

Void-Free Fluxless Solder Bonding of CPV Solar Cells

Wei Shi, Paul Barnes, David Muhs
 SST International
 9801 Everest Street
 Downey, CA, 90242
 Phone: (562) 803-3361, Fax: (562) 803-4043
 E-mail: wshi@sstinternational.com

Abstract

In order to obtain low thermal resistance and high reliability for thermal management of concentrating photovoltaic (CPV) modules, vacuum solder reflow technologies for void-free and fluxless bonding processes have been reviewed in this paper. Surface oxides of solder alloys that utilize elements in the top side of the Ellingham Diagrams are much easier to be decomposed in vacuum. Surface oxides of solders that are alloyed with multiple elements are easier to remove than pure-metal oxides. Without the very low oxygen partial pressures and corresponding high vacuum levels that are required by the Ellingham Diagrams, void-free soldering results using various types of solders such as AuSn, InAg, InSn, SnAgCu and SnAgInCu have been obtained. Without any special surface treatment such as forming gas, formic acid gas, plasma, ultrasonic, nitrogen or chemicals, this technology is very promising and reliable. It will meet the thermal, mechanical and reliability requirements of CPV or other high-power optoelectronic packages.

Keywords: Fluxless, Solder, Void, Vacuum, CPV, Thermal

1. Introduction

In photovoltaic systems, the junction temperature of the cell must be well managed for purposes of efficiency and reliability; through effective design and systematic implementation of thermal, material, mechanical and process elements. In concentrating photovoltaic (CPV) or high concentrating photovoltaic (HCPV) systems, through optical concentration, the solar intensity can reach 200~1000 suns, with the cell being heated by a heat flux of 20~75W/cm² [1]. Regardless of whether the system is being cooled with natural convection or a heat pipe, the module-level cooling technologies for CPV or HCPV make it very challenging to achieve the goals of:

- 1) Junction operating temperature < 60 °C
- 2) Life time > 30 years

These challenges can be illustrated through a typical CPV structure as shown in Fig. 1, which not only covers thermal design, but also mechanical design, material selection, manufacturing processes and cost. Normally, the solar cell (GaAs or Si based) is about 100~200 μm thick, with the Au backside metallization a couple microns thick. The CPV cell is soldered to a ceramic substrate for CTE mismatch

and electrical connections. The substrate is then bonded to the heat spreader with another solder layer.

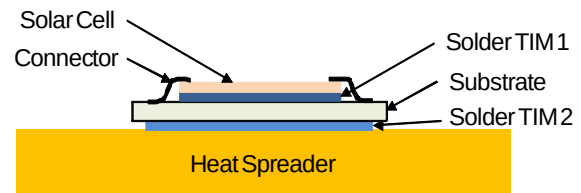


Fig. 1: A typical structure of CPV module.

Obviously, the ceramic substrate and the second layer of thermal interface material (TIM) increase the thermal resistance significantly, because the thermal conductivity of ceramic is normally much lower than that of metal (like Cu) and the heat spreading resistance of the ceramic layer is much higher. For example, bonding the cell to a CTE-matched heat spreader with high thermal conductivity, or bonding the cell with thick soft solder that can absorb the CTE stress between the cell and heat spreader, are definitely options to be considered. In so many architectural designs, there are many complicated tradeoffs; among these are thermal resistance, CTE mismatch, costs (of materials and equipment) and manufacturability. These need a thorough and systematic evaluation to

optimize the CPV's efficiency, reliability and cost. In this paper, we will present a void-free, fluxless soldering method to the CPV module designers to help solve these challenges.

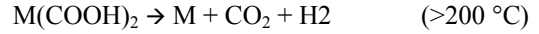
As a rule of thumb in thermal design, the heat from the cell must be transferred to a heat spreader through a layer of TIM, with thermal resistance as low as possible. The thermal resistance of the TIM layer plays a key role in the total thermal resistance of the whole module. The TIM is one of the most critical materials in the reliability of the whole module. Void-free bonding quality is required in the manufacturing line, because voids in the solder TIM can cause multiple impacts such as:

- 1) Increase in the thermal resistance, thereby reducing the CPV's efficiency. The efficiency drops approximately 0.1% for every 1 °C rise in junction temperature [2].
- 2) Create hot spots on the cell, which may degrade the device performance and reliability.
- 3) Degrade the reliability with poor bonding strength.

