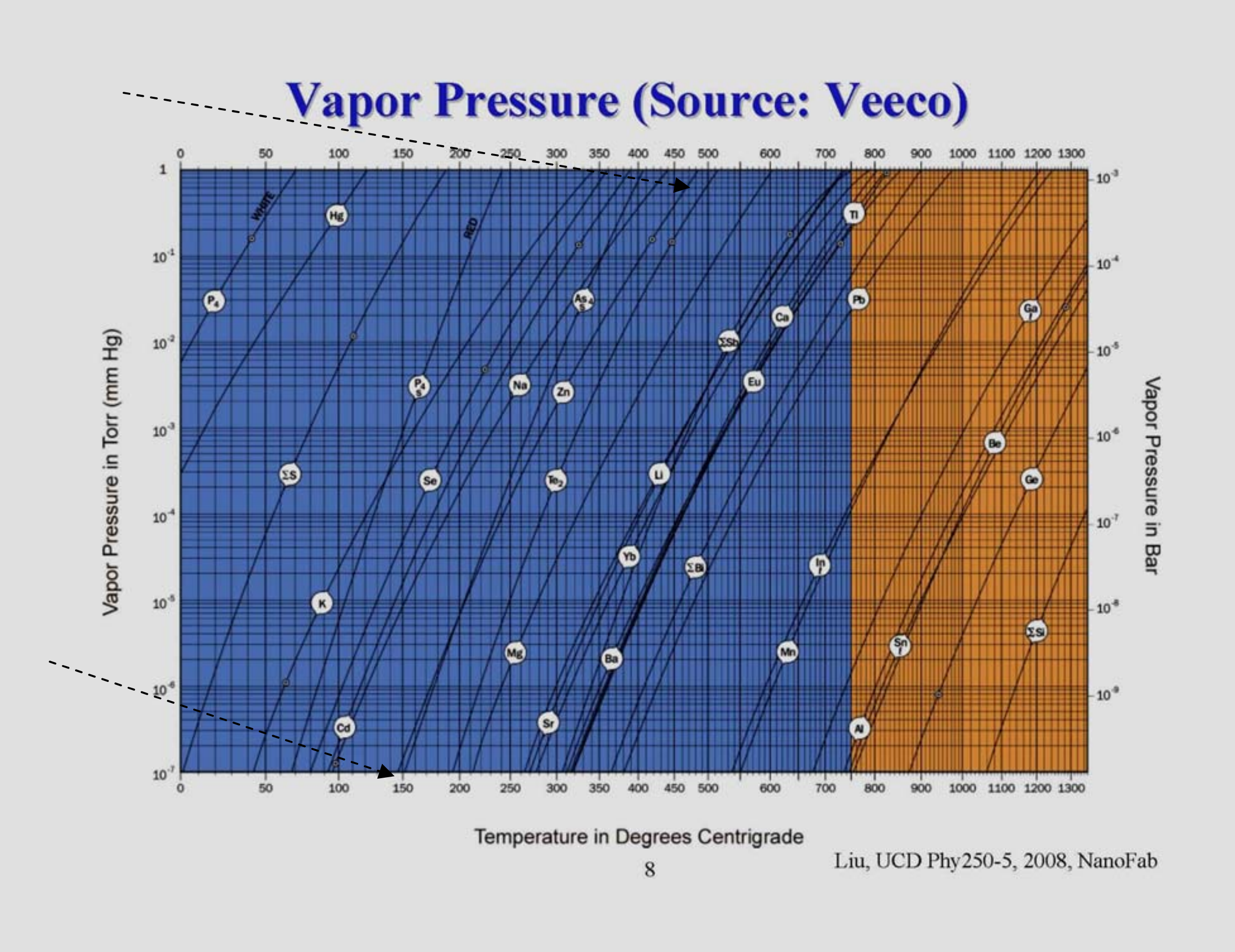

Fig. 1. Vapor pressure of the elements, Zn indicated by arrows (1).

The vapor pressure of Zn over solid Zn is measurable at temperatures as low as 150°C as indicated by the arrows in Fig. 1 and increases rapidly to 1 Torr at a temperature of 450°C. This property suggests that any Zn present in the metallic state and at the surface of the internal components of the TPBARs may be volatilized. The data further indicate that a substantial Zn pressure exists at temperatures consistent with the lithium trap. Thus, as well known, the Zn pressure is significant over the extraction conditions and metallic Zn may volatilize and deposit at low temperature and higher pressure areas within the TEF piping. The vapor pressure of ZnO is low at temperatures up to 1100°C due to in large part to its melting point of 1975°C (Ref. 2). It sublimes at temperatures over 1400°C. Consequently vapor transport of ZnO is highly unlikely.

