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Thermodynamic evaluation of oxidation during brazing process of medium-voltage electrical circuit breakers

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Key words:

Vacuum circuit breakers;
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vacuum interrupters;
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vaporization; condensation;
oxygen transport;
oxygen impurity;
vacuum conditions;
vacuum furnace

Abstract – The present study is a thermodynamic analysis of the different molecular flows occurring during the vacuum brazing of electrical vacuum bottles also called Vacuum Interrupters (mentioned later as VI). Among the available impurities either coming from the Vacuum Interrupters components materials or from vacuum technology, the analysis is focused on the oxygen since this impurity leads to formation of the more stable compounds, i.e. oxides. During the brazing cycles the resistors of the vacuum furnace and the VI materials including some braze components are the main sources of vapours that partly escape or make deposits on colder parts of the furnace. Vaporization and condensation processes are evaluated, their matter flows quantified and finally their interaction with residual oxygen calculated through a balance between input oxygen from vacuum or neutral gas and the different sources of oxygen coming from the parts under treatment. The enrichment of the VI materials and deposits with oxygen is evaluated as well as the limits required for vacuum conditions. The main conclusion is that present vacuum conditions allow correct working of the brazing sequence but in any other temperature steps or ramps, oxygen is trapped as oxides at the surface of the parts or accumulated in the bulk materials of the furnace.

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To protect an electrical circuit from a damage caused by overload or short circuit, circuit breakers are used. For medium-voltage class, i.e., between 1 and 50 kV_{AC}, Vacuum Interrupters (VIs) are today one of the dominant technology worldwide installed as switchgears: the current interruption is made by creating and extinguishing an electrical arc in a vacuum container [1–3]. Vacuum (typically $\approx 10^{-4}$ Pa, for a new VI) has good dielectric properties remarkable enough to use it has a mean to break a defect current. By removing absorbed gases and impurities from the metallic parts before or during the device manufacturing, certain chemical compounds detrimental to the arc control system efficiency are eliminated. The VIs can operate up to 36 kV (for medium voltage range)

and pressure level below 0.01 Pa (10^{-4} mbar) is guaranteed 30 years.

Sometimes, despite of high quality vacuum conditions during brazing process, some coloured layers with a varied degree of adherence are observed on metals, ceramics, and on alloys parts. These coloured layers may be observed after brazing treatment on around 15% of the parts in one furnace load and microscopic studies show that these layers are oxides. The thickness of these oxide films alternately increase or decrease due to the daily brazing cycles changes in furnace temperature as there are several VI ranges to manufacture. This is mandatory to master this oxide layer deposit mainly depending on temperature because brazing cycles generate more or less desorbed oxygen flows during the next temperature ramp. To understand the origin of these oxide layers

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Fig. 1. Description of main parts of a Schneider vacuum circuit breaker for medium voltage.

1 and quantify their thicknesses, the purpose
2 of the present study is: (i) to identify the
3 vapour composition during brazing process
4 under vacuum; (ii) to analyse the exchanges
5 of the molecular flows between different
6 parts of the furnace/VI and thus evaluate
7 the deposits; (iii) to evaluate the influence
8 of cooling gas as well as of pumping pres-
9 sure limits on the oxides formation. Thermo-
10 dynamic calculation of the vaporization and
11 condensation of different components (i.e.
12 metallic parts and brazing material) as well
13 as of adsorption of oxygen are performed.
14 The present work on vacuum bottles seal-
15 ing is to determine the critical level for the
16 residual vacuum in the furnaces and to spot
17 which kind of gaseous species have a ma-
18 jor significance during brazing cycle on the
19 furnace specifications degradation.

20 1 Methods

21 1.1 Brazing furnace description 22 and basic operation conditions

23 Each subassembly of a Schneider Electric
24 VI is composed by electrical rod (conduc-
25 tor), contact tip, and shields (Fig. 1). There is
26 one fixed subassembly and one moving sub-
27 assembly equipped with a bellows to allow
28 the sliding movement. These components
29 are brazed altogether. The different brazed

joints are: bellows to-rod, flange to insula-
tor, flange to bellows, rod to contact tip, and
bellows to shield.

At Schneider Electric Company brazing
operations are made in a secondary vac-
uum type industrial furnace (ECM Tech-
nologies, Technisud, 38029 Grenoble at
www.ecm-furnaces.com). A typical indus-
trial brazing furnace is described in Fig-
ure 2a. The central part of the furnace is
the casing. It is built as practically a closed
box with packed thermal shields and resis-
tors holders. The casing is mainly pumped
by the front and back apertures A VI load
(about 100 VIs) brazed in an only one cy-
cle is heated using arrays of molybdenum
heating elements hold inside the casing and
close to its internal side (first thermal shield).
The arrays surround the whole parts and, in
this manner, heat can be provided homoge-
neously. The heating elements, with a large
surface of 5.19 m² are made of molybdenum.
The first thermal shield is made of molybde-
num too and others in stainless steel. Their
number guarantees a good thermal shield-
ing and a homogeneous temperature of the
load Typically, the temperature gradient be-
tween the load and the first thermal shield
amount to 10 to 20 K degree difference, the
thermal shield temperature being lower than
the load temperature.

Fig. 2. Schematic description of a ECM vacuum furnace for brazing process of vacuum circuit breakers: (a) general view, (b) Details for location of different temperature measurements.

1 Vacuum, typically 0.0002 Pa ($2 \times$
2 10^{-6} mbar) at room temperature before the
3 heating cycle is obtained using a secondary
4 cryopump ($\approx 14000 \text{ l s}^{-1}$ through a 40 cm
5 pumping orifice diameter) and primary dry
6 pumps.

7 Inside the furnace, there are four loca-
8 tions (Fig. 1b) for temperature recordings
9 using K type thermocouples. In the furnace
10 gate a viewing port (0.07 m diameter) and
11 apertures in thermal front shields allow vi-
12 sual observations and temperature determi-
13 nations using a pyrometer. For the studied
14 brazing cycle, the furnace is heated in two

temperature ramps: – first a 5 K step per
minute until 1068 K and then a temperature
plateau is maintained 100 min – second a 3 K
step per minute until 1163 K and a final tem-
perature plateau for brazing is maintained
10 min. After switching off heating and de-
creasing the temperature inside the furnace
down to 998 K a nitrogen gas is flushed
(99.95%) ($\text{H}_2\text{O} < 10 \text{ ppm}$, $\text{O}_2 < 10 \text{ ppm}$)
in the furnace close to one atmosphere and
vented using a stator-less turbine located at
the rear aperture of the casing in order to
increase the cooling rate of the load.