The relationship between the junction temperature and voids (amount, size and distribution) can be obtained through either thermal simulation or experimental correlation for the specific CPV module. The threshold of the voiding level may vary for different CPV modules. The higher the solar concentration level of the CPV, the lower the thermal resistance must be [2], requiring more crucial limits on the voiding level of the solder TIM.

In traditional solder reflow, the surface oxides of solder are normally removed with chemical fluxes, which typically produce voids in the solder layer. This soldering process is not suitable for most optoelectronic devices because contamination from flux residuals or volatiles may degrade the optical performance. In fluxless soldering, the solder surface oxides can normally be removed by:

- 1) Vacuum. The details will be discussed in the following sections of this paper.
- 2) Forming gas, which is usually comprised of 5% hydrogen and 95% nitrogen gases. The hydrogen can reduce the oxides of the metals that sit above the line of $2H_2 + O_2 = 2H_2O$ in Ellingham Diagrams, [3] as shown in Fig. 2. For example, the oxides of Au_2O_3 , Ag_2O , PbO and Cu_2O should be relatively easier to remove using hydrogen, when compared to SnO_2 . In some cases, however, H_2 may degrade the performance of the GaAs devices [4].
- 3) Formic acid gas [5], based on the reactions of: $2HCOOH + MO \rightarrow M(COOH)_2 + H_2O$ ($>150^\circ C$)



where, M denotes metal. Obviously, there are a couple of concerns in this type of gaseous solder flux, such as the acid gas may damage optical films that cover the solar cell, the volatile residuals may be entrapped by the molten solder generating voids, and the cleaned solder surface may be re-oxidized by H_2O if the outgassing is insufficient.

- 4) Plasma or ultrasonic cleaning. These are not suitable for the production of solar cells, because the film or device may be damaged.

As another fluxless soldering method, rather than using a solder preform, layers of the individual metals of the solder alloy can be pre-deposited on the bonding surfaces, then reflowed by Solid-Liquid Diffusion Bonding [6] in vacuum. However, the total thickness of the solder layer is very thin using this method.

In this paper, we will be focusing on vacuum fluxless soldering, which is superior to other reflow methods in the aspects of quality, cost and manufacturability. We present this reflow method, with 30-plus years of industrial applications, to CPV designers for their systematic consideration of module-level cooling solutions including thermal design, mechanical design, material selection, process development and equipment selection.

2. Vacuum Reflow

It is well known that a vacuum can prevent further oxidation of the solder surface when solder is being heated. According to the Ellingham Diagrams [3], when the partial pressure of oxygen p_{O_2} lies below the equilibrium line, the surface oxide will decompose into metal and oxygen gas, because the vacuum provides the driving force for such a reduction reaction. Unfortunately, very little information is available on the oxidation of alloys (most solders are alloys) which are no longer in the standard state, as pure metal is, in the Ellingham Diagrams [3].

As discussed in reference [7], the activity (ability to participate in a reaction) of an alloy is lower than that of its pure metal,

$$\Delta G = \Delta G^\circ - RT \ln a_M \quad (\text{Eq. 1})$$

where, ΔG is the Gibbs free energy, ΔG° is the Gibbs free energy at the standard state, R is the molar gas constant, T is the temperature, a_M is the activity of the metal in the alloy, $a_M = p_{(\text{metal in std state})} / p_{(\text{metal in alloy})}$, which is proportional to the concentration of this metal in its alloy form [7],

$$a_i = \gamma_i X_i \quad (\text{Eq. 2})$$

where, X_i denotes the concentration of the metal i . γ_i is called the activity coefficient [7], which is very difficult to determine. For instance, the oxidation of 80Au20Sn surface becomes more difficult than the oxidation of pure Sn. Therefore, the oxide of 80Au20Sn is relatively easier to reduce in vacuum.