The other mechanism for Zn deposition in TEF piping is Zn source material that lies within the TPBAR components, such as the liner, getter, pellets, and coated cladding. A mechanism for this material to be released requires the formation of the activated product and the solid state diffusion of the product to the surface and the subsequent volatilization. The solid state mobility of Zn in an alloy will be primarily dependant on the composition and temperature.

Unfortunately, no diffusion coefficient for Zn in Zr metals was readily found, however, values for diffusivity from the vacuum dezincification of Zn-Cu and Zn-Ni were (Ref. 3). Based on engineering estimates, it is expected that the diffusivity will range from 10^{-15} to 10^{-8} cm^2/s over the temperature range RT to 1100°C. Depending on the time (distance = $\sqrt{Dt}$), diffusional distances of several mils can be achieved that will provide subsurface Zn source terms. The reference document clearly shows void formation in these high Zn alloys (65 Cu/35 Zn) with almost complete dezincification for brass alloys 0.1 mm thick thermally treated at temperatures of 750 and 850°C after 30 minutes to 8 hours. The mechanisms of diffusion and thermal vaporization of metallic Zn are more credible than ZnO vaporization.

Thermochemical Reactions

The possibility of ZnO reduction to metallic Zn and an oxide product due to solid state or gas reactions was also investigated. The propensity for zinc oxide reduction using gas phase reduction with H_2 and CH_4 singly and in conjunction with several TPBAR prominent metals is shown in Fig. 2. This series of equilibrium calculations show, that with the species identified, only a gas reaction with Zr present in addition to CH_4 will result in reduction of ZnO and only at temperatures in excess of 872°C, the point at which the dark solid line crosses the x-axis, (Ref. 5). Note that hydrogen reduction of ZnO is not a favorable reaction from 0 up to 1100°C.

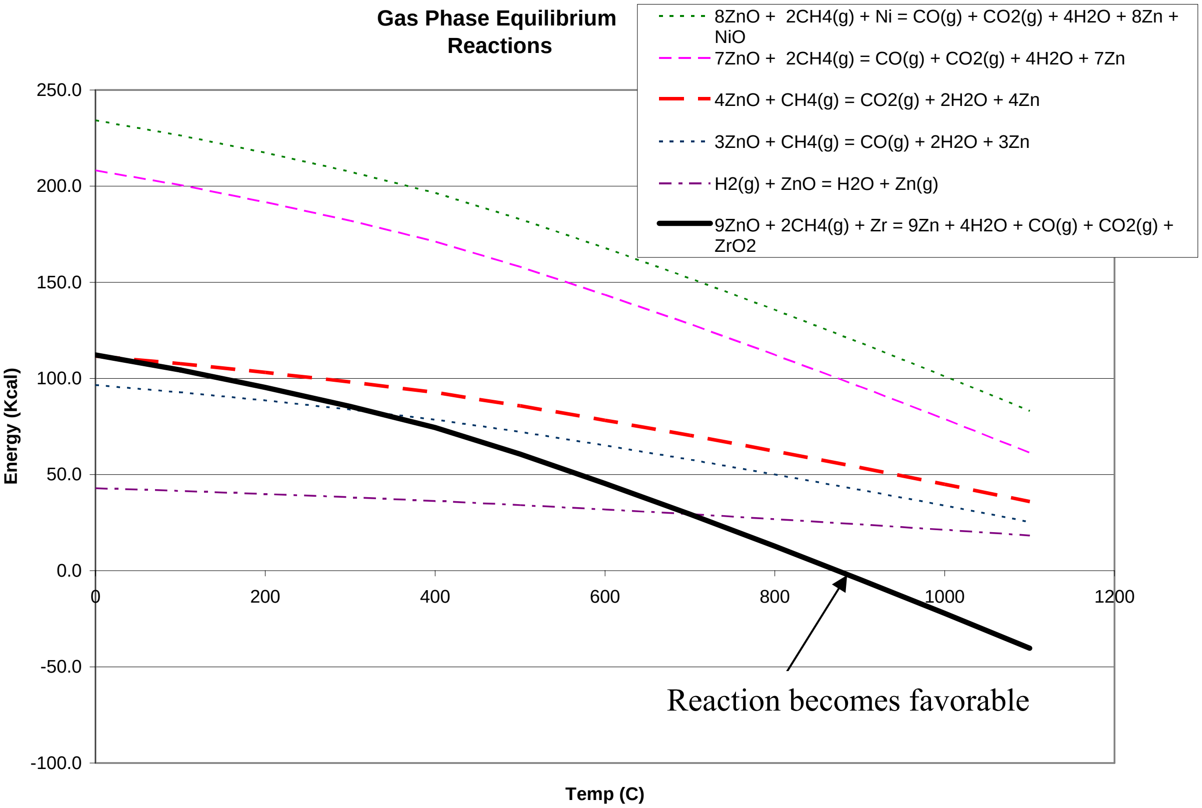

Fig. 2. Gas - ZnO equilibrium reactions (calculated using Ref. 4).