Fig. 3. Insulators (Al_2O_3) of VCB: (a) original insulator part before brazing process; (b) insulator with deposits after brazing process.

1 **1.2 Characterization of oxides**
2 **deposits**

3 Two types of deposit morphologies on insu-
4 lators may be observed after a brazing cycle:
5 (i) a red to gray or green gradual coloured
6 deposit as presented in Figure 3 that can be
7 more or less easily hand-cleaned with a stuff
8 and, (ii) an strongly adhesive metallic mirror
9 deposit.

10 In the first and currently case, the EDX-
11 ray microanalysis on samples without de-
12 posits (see Figs. 3 and 4b) reveals the
13 presence of Silicon (45.3 at%), Aluminum
14 (19.0 at%), and Oxygen (24.2 at%), charac-
15 teristics of the alumina ceramic and silica based
16 glaze. The presence of Potassium (5.6 at%),
17 Sodium (1.9 at%), Magnesium (1.3 at%), Cal-
18 cium (1 at%) and Manganese (0.5 at%) is jus-
19 tified by the method of preparation of ceram-
20 ics and its glazing. For sample with visible
21 deposits (see Fig. 3b) and according to the
22 spectra after removing the above contribu-
23 tions of substrate chemical species, the de-
24 posit is characterized by the major presence
25 of Copper (2.5 at%), a small contribution of
26 Molybdenum (1.7 at%), and some traces of
27 Iron (0.5 at%).

28 The second case is related to some rare
29 brazing cycles which were associated to
30 overheating of the supplementary central re-
31 sistor since the deposit analysed by MEB (see
32 Fig. 4a) revealed some small like-droplets
33 at the surface – or probably crystal growth
34 structures – and the EDX analysis (see

Fig. 4b) shows the only contribution of pure
molybdenum.

35 **1.3 Thermodynamic data**
36 **and calculation method**

37 The casing in which is performed the braz-
38 ing process is a closed thermal shield hous-
39 ing with the only two apertures (described
40 before) and it can be considered analogous
41 to a Knudsen effusion cell – a basic vessel
42 to study high temperature equilibrium va-
43 porization processes [4] – with the ratio s/S
44 between the cross-section “s” of the effusion
45 orifice located in its lid and the surface “S”
46 of the vaporizing sample disposed inside the
47 cell. This ratio is usually taken $\leq 10^{-2}$ [5] in
48 order to obtain equilibrium conditions for
49 vaporisation of surfaces at least when reac-
50 tions of vaporisation are fast enough (evapo-
51 ration coefficient of metals, usually, is >0.1).
52 Here, the orifices for gas or vapours effusion
53 out of the casing are the front aperture facing
54 the viewing port (fitted with retractable ther-
55 mal shields as explained before) and the rear
56 aperture (fitted with a stator-less turbine for
57 venting the cooling gas). The “equivalent”
58 sample vaporizing surface in the brazing
59 furnace is all the surfaces of different parts
60 of Vis which vaporize from one furnace load
61 during the brazing process. In Table 1, the
62 only surfaces which are presented are the VI
63 inner and outer surfaces “exposed to vac-
64 uum” inside the furnace volume, excluding
65 for example the hidden surfaces in contact
66
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Fig. 4. (a) Scanning electron micrograph of a sample with deposits on ceramic parts which were associated to overheating of a supplementary central resistor. (b) The representative EDX spectra of a sample without deposits and for one with deposits on ceramic parts.

Table 1. Vaporization and condensation surfaces in the brazing oven which are taken into account for flow calculations.

Components of VCB		Surface exposed** to vacuum /m ²	Ratio <i>s</i> / <i>S</i> Escaping flow/evaporation flows**	Surface exposed to vacuum /%	Total surface per load that vaporizes /m ²
Conductors (Cu OFHC)		1.8	0.003	27.9	
Contacts (Cu-Cr alloy)		0.576	0.0094	8.9	
Flanges – bowls (Cu-Ni alloy)		3.96	0.0014	61.3	
brazed joints (Cu-Ag-Ni alloy)	conductors with bellows shields	0.029			6.458
	bellows with bellows shields.	0.058	0.044	1.9	
	insulator with flange	0.029			
	bellows with flange	0.006			
Casing deposit (mainly Ag-Cu alloy)	First Mo thermal shield	6.154	0.0008	100	6.154
Resistor (Mo)		5.197	0.001	200	5.197
Apertures of the casing	Front aperture	0.0004			0.0054
	Rear aperture (fitted with the turbine)	0.005			

* “exposed to vacuum” means only the parts surfaces vaporizing i.e. surrounded by vacuum. The parts surfaces which are hidden by the working platform or by the solder were not taken into account.

** Escaping flow from apertures reported to each vaporizing parts surface.

1 with the carrier platform (holders) or those
2 at the brazed interfaces. The above criteria
3 ($s/S < 10^{-2}$) for equilibrium vaporization in
4 the casing is fulfilled as presented in Table 1.

5 Matter flow vaporization and conden-
6 sation calculations are performed consid-
7 ering that a thermodynamic equilibrium is
8 established between the condensed sample
9 i.e. each loaded part surface and its vapour
10 phase – and the casing volume. Due to some
11 condensation on the casing first thermal
12 shield – which is the first cold temperature
13 encountered by the vaporizing flows – the
14 internal surface of the casing is taken into ac-
15 count for the vaporization of these deposits.
16 All surfaces are considered to vaporize at
17 equilibrium since the balance of evaporat-
18 ing and condensing flows are close to 1, ex-
19 cept for molybdenum based gaseous species
20 that may come from the resistor and vapor-
21 ize at higher temperature than the casing
22 and the load temperature and this feature
23 let these species condense instantaneously
24 Consequently no molybdenum species back
25 flow on the resistor can occur and the Mo
26 and related species vaporization is consid-
27 ered as free vaporization. For free vaporiza-
28 tion it may exist a “so-called” evaporation
29 coefficient [6] usually quoted as α_i (i for each
30 gaseous species). At equilibrium this coeffi-
31 cient equals 1 but in case of some low kinetic
32 process at vaporization $\alpha_i < 1$ and some-
33 times very low for complex species ($\approx 10^{-4}$
34 to 10^{-6}) vaporizing from some condensed
35 phases as amorphous. However we shall
36 consider that these species evaporate at equi-
37 librium for molybdenum or molybdenum
38 oxide which corresponds to the maximum
39 vaporization rate.