In the aspect of the soldering environment, a vacuum level of $10^{-6} \sim 10^{-7}$ Torr is believed to be good enough for fluxless soldering [4]. Kuhmann *et al* [9] measured the growth of oxide at different oxygen partial pressures, temperatures and time on the solders of AuSn, InSn and SnPb by using in-situ Auger electron spectroscopy (AES). They found that Sn segregates to the surface and can be oxidized rather than the Au. They used hydrogen to reduce the oxygen partial pressure through the reaction of:

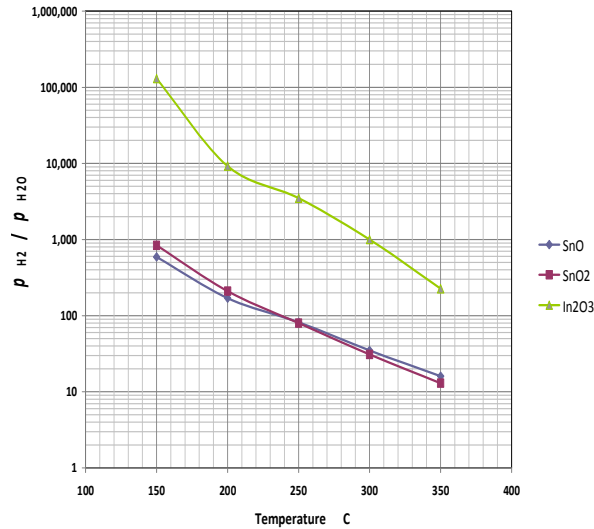
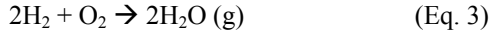


Fig. 3: Partial pressure ratio ($p_{\text{H}_2}/p_{\text{H}_2\text{O}}$) for $\Delta G=0$ [9]

As indicated in Fig. 3, in the temperature range of 150~200 °C, the hydrogen partial pressure must be about 590~840 times the water vapor partial pressure to decompose SnO₂. We can also see that indium oxide is more difficult to remove than tin oxides. However, within the authors' knowledge, there is no study relating to oxygen partial pressure reduction by carbon.

Based on the calculations, Reference [10] gives ($p_{\text{H}_2}/p_{\text{H}_2\text{O}}$) ratio to be 1.5×10^2 for SnO₂ at a temperature of 500K, which is in general agreement with Fig. 3. However, Reference [10] gave that

$p_{\text{H}_2}/p_{\text{H}_2\text{O}} = 9.5 \times 10^{-5}$ for In₂O₃ at 500K, and concluded that the oxidation of the indium-based alloy is relatively easily decomposed in a hydrogen atmosphere. To clear up this type of disagreement, it seems that further fundamental research is needed.

In a typical SST vacuum reflow oven, as shown in Fig. 4, we use graphite as the resistive heater in which the package is sitting.

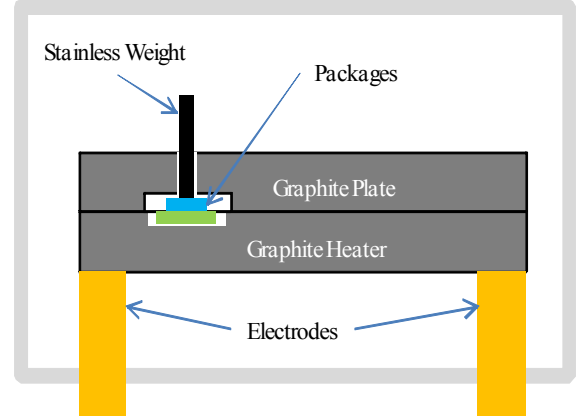


Fig. 4: Schematic structure of the heating method.