Solid-Solid chemical reactions were also considered. The propensity for solid state reduction reactions for ZnO and other metals of construction and interest is shown in Fig. 3. The calculations presented here show several metal oxide combinations that could lead to reduction of ZnO and concurrent oxidation of the metallic alloy species. For simplicity sake, these calculations do not account for the variability of the composition effects and the changes in free energy due to heats of solution. Rather they are intended purely as a guide to demonstrate feasibility. Also note that for the solid state reactions to occur, the reactants must be in contact, for instance, for the Zr reaction with ZnO the ZnO must be in contact with the Zr. For crud and associated external ZnO contamination, this is a highly unlikely situation. It is possible for the ZnO to be reduced by Cr, which is present in the TPBAR cladding, although it is moderately oxidized / corroded after irradiation. A detailed assessment of ZnO reduction with prototypic quantities of all the pertinent chemical species could be conducted, but is of little additional value, in my opinion.

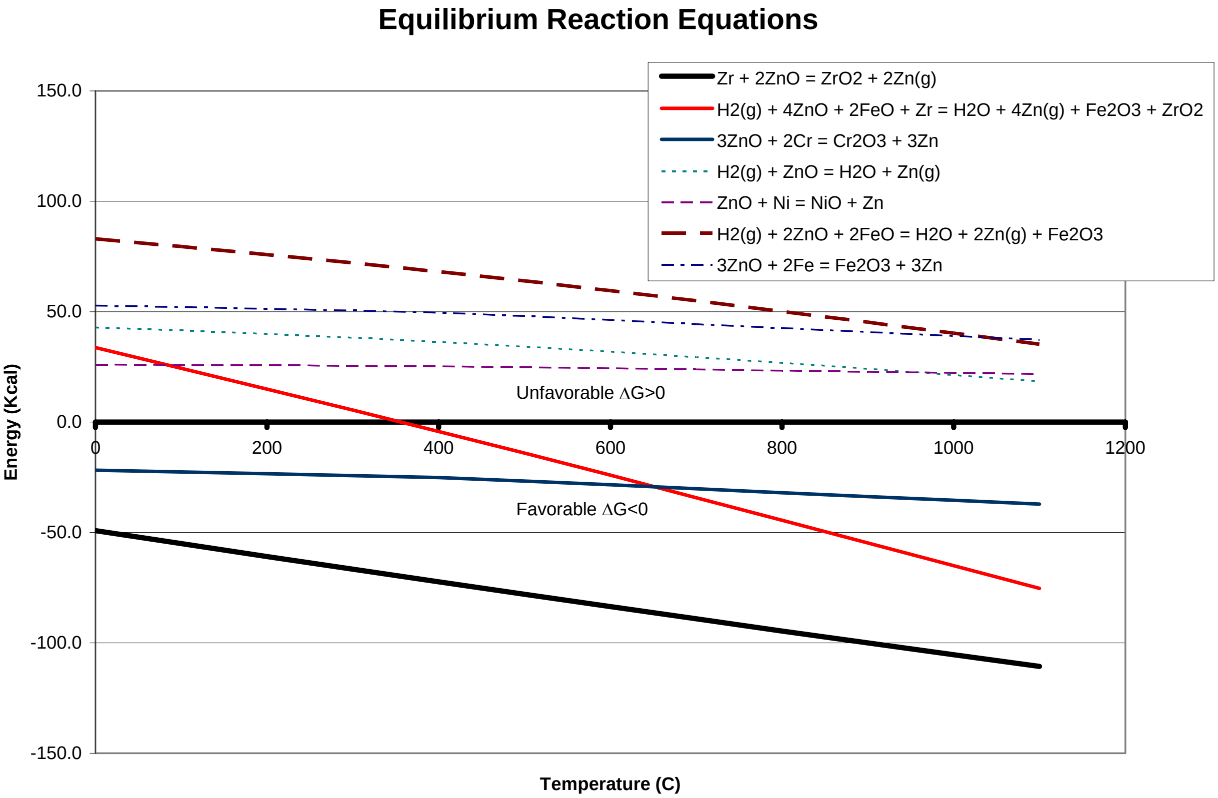

Fig. 3. Gas solid phase equilibrium (calculated using Ref. 4)

References

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