40 The SGTE-Alloy Phase Diagrams Ther-
41 modynamic database [7] – a database where
42 the basic binary alloys corresponding to the
43 VI parts are stored – was used to calculate
44 the gaseous phase formed during the braz-
45 ing process, and it was operated with the
46 FactSage [8] software with “Equilib module”
47 which performs the thermochemical equi-
48 librium calculations based on Gibbs energy
49 minimization. Because oxygen combination
50 with the present alloys components is the
51 main key point of this study, we completed
52 SGTE alloys phase diagrams information
53 with the following binary and ternary sys-

tems the thermodynamic and phase diagram
data of which were already optimized in sci-
entific literature: Cu-O [9, 10], Ag-O [9, 11]
Cr-O [12], Ni-O [13], Cu-Ag-Ni [14], and
Cu-Ag-O [15]

For an alloy composed by an homoge-
neous phase or for diphasic systems like
Mo(s)-MoO₂(s) as an example, the partial
vapour pressure of the j gaseous species
is related to temperature by the simple
relation,

$$\ln p_j = -\frac{\Delta_{vap}H_j(\bar{T})}{RT} + \Delta_{vap}S_j(\bar{T}) \quad (1)$$

in which the partial enthalpy $\Delta_{vap}H_j(\bar{T})$ and
entropy $\Delta_{vap}S_j(\bar{T})$ of vaporization of the j
molecule at mean temperature are constants
in our temperature range. For this reason,
we used the final relation for partial pres-
sures calculations as,

$$\log_{10} p_j = \frac{A}{T} + B. \quad (2)$$

In case of phase change – as for braze melting
– a new relation is used for the new phase
in the temperature range where this phase
is stable. The whole set of known gaseous
species vapour pressures and related coeffi-
cients are summarized in Table 2.

Those partial pressures relations were
then introduced in Visual Basic from Ex-
cel (Microsoft Office Package) in order to
calculate the different matter flows and to
solve flow balances. The molar flow F_j of any
 j gaseous molecule (i.e. Cu, Cu₂, Cr, CrO,
CrO₂, Ag, Ni, O, O₂, etc.) vaporized from
each part surface exposed to vacuum dur-
ing one brazing cycle was calculated along
any temperature cycle using the equation
for steady-state effusion of dilute gases in
vacuum, known as the Hertz-Knudsen rela-
tion [4]:

$$F_j = \frac{\alpha_j p_j S_{vap}}{\sqrt{2\pi M_j RT}} \Delta t \quad (3)$$

where:
 F_i – is the molar flow of j molecule
(mol.m⁻².s⁻¹);
 Δt – is the cycle time unit (in s) selected
from temperature recordings: here 30 s;
 α_j – the evaporation coefficient we set equal
to 1 for equilibrium conditions (see text
above);

Table 2. Coefficients for the calculation of partial pressures of vaporization as a function of the inverse of temperature for the different parts materials i.e. conductors, contacts, flanges brazing joints and resistor (Mo). Their behaviour with temperature is given as $\log_{10}(p/Pa) = A/(T/K) + B$.

VCB parts and material	Gaseous Species	A	B	Temperature range /K
Conductors	Cu(g)	-17559	11.7163	300–1300
OFHC Cu	Cu ₂ (g)	-24523	13.4940	
Pure Cu				
Contacts	Cu(g)	-17 558	11.7139	300–1300
Molar fractions	Cu ₂ (g)	-24 520	13.4891	
X _{Cu} = 0.71	Cr(g)	-21 898	13.4678	
X _{Cr} = 0.29 alloy	Cr ₂ (g)	-32 658	14.5295	
Flanges/bowls	Cu(g)	-17 518	11.5597	300–1300
Molar fractions	Cu ₂ (g)	-24 440	13.1807	
X _{Cu} = 0.68	Ni(g)	-21 800	12.2498	
X _{Ni} = 0.32 alloy	Ni ₂ (g)	-33 324	13.7763	
Solder	Ag(g)	-14 812	6.6009	300–1240 (solid phase)
Molar fractions	Ag ₂ (g)	-21 014	8.3602	
X _{Cu} = 0.3967	Cu(g)	-17 580	6.7545	
X _{Ag} = 0.5918	Cu ₂ (g)	-24 535	8.5380	
X _{Ni} = 0.0115	Ni(g)	-21 962	7.6329	
Solid alloy	Ni ₂ (g)	-33 656	9.5469	
	AgCu(g)	-23 393	8.7764	
Solder	Ag(g)	-13 915	10.8224	1240–1300 (liquid phase)
Molar fractions	Ag ₂ (g)	-19 094	11.6741	
X _{Cu} = 0.3967	Cu(g)	-17 316	11.4929	
X _{Ag} = 0.5918	Cu ₂ (g)	-23 919	12.9368	
X _{Ni} = 0.0115	Ni(g)	-21 689	12.3601	
Liquid alloy	Ni ₂ (g)	-33 176	14.0645	
	AgCu(g)	-22 093	12.5945	
Deposits	Ag(g)	-14 820	11.6353	400–1020 (Cu–Ag sol.)
Ag _{0.97} -Cu _{0.03} alloy	Ag ₂ (g)	-21 036	13.4534	
/mol. Frac.	Cu(g)	-17 594	11.8021	
	Cu ₂ (g)	-24 610	13.7119	
	AgCu(g)	-23 421	13.8845	
Deposits	Ag(g)	-14 661	6.4220	1020–1120 (liquid phase)
Ag _{0.97} -Cu _{0.03} alloy	Ag ₂ (g)	-20 636	7.9164	
/mol. Frac.	Cu(g)	-15 834	4.5497	
	Cu ₂ (g)	-21 006	4.0942	
	AgCu(g)	-21 414	6.3007	
Deposits	Ag(g)	-13 911	5.8060	1120–1300 (liquid phase)
Ag _{0.97} -Cu _{0.03} alloy	Ag ₂ (g)	-19 085	6.6407	
/mol. Frac.	Cu(g)	-15 700	4.1426	
	Cu ₂ (g)	-20 687	3.2355	
	AgCu(g)	-20 472	5.2270	
OFHC Cu - Cu ₂ O	Cu(g)	-17 544.4	6.7027	400–1300 K
	Cu ₂ (g)	-24 482.1	8.4557	
	CuO(g)	-24 940.7	8.7874	
	O ₂ (g)	-17 703.3	7.7173	
	O(g)	-21 979.5	7.1872	
	O ₃ (g)	-33 971.7	8.0012	

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Table 2. Continued.