In the SST 3150 oven with a turbo pump, the typical chamber pressure reaches about 6×10^{-6} Torr when the heater gets to about 350 °C. Without using any nitrogen purge of the chamber, the residual gas analyzer indicates partial pressures as follows:

$$\begin{aligned} p_{\text{H}_2\text{O}} &= 6 \times 10^{-6} \text{ Torr} \\ p_{\text{N}_2} &= 5 \times 10^{-7} \text{ Torr} \\ p_{\text{CO}_2} &= 3 \times 10^{-7} \text{ Torr} \\ p_{\text{H}_2} &= 2 \times 10^{-7} \text{ Torr} \\ p_{\text{O}_2} &= 7 \times 10^{-8} \text{ Torr} \end{aligned}$$

This is a worst case condition for the SST 3150 oven. We have the option to use a cryo pump to drive the water vapor pressure lower. Unfortunately, residual gas analysis cannot differentiate between N₂ and CO because of the same molecular mass. Boldyreva *et al* [11] studied carbon oxidation kinetics at low temperatures, and showed the product ratio of CO/CO₂ = 1 in the temperature range of 380~440 °C. There was no data available on the partial pressure of CO in vacuum, in the temperature range of 150~350 °C.

So, if the fact can be confirmed that oxygen partial pressure can be reduced through the reactions of:



in the common solder baking and reflow temperature range of 150~350 °C in a vacuum chamber, then the C and CO will help to remove the solder oxide too, according to the Ellingham Diagrams [3]. The graphite heater is not appreciably consumed so as to impact its long term use.

In the 30-plus years of experience at SST, hermetic seals have been accomplished with various eutectic solders such as AuSn, InAg, SnAgCu, InSn and so on. As shown by X-ray images in Fig. 5, the void-free soldering results were successfully achieved by using 10^{-2} ~ 10^{-6} Torr vacuum, without any application of hydrogen, forming gas or formic acid gas.

Based upon our experience, it seemed that the fundamentals required for oxide decomposition of the above solders can be obtained with SST ovens at vacuum levels in the range of 10^{-2} ~ 10^{-6} Torr. We are interested in further research on oxide decomposition of solder alloys in this environment.

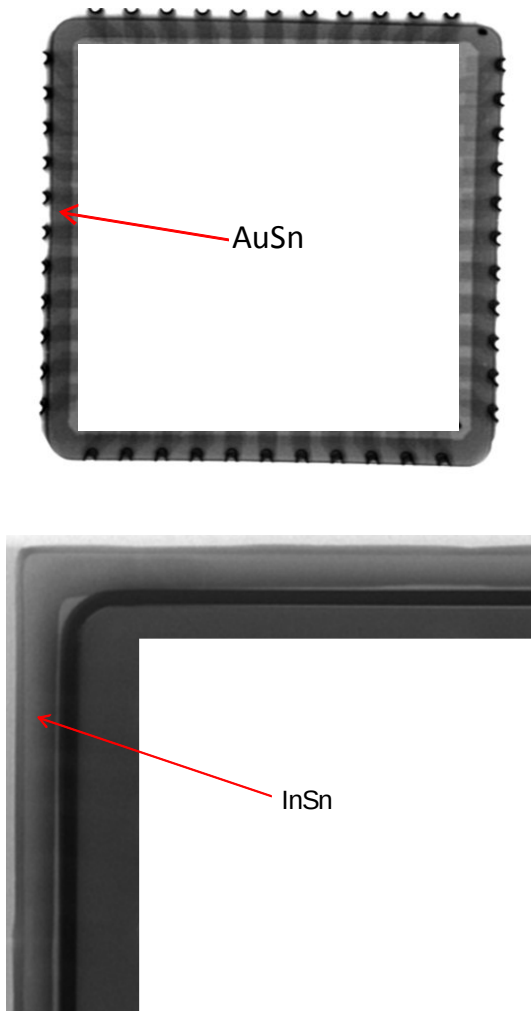


Fig. 5: Seal ring soldering in SST ovens.