Flanges/Bowls $X_{\text{Cu}} = 0.68$ $X_{\text{Ni}} = 0.32$ + NiO	Cu(g)	-17 540.8	6.6206	400–564 K
	Cu ₂ (g)	-24 518.3	8.3807	
	Ni(g)	-21 975.9	7.6642	
	Ni ₂ (g)	-33 676.2	9.5979	
	CuO(g)	-28 551.6	9.6320	
	NiO(g)	-27 283.7	9.6248	
	O ₂ (g)	-24 936.0	9.5790	
	O(g)	-25 541.4	8.0057	
	O ₃ (g)	-44 795.2	10.7426	
Flanges/Bowls $X_{\text{Cu}} = 0.68$ $X_{\text{Ni}} = 0.32$ + NiO	Cu(g)	-17 462.8	6.4967	564–1400 K
	Cu ₂ (g)	-24 286.8	8.0071	
	Ni(g)	-21 636.1	7.0711	
	Ni ₂ (g)	-33 015.6	8.4398	
	CuO(g)	-28 528.1	9.6215	
	NiO(g)	-26 899.8	8.9792	
	O ₂ (g)	-25 041.2	9.7978	
	O(g)	-25 686.9	8.2710	
	O ₃ (g)	-45 001.8	11.1490	
Contact pads (Cu,Cr,O) – Cr ₂ O ₃	Cu(g)	-17 471.8	6.6221	300–1348 K
	Cu ₂ (g)	-24 298.3	8.2521	
	Cr(g)	-21 797.6	8.35600	
	Cr ₂ (g)	-32 417.6	9.2715	
	CuO(g)	-35 700.9	9.2744	
	CrO(g)	-29 161.8	9.8493	
	CrO ₂ (g)	-33 457.5	10.2681	
	CrO ₃ (g)	-42 128.5	9.83673	
	Cr ₂ O(g)	-33 480.0	11.0282	
	Cr ₂ O ₂ (g)	34 070.7–	10.8292	
	Cr ₂ O ₃ (g)	41 775.0	12.9331	
	O ₂ (g)	-39 369.2	8.8592	
	O(g)	-32 858.3	7.8053	
	O ₃ (g)	-66 499.3	9.7368	
Contact pads (Cu,Cr,O) – Cr ₂ O ₃	Cu(g)	-16 400.3	5.8111	1348–1600 K
	Cu ₂ (g)	-22 056.9	6.5501	
	Cr(g)	-21 389.9	8.0362	
	Cr ₂ (g)	-31 624.7	8.6373	
	CuO(g)	-34 541.5	8.3890	
	CrO(g)	-28 631.3	9.4232	
	CrO ₂ (g)	-32 892.0	9.8095	
	CrO ₃ (g)	-41 678.4	9.4682	
	Cr ₂ O(g)	-32 497.4	10.2424	
	Cr ₂ O ₂ (g)	-33 193.3	10.1247	
	Cr ₂ O ₃ (g)	-41 037.1	12.3383	
	O ₂ (g)	-39 224.8	8.7351	
	O(g)	-32 884.0	7.8233	
	O ₃ (g)	-66 401.4	9.6458	
(Ag,Cu,Ni,O) – NiO solder	Ag(g)			Différentes phases
	Ag ₂ (g)			
	Cu(g)			
	Cu ₂ (g)			
	Ni(g)			
	AgCu(g)			
	CuO(g)			
	AgO(g)			
	NiO(g)			
	O ₂ (g)			
	O(g)			

Table 2. Continued.

Ag _{0.97} -Cu _{0.03} - Cu ₂ O Deposits	Ag(g)	-14 787.6	6.5820	300–784 Kr
	Ag ₂ (g)	-20 955.4	8.3206	
	Cu(g)	-17 566.9	6.7561	
	Cu ₂ (g)	-24 539.1	8.5928	
	AgCu(g)	-23 345.2	8.7578	
	CuO(g)	-24 994.2	8.9058	
	AgO(g)	-24 484.2	8.9589	
	O ₂ (g)	-17 762.8	7.8497	
	O(g)	-21 996.645	7.2167	
	O ₃ (g)	-34 047.314	8.1619	
Ag _{0.97} -Cu _{0.03} - Cu ₂ O Deposits	Ag(g)	-14 663.9	6.4224	784–1200 K
	Ag ₂ (g)	-20 643.3	7.9181	
	Cu(g)	-15 856.7	4.5735	
	Cu ₂ (g)	-21 052.8	4.1427	
	AgCu(g)	-21 441.5	6.3259	
	CuO(g)	-26 355.2	10.6432	
	AgO(g)	-27 431.8	12.7196	
	O ₂ (g)	-23 909.3	15.6945	
	O(g)	-25 145.8	11.2372	
	O ₃ (g)	-43 322.7	20.0001	
Ag _{0.97} -Cu _{0.03} - Cu ₂ O Deposits	Ag(g)	-13 717.0	5.6487	1218–1500 K
	Ag ₂ (g)	-18 686.1	6.3172	
	Cu(g)	-17 570.1	5.6855	
	Cu ₂ (g)	-24 414.8	6.3118	
	AgCu(g)	-22 133.6	6.6014	
	CuO(g)	-24 130.6	9.1011	
	AgO(g)	-22 545.3	9.2906	
	O ₂ (g)	-16 055. 2	10.4048	
	O(g)	-21 282.4	8.6464	
	O ₃ (g)	-31 619.3	12.1308	
Mo(s) – MoO ₂ (s)	Mo(g)	-33 948	7.5034	1000–2000 K
	O(g)	-28 174	7.7433	
	O ₂ (g)	-29 830	8.5864	
	O ₃ (g)	-33 121	9.6700	
	MoO(g)	-28 543	10.0078	
	MoO ₂ (g)	-25 587	9.5608	
	MoO ₃ (g)	-30 073	11.6708	
	Mo ₂ O ₆ (g)	-36 295	14.4155	
	Mo ₃ O ₉ (g)	-44 062	16.1263	
	Mo ₄ O ₁₂ (g)			

1 p_j – is the partial pressure of the molecule or
2 gaseous species j (Pa);
3 S_{vap} – is the vaporizing surface from one
4 material in a load (m²) (for more details see
5 Tab. 1);
6 R – is the ideal gas constant =
7 8.3145 J.mol⁻¹.K⁻¹;
8 T – is temperature (K);
9 M_j – molar mass of the j gaseous species
10 (kg.mol⁻¹).

During the vaporization and condensa- 11
tion processes, the only atomic flows F_i for 12
any i component are considered as issued 13
from different j molecules and the following 14
relation is used: 15

$$F_i^{evap} = \sum_j v_i \frac{p_j S_{vap}}{\sqrt{2\pi M_j RT}} \Delta t \quad (4)$$

relation in which v_i is the stoichiometric co- 16
efficient of the atom i in the j vaporized 17

Fig. 5. Vaporization of the Mo resistor as pure Mo(g) under Ultra High Vacuum or Mo gaseous oxides when MoO₂(s) is formed at its surface and condensation on loaded parts. The vaporization and condensation yield is presented as equivalent layers thickness in microns per hour

1 molecule. In case of condensation on another
2 surface the same relation is applied, chang-
3 ing the surface value.

4 2 Results related to the only 5 vaporization of different 6 materials

7 2.1 Vaporization flows of Mo from 8 the resistor during one brazing 9 cycle

10 In a first step, the vaporization of the resistor
11 is calculated with its associated Mo flows as
12 a function of the resistor temperature since
13 the maximum available temperature before
14 the occurrence of Mo deposits in the cas-
15 ing is to be known in order to fix a limit to
16 the electrical power input. The total evap-
17 orated Mo flow is calculated according to
18 relation (4) at any temperature T and total
19 resistor surface available. This total vapor-
20 ized flow may be condensed either on the
21 casing first thermal shield – species emitted
22 from the back surface of the Mo resistor – or
23 on the loaded parts from the front surface

of the Mo resistor. As these surfaces are at
very low temperature compared to the resis-
tor (at least 300 K gradient) the Mo species
condense readily. The deposition on the first
thermal shield made of Mo has no influence
on other deposits as the Mo cannot be re-
emitted at the casing temperatures. Taking
into account of the respective surfaces of the
front surface of the resistor and the loaded
parts, the deposit thickness can be evaluated
using the respective surfaces as presented
in Figure 5. As the surfaces ratio is close to
1, the two curves for pure Mo vaporization
and deposition are very close, the deposi-
tion thickness being slightly lower than the
evaporation thickness.

However, in case of frontal situation be-
tween the resistor and some loaded parts
– parts close to the resistor and deposits
observed during some brazing cycles –, the
ratio of evaporated surface to condensed
surface becomes equal to 1 and the deposit
thickness tends to be equal to the evap-
oration rate thickness. This represents the
maximum deposit thickness as presented in
Figure 5 for pure Mo.

1 In case of increasing background oxygen
2 pressure in the furnace and consequently in
3 the casing *via* its two main orifices the Mo
4 resistor may finally evaporate through sev-
5 eral gaseous oxides the partial pressures of
6 which increase with oxygen incident flow
7 up to the apparition of the diphasic Mo-
8 MoO₂(s) at the surface of the resistor. Taking
9 into account of the formation of this diphasic
10 at the surface of the resistor, same vaporiza-
11 tion calculations are performed and reported
12 as MoO₂(s) deposits in Figure 5. The depo-
13 sition rate increases by a factor 10⁴ to 10⁵
14 mainly due to the high volatility of molyb-
15 denum oxides. If a deposition limit is fixed
16 at 10⁻² micron h⁻¹, the maximum available
17 temperature for the Mo resistor in high vac-
18 uum is about 1930 K (1660 °C) meanwhile
19 the oxygen background decreases this maxi-
20 mum temperature down to 1430 K (1160 °C).
21 Note that between the two situations – pure
22 Mo vaporization and diphasic vaporization
23 from the resistor material – intermediate
24 steady-state vaporizations occur as calcu-
25 lated hereafter when considering the steady-
26 state pumping of oxygen species between
27 the casing and the furnace housing.

28 2.2 Vaporization flows of loaded 29 parts during one brazing cycle

30 Among all parts existing in the industrial
31 furnace our vaporization calculations take
32 into account the only loaded parts because
33 they are foreseen as major contributors to
34 further deposits: conductors (Cu-OFHC),
35 contacts (Cu-Cr alloys), flanges (Cu-Ni al-
36 loys), and braze materials (Cu-Ag-Ni alloys)
37 (refer to Tab. 2 for compositions). All gaseous
38 species known and compiled in the data
39 bank are used in the calculations, i.e. Cu(g),
40 Cu₂(g), Cr(g), Cr₂(g), Ni(g), Ni₂(g), Ag(g),
41 Ag₂(g) and AgCu(g). As the dimers and the
42 hetero-atomic AgCu molecules have pres-
43 sures lower than 10⁻³ times the monomer
44 pressures, the evolution of partial pressures
45 of the only main gaseous molecule versus
46 the inverse of temperature are presented for
47 all the present materials used to build a VI
48 as coefficients in Table 1 and pressures in
49 Figure 6. This inter-comparison of partial
50 pressures over parts in the furnace shows
51 that the same gaseous species originating

from one pure material has higher pressures 52
than from another alloyed part: – for in- 53
stance Cu(g) pressure from conductors is 54
higher than from braze even if the difference 55
does not appear important – whereas some 56
species like Ag(g) comes from the only braze 57
material. 58

Consequently, some matter transport via 59
the gaseous phase will occur during the 60
brazing cycle between these different ma- 61
terials or parts. More, as the first thermal 62
shield of the casing is at slightly lower tem- 63
perature (measured as 10 to 20 K) than the 64
loaded parts, the vapours will go first to this 65
cold point and partly condense and partly re- 66
evaporate. Another small proportion (<10⁻²) 67
of vapours escapes by effusion through the 68
two apertures of the casing. The main ques- 69
tion is “what is the real pressure or the 70
real partial pressures?” existing in the cas- 71
ing during the brazing cycle since thermo- 72
dynamic calculations can be performed for 73
only constant temperature and for a unique 74
sample in its stable state. To understand 75
what sort of steady-state is established in the 76
casing during brazing we consider two lim- 77
iting conditions: 78