Another reason to use vacuum reflow is that the lower vapor pressure could improve the wettability of the solder. Even if the oxide of the solder surface is totally removed before melting, via a flux or fluxless process, it will inevitably result in some voiding because of the entrapment of air into the liquid solder. From the surface energy at the thermal and mechanical equilibrium,

$$\gamma_{ab} = (\partial F / \partial A_{ab})_{T, \mu} \quad (\text{Eq. 6})$$

where, F is the surface free energy, A_{ab} is the area of the interface between (a) and (b) phases, γ_{ab} is the interface energy, we can see the surface tension γ_{ab} is the function of free energy, area, temperature T and viscosity μ .

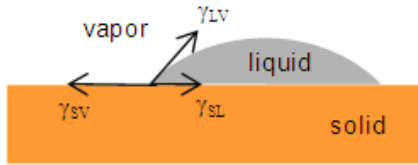


Fig. 6: Schematic of liquid-vapor-solid interfaces.

As illustrated in Fig. 6, Young's equation depicts the force balance along the bonding surface.

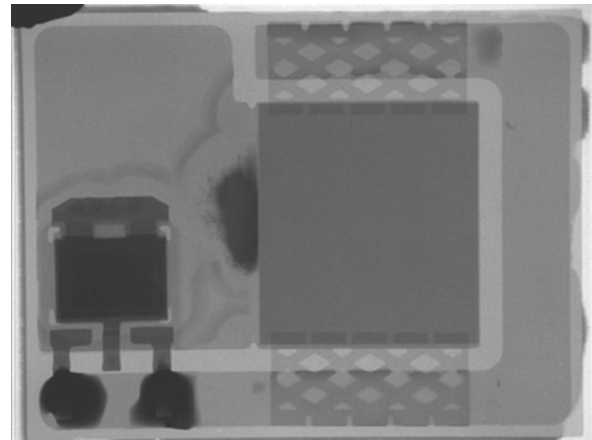
$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \quad (\text{Eq. 7})$$

It is clear that [8], to get better wettability, γ_{SV} can be increased through the removal of the surface oxides, γ_{SL} decreases by lifting the melting temperature, while the γ_{LV} can be reduced by the lower vapor pressure which is created by vacuum. Young's equation is only applicable to the initial moment when the solder melts, after which the interfacial tensions will experience a dynamic variation due to chemical reactions between solid and liquid. More detailed discussions under the conditions of chemical equilibrium and non-equilibrium are available in reference [12].

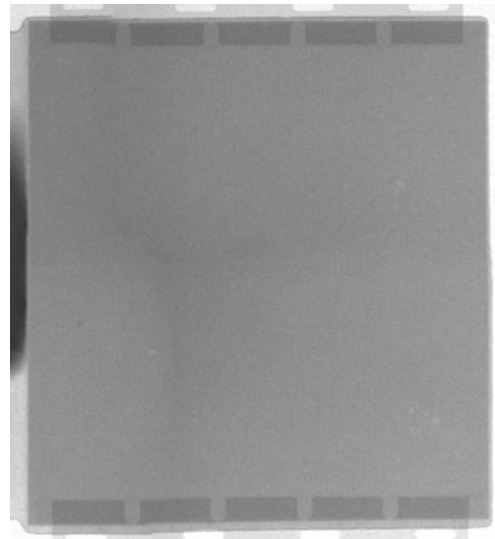
3. Results on a CPV Module

For the purpose of demonstrating the vacuum oven capability only, a piece of 100 μm thick 88.5Sn8In3Ag0.5Cu [13], $T_m=196\sim202^\circ\text{C}$, solder preform was placed as the TIM2 layer (see Fig. 1) to bond a 25 x 20 mm CPV module onto a piece of Cu heat spreader. Both bonding surfaces are properly plated with Au for soldering. It was reflowed at 235 $^\circ\text{C}$ for 5 min with the vacuum level of 10^{-2} Torr in an SST 3130 oven. The solder preform was not cleaned with any chemical, forming gas, formic acid gas, hydrogen or anything else.