1. For vaporization of parts with no mat- 79
ter back flow – open sky under vacuum 80
or the casing assuming a total condensa- 81
tion of vapours (like a cold point at more 82
than some 100 K below or induction fur- 83
nace with cold thermal shields) the total 84
flow of vaporization is calculated from 85
the sum of parts vaporization flows. The 86
mean flow molar fraction escaping from 87
the parts during a brazing cycle has been 88
calculated and is mainly $X_{Cu} = 0.39$ and 89
 $X_{Ag} = 0.61$ since other components are 90
at very low partial pressures and their 91
contribution is negligible. 92
2. For vaporization of parts under isother- 93
mal conditions – i.e. a first thermal shield 94
of the casing at the same temperature 95
as the loaded parts – the condensation 96
flow coming back to the parts is the same 97
as the vaporization flow, the only differ- 98
ence in the flows is coming from the two 99
apertures that let escape a small effusing 100
flow (same proportion as $s/S \leq 10^{-2}$). 101
At that time quasi-equilibrium condi- 102
tions are established in the casing: par- 103
tial pressures are thus for each species 104

Fig. 6. Temperature-dependence of partial vapour pressures of gaseous species vaporizing from the different materials of the VCB. The only main gaseous species are presented: Cu(g) from conductors (pure Cu), from CuNi bowls, from CuCr contacts and from the AgCuNi solder, Cr(g) from contacts, Ni(g) from bowls-flanges; Ag(g) from the solder material.

the partial pressure as calculated in Figure 6. But yet the partial pressures for any gaseous species cannot be summed and the value to be retained is the one coming from the main source material (i.e. the one with the greatest activity, i.e. pressure): for instance the Ag(g) pressure is controlled by the braze, the Cu(g) pressure controlled by the pure Cu parts. Indeed, parts made of alloys have activities lower than one (one is for pure components) and cannot generate higher pressures than pure components. For these alloyed parts, some incorporation of material can occur by adsorption from the vapour pressures in excess of their own ones and then followed by bulk diffusion to generate new alloys. Neglecting these phenomena that are considered to have low rates and not important for the duration of one brazing cycle, the gas phase composition is readily calculated from the only maximal partial pressures as,

See equations (5) and (6) next page.

taking into account of the only main components Cu and Ag in the vaporization process.

The resulting gas phase composition (molar fraction X_{Ag} of Ag, with $X_{Cu} = 1 - X_{Ag}$) is presented in Figure 7 showing a composition very rich in Ag (like pure Ag) at low temperature that becomes an alloy (Ag,Cu) with small Cu content (1 to 2% mole fraction) and a very small content with Ni and Cr (like impurities). This composition corresponds to quasi-equilibrium conditions that are established in the casing for the vapours.

During a brazing cycle, the first thermal shield temperature is measured along any brazing cycle to be slightly lower than the load temperature and the present gaseous phase (item 2 above) at quasi-equilibrium will partly condense on this shield and re-evaporate causing a matter back flow towards the loaded parts which becomes different from the one at equilibrium temperature of the loaded parts. Thermodynamic calculations of the phase composition condensed on the shield as well as its re-vaporization is performed starting from the above gas phase composition (isothermal conditions as for item 2) and decreasing the temperature by 0, 10 and 20 K for

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$$X_{Cu} = \frac{p_{Cu}^{conductors} + 2p_{Cu_2}^{conductors}}{p_{Cu}^{conductors} + 2p_{Cu_2}^{conductors} + p_{Ag}^{solder} + 2p_{Ag_2}^{solder} + p_{AgCu}^{solder}} \quad (5)$$

and

$$X_{Ag} = \frac{p_{Ag}^{solder} + 2p_{Ag_2}^{solder} + p_{AgCu}^{solder}}{p_{Cu}^{conductors} + 2p_{Cu_2}^{conductors} + p_{Ag}^{solder} + 2p_{Ag_2}^{solder} + p_{AgCu}^{solder}} \quad (6)$$

Fig. 7. Gas phase composition – molar fraction of Ag in the practically pure [Ag-Cu] system - issued from the vaporization of the loaded parts in the casing during one brazing cycle as a function of temperature of the load.

1 brazing cycle temperatures in the range 900
2 to 1300 K (in this range partial pressures are
3 high enough to generate matter flows). The
4 composition of the deposit is presented in
5 Figure 8 and the ratio of condensed phase
6 on the casing inner wall to vapour phase ratio
7 (partition coefficient) in Figure 7.

8 In Figure 8, for a 0 K gradient (isothermal
9 conditions) the sampled gas phase should
10 not precipitate a condensed phase but here
11 it precipitates because the original gas phase
12 composition is not an equilibrium one – i.e.
13 this phase results from a mixing of Cu +
14 AgCu different vaporizing materials, and
15 there is an excess of Cu(g) molecules. This
16 feature explains the low values of the Ag
17 concentration observed for 0 K gradient (on
18 the y axis). When a temperature gradient is
19 established the condensed composition re-

cover a value close to the one calculated
in the above condition of quasi-equilibrium
(inlet flow in the thermodynamic calculations).
The composition of the deposit on the casing
is close to the vapour one, a little bit richer
with Ag. In Figure 9 the partition coefficient
corresponds to the proportion of condensed
phase reported to the gas phase (as a matter
flow) as a function of the temperature
gradient between the furnace and the first
thermal (inner) shield of the casing. At high
temperature the condensed phase on the casing
becomes liquid for small gradients and this
feature explains the apparent re-increasing
value at 0 K gradient for 1300 K. The
knowledge of partition coefficient value
allows the estimate of the total matter
condensed on 1 m² of casing during one
brazing cycle from the incident Knudsen

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Fig. 8. Composition of the deposits – practically in the pure [Ag-Cu] binary system – on the first inner thermal shield of the casing as a function of the temperature gradient between the load and this shield for different treatment temperatures.

Fig. 9. Partition coefficient between the solid phase as condensed on the casing and the gaseous phase vaporizing from the load.