As shown by the X-ray image in Fig. 7 (a), the void-free soldering in the TIM2 layer was obtained across the whole module area except some tiny voids at the right bottom corner (which can be improved by using a more uniform pressing force). The thickness variations of the solder that originally spread from the diode along the substrate top surface can be seen in the left center area. Under the cell area, through where the majority of the heat will be dissipated, void-free bonding in the TIM2 layer was achieved. We believe that this voiding level can definitely meet the CPV's requirement of low thermal resistance. Given that the solder material and thickness are good enough for CTE mismatch, long life reliability can also be expected. We anticipate performing further analysis such as CSAM of the TIM2 layer, SEM of the cross section, and reliability tests to fully validate the soldering quality.



(a)



(b)

Fig. 7: CPV receiver attached to a heat spreader with SnInAgCu solder. (a) General view (b) Magnified view under the cell

A variety of vacuum oven configurations are available, offering additional options to users:

- 1) Lower water vapor partial pressure with cryo pumps.
- 2) Alternative environments using nitrogen, hydrogen, forming gas, formic acid gas or more.
- 3) Higher throughputs through integrating multiple chambers or larger working areas (Fig. 8).



Fig. 8: (a) SST Model 5100 vacuum oven with (b) 30 x 30 cm work area.

4. Summary

Through the above discussion on the fundamental theories and real bonding results, fluxless vacuum reflow is shown to be very suitable for the packaging of solar cells, like CPV, for void-free bonding quality, because it:

- 1) Prevents or reduces oxides by decomposition.
- 2) Improves the wettability by lower vapor pressure.
- 3) Prevents contamination to optical films.

This soldering process will help CPV designers to implement low-thermal-resistance designs. A systematic design based on thermal, mechanical, material and soldering processes is very important.

References

1. William G. Anderson, Sanjida Tamanna, David B. Sarraf, Peter M. Dussinger, and Richard W. Hoffman Jr., "Heat Pipe Cooling of Concentrating Photovoltaic (CPV) Systems", American Institute of Aeronautics and Astronautics (web search).
2. Anja Royne, Christopher J. Dey, David R. Mills, "Cooling of photovoltaic cells under concentrated illumination: a critical review", Solar Energy Materials & Solar Cells, Vol. 86, pp. 451–483, 2005.
3. http://web.mit.edu/2.813/www/readings/Ellingham_diagrams.pdf
4. D. M. Jacobson, S.P. Sangha and J. Hopkins, Design Rules for Fluxless Soldering, The GEC Journal of Technology, Vol. 15, No. 2, 1998.
5. Wei Lin and Y.C. Lee, Study of Fluxless Soldering Using Formic Acid Vapor, IEEE Transactions on Advanced Packaging, Vol. 22, No. 4, November, 1999.
6. Chin C. Lee and Selah Choe, Fluxless In-Sn Bonding Process at 140 C, Materials Science and Engineering, A 333, pp.45-50, 2002.
7. http://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/non_standard.php
8. Giles Humpston, David M. Jacobson, Principles of Soldering, ASM International, Materials Park, Ohio, Chapter 3, pp. 107-108, 2004.
9. Jochen F. Kuhmann, Andrea Preuss, Barbara Adolphi, Karsten Maly, Thomas Wirth, Werner Oesterle, Wolfgang Pittroff, Gerd Weyer, and Marco Fanciulli, "Oxidation and Reduction Kinetics of Eutectic SnPb, InSn, and AuSn: A Knowledge Base for Fluxless Solder Bonding Applications", IEEE Transactions on Components Packaging, and Manufacturing Technology – Part C, Vol. 21, No. 2, April, 1998.
10. Mulugeta Abtey, Guna Selvaduray, "Lead-free Solders in Microelectronics", Materials Science and Engineering, Vol. 27, 2000, pp. 95-141.
11. N. A. Boldyreva, V. Ya. Zabuga, G. G. Tsapyuk, and D. F. Datsenko, "Low-Temperature Carbon Oxidation in a Gradient-Free Reactor", Theoretical and Experimental Chemistry, Vol. 24, No. 6, November, pp. 726-728, 1988.
12. I.A. Aksay, C.E. Hoge, and J.A. Pask, "Wetting under Chemical Equilibrium and Nonequilibrium Conditions", The Journal of Physical Chemistry, Vol. 78, No. 12, pp. 1178-1183, 1974.
13. Hwang, Jennie S., *etal*, US Patent 6176947