1 flow coming from the vapour, taking into
2 account of the cycle duration. Our calcula-
3 tions give 0.0672 moles of $\text{Ag}_{0.97}\text{-Cu}_{0.03}$ al-
4 loy (molar fractions) deposited per brazing
5 cycle, corresponding to a layer of $0.69\ \mu\text{m}$
6 thickness.

7 As the deposited layers for each cycle
8 are very thin (thickness $\approx 0.7\ \mu$) and prob-
9 ably not high density with an appreciable
10 specific surface, it will probably react with
11 oxygen at least during the opening of the
12 furnace for next loading or with other possi-
13 ble sources of oxygen during the cooling as
14 for instance the oxygen content of the flush-
15 ing N_2 gas or the residual background of the
16 vacuum pumping. To evaluate the oxygen
17 affinity of these Ag-Cu deposits, thermody-
18 namic equilibrium calculations with the de-
19 posit composition were performed with in-
20 creasing oxygen content in order to observe
21 the formation of the first solid oxide and
22 to quantify the quantity of oxygen that can
23 be dissolved in this deposited alloy layer.
24 Cu_2O solid is calculated as the first and only
25 formed oxide from room temperature until
26 1360 K that appears when the oxygen solu-
27 bility limit is reached for the Ag-Cu deposits.
28 Then we focused the calculations on the be-
29 haviour of the Ag-Cu-O system (at the above
30 deposit composition) – mainly the oxygen
31 pressure and the oxygen solubility at the ox-
32 ide formation – in order to evaluate the ex-
33 tent of oxygen dissolution in the alloy that
34 can be a tank which during next cycles of
35 brazing processes generates memory effects
36 (at least oxygen desorption). Indeed, under
37 temperature decrease at the end of a braz-
38 ing cycle, the deposited alloy ($\text{Ag}_{0.97}\text{-Cu}_{0.03}$)
39 in one cycle can adsorb oxygen until dis-
40 solution as well as other oxygen contain-
41 ing gaseous species as for instance $\text{CO}(\text{g})$
42 or gaseous oxides, whereas during the next
43 cycle under temperature rising the deposit
44 can desorb its oxygen via different gaseous
45 species. More, the thickness of the former de-
46 posited layers can be only increased at each
47 brazing cycle although some vaporization
48 also occurs and finally the oxygen storage
49 capacity increases.

50 The deposited alloy composition is
51 drawn in Figure 10 on the Ag-Cu binary
52 phase diagram. The deposit is mainly pure
53 Cu with a small quantity of [Ag,Cu] solid so-

lution between 400 and 1020 K, then [Ag,Cu] 54
solid solution in the range 1020–1120 K, and 55
above it is a liquid. As calculated above, for 56
all these ranges the oxygen effect – at satu- 57
ration - is the only formation of Cu_2O ox- 58
ide. The calculated main gaseous species in 59
the vapour phase of the [Ag, Cu,O - Cu_2O] 60
system at the composition of the deposits is 61
 $\text{O}_2(\text{g})$ and its partial pressure at the solubility 62
limit is represented by the relations: 63

$$\log p(\text{O}_2)/\text{Pa} = -17776/T + 12.8682 \quad (400\text{--}1020\ \text{K})$$

Triphasic Cu-Ag(Cu) solution (7)

$$\log p(\text{O}_2)/\text{Pa} = -23920/T + 20.716 \quad (1020\text{--}1120\ \text{K})$$

for (Ag, Cu) solution (alloy) (8)

$$\log p(\text{O}_2)/\text{Pa} = -37624/T + 32.288 \quad (1120\text{--}1300\ \text{K})$$

for the liquid phase. (9)

For the same system, the temperature de- 66
pendence of the oxygen mole fraction (X_{O}) 67
at saturation in the solid and liquid solutions 68
(maximum oxygen solubility) is described 69
by the equations: 70

$$\log X_{\text{O}} = -10480/T + 3.9889 \quad (400\text{--}1020\ \text{K})$$

(10)

$$\log X_{\text{O}} = -13296/T + 7.6565 \quad (1020\text{--}1120\ \text{K})$$

(11)

$$\log X_{\text{O}} = -18974/T + 12.56 \quad (1120\text{--}1300\ \text{K}).$$

(12)

3 Results: Steady-state equilibria 71 with background oxygen 72

3.1 Influence of the flushed N_2 73 cooling gas on formation 74 of oxides deposits (layers) 75

In order to decrease the room temperature 76
recovering time of the load which may be 77
very long under vacuum, a nitrogen flush- 78
ing gas is used assisted by venting the gas in 79
the furnace with a turbine. The oxygen quan- 80
tity introduced in the furnace by the cooling 81
gas, is calculated using ideal gas law and 82
impurities data furnished by the supplier: 83

$$N_{\text{O}_2} = \frac{[\text{O}_2]pV}{RT} \quad (13)$$

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Fig. 10. Optimized [Ag-Cu] binary phase diagram from thermodynamic and phase diagram data issued from literature.

1 where:
 2 $[\text{O}_2]$ – oxygen impurities content (10 ppm in
 3 volume) $/\text{m}^3$;
 4 p – final furnace pressure/Pa (101 325 Pa);
 5 V – furnace volume/ m^3 (2.4 m^3) or total vol-
 6 ume of the introduced flushing gas;
 7 R – ideal gas constant ($\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$);
 8 T – temperature (K).
 9 Note that the cooling gas is flushed to fill
 10 up and then maintain the furnace at a pres-
 11 sure slightly under 1 bar during the cooling
 12 cycle and consequently the total cooling gas
 13 volume amounts to the furnace volume.

14 A first step is to evaluate the possibil-
 15 ity of oxides formation at the surface of the
 16 parts or any deposit when comparing differ-
 17 ent oxygen potentials. For this we compare
 18 the temperature dependence of the final oxy-
 19 gen impurity partial pressure imposed by
 20 the flushing gas (furnace filled at 1 bar) in
 21 Figure 11 with the one existing at saturation
 22 of the one brazing cycle formed deposit or
 23 of the different alloys of the loading. Remind
 24 that the formed oxide is first the $\text{Cu}_2\text{O}(\text{s})$ ex-
 25 cept for the [Cu-Cr] contacts where $\text{Cr}_2\text{O}_3(\text{s})$

may be formed and [Cu-Ag-Ni] braze where
 $\text{NiO}(\text{s})$ may be formed.