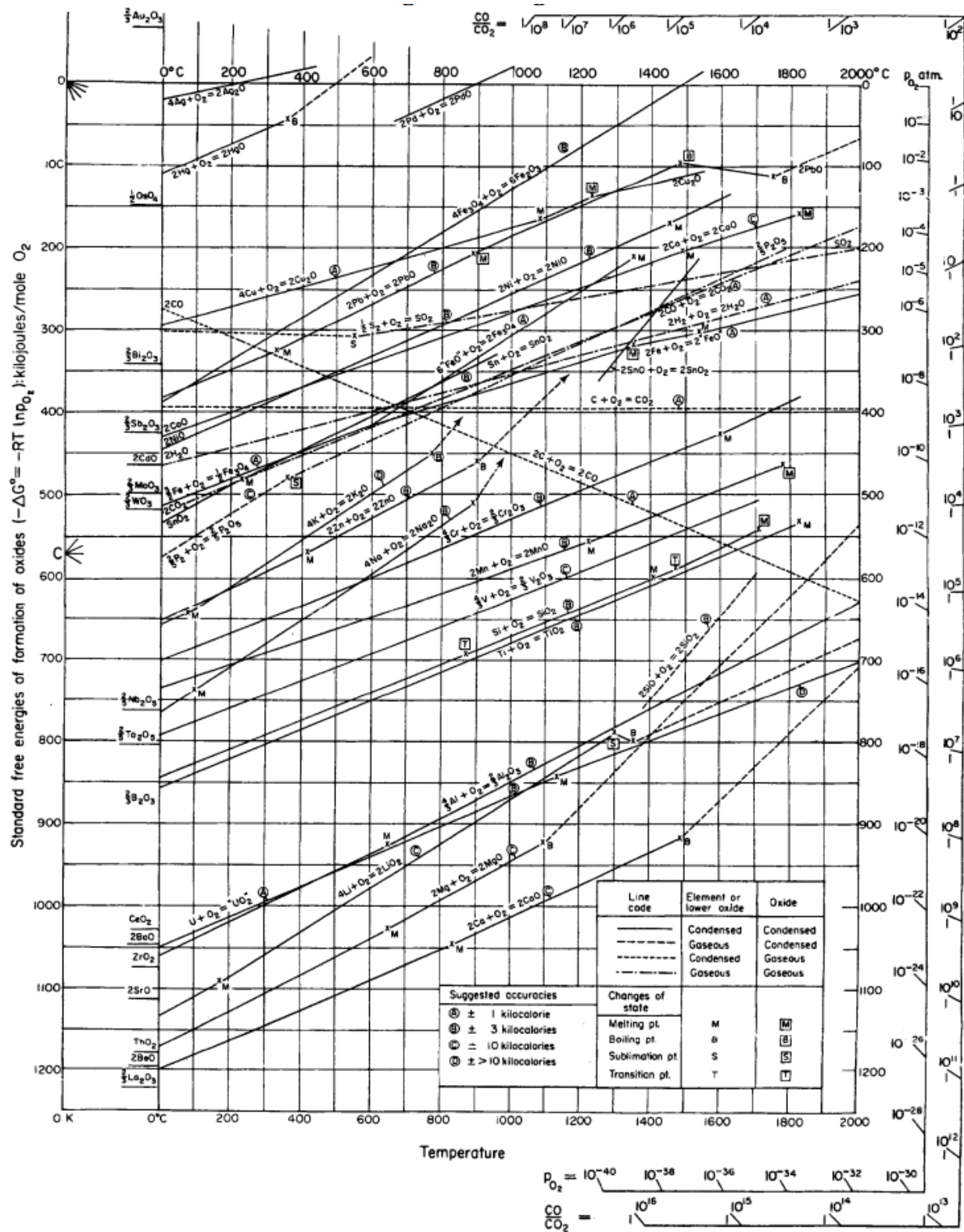


Fig. 2: Ellingham Diagrams [3].