We observe that whatever would be the
 temperature at the input of the flushing
 gas, the nominal oxygen partial pressure
 in the flushing gas is sufficient to oxidize
 the deposits and the parts surfaces, and
 this feature is most probable when tempera-
 ture decreases although the reaction kinetics
 becomes unfavourable.

A second step is to compare the oxy-
 gen quantities introduced in the furnace by
 the flushed gas volume during the cooling
 and that for saturation of the deposits, this
 last material being probably the most reac-
 tive due to its “native” nature. In Figure 12
 we compare the oxygen quantity introduced
 when flushing the furnace (one full gas
 load) with the oxygen quantity for satura-
 tion of the one brazing cycle deposit. We ob-
 serve that the recent and last deposited layer
 should be readily saturated below 1330 K,
 and consequently there is enough oxygen to
 also react with the parts namely when tem-
 perature decreases.

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Fig. 11. Comparison of the decimal logarithm of $O_2(g)$ equilibrium partial pressures at the first oxides formation of the different materials of the load with the partial pressure of $O_2(g)$ in the flushing gas.

Fig. 12. Comparison of the decimal logarithm of the number of O moles at saturation in the one brazing cycle [Ag-Cu] deposit on the casing and the number of O moles contained in the flushing gas.

1 As the parts contain larger quantity of
2 materials and large surfaces the primary ef-
3 fect of oxygen will be its competitive dissolu-
4 tion in the different parts and in the deposit,
5 leading to non-saturation of the deposits
6 from only one brazing cycle. This situation
7 will change after a great number of cycles
8 since the successive deposited layers of [Ag-
9 Cu] alloys should accumulate more oxygen
10 than other parts materials.

11 3.2 Influence of residual pumping 12 pressure on steady-state 13 formation of surface oxides 14 at resistor

15 Under high vacuum, i.e. in the molecular
16 regime, the oxygen partial pressure value in
17 the furnace is not the pertinent parameter
18 that determines the formation of an oxide at
19 the surface of any metallic part when some
20 volatile oxides are formed. Indeed, under
21 vacuum, the metallic surfaces are not sub-
22 mitted directly to an oxygen partial pressure
23 in the sense of an applied mechanical pres-
24 sure but are submitted to impinging inci-
25 dent molecular flows from the background
26 gas containing oxygen or molecules with
27 oxygen (O_2 , O, CO, H_2O , etc.) coming from
28 the pumps at room temperature – pumps
29 work as a dynamic join with a residual back
30 flow corresponding to their pressure limits)
31 – whereas the metal plus or minus satu-
32 rated with oxygen can also evaporate oxy-
33 gen and/or volatile oxides when temper-
34 ature increases. Consequently the oxygen
35 partial pressure at the surface of the parts is
36 determined by the steady-state atomic flow
37 balance of incident and evaporated oxygen
38 atomic flows at the surface.

39 The total evaporated flow of oxygen – F_O
40 (tot.evap.) in number of O moles – is writ-
41 ten taking into account the known gaseous
42 molecules and for each VI part in Table 3.
43 The incident oxygen flow on the parts and on
44 the deposit at first thermal shield during the
45 brazing treatment is coming from the back-
46 ground vacuum in the furnace (cold walls
47 at temperature $T_{\text{housing}} \approx 300$ K) through the
48 two casing orifices (total surface S_{orif}).

49 The oxygen pressure at walls in the fur-
50 nace $p_{O_2}^{\text{furnace}}$ is fixed as a steady-state pressure
51 by the vacuum pumping capacities. Note

that this pressure is not constant when the
parts are degassing due to limiting values
of the pumping capacity and a succession
of steady-states is followed by the vacuum
gauges, but finally after a while this pres-
sure will reach the vacuum limits as fixed by
the manufacturer. The vacuum limit in the
present furnace is $\approx 2 \times 10^{-6}$ mbar range. This
range is depending on the degassing regime.
As the pumping device and the furnace itself
operates under reductive conditions due to
predominantly metallic parts (a quadrupole
filter can control this feature) we can con-
sider that the oxygen species ($O_2(g) + O(g)$
+ $CO(g) + H_2O(g)$) are in the range 10% to
1% of the total measured pressures (mainly
 $N_2 + H_2 +$ hydrocarbons) in the ultimate
background vacuum and consequently the
equivalent oxygen partial pressure ranges
from $\approx 2 \times 10^{-10}$ to 2×10^{-11} bar.

This total incident atomic O flow on the
parts is thus, flowing through the casing
orifices,

$$F_O^{\text{inc}} = \frac{2p_{O_2}^{\text{furnace}}S_{\text{orif}}}{\sqrt{2\pi RT_{\text{Housing}}M_{O_2}}} \quad (14)$$

This incident flow into the casing will react
with the different parts as the resistor or the
load and thus form oxides – solid or gaseous.
Before the formation of solid oxides, the only
formation of gaseous oxides added to $O(g)$
and $O_2(g)$ evaporating from the different
metallic surfaces balances the incident oxy-
gen flow and a steady-state is established be-
tween oxygen condensation/adsorption and
total oxygen vaporization/desorption. The
steady-state oxygen flow equilibrium for in-
stance at the surface S_r of the resistor at tem-
perature T is for instance,

$$\begin{aligned} \frac{2p_{O_2}^{\text{furnace}}S_{\text{orif}}}{\sqrt{2\pi RT_{\text{Housing}}M_{O_2}}} &= \frac{2p_{O_2}S_r}{\sqrt{2\pi RTM_{O_2}}} \\ &+ \frac{p_{O_2}S_r}{\sqrt{2\pi RTM_{O_2}}} + \frac{p_{MoO}S_r}{\sqrt{2\pi RTM_{MoO}}} \\ &+ \frac{2p_{MoO_2}S_r}{\sqrt{2\pi RTM_{MoO_2}}} + \frac{3p_{MoO_3}S_r}{\sqrt{2\pi RTM_{MoO_3}}} \\ &+ \frac{6p_{Mo_2O_6}S_r}{\sqrt{2\pi RTM_{Mo_2O_6}}} + \frac{8p_{Mo_3O_8}S_r}{\sqrt{2\pi RTM_{Mo_3O_8}}} \\ &+ \frac{9p_{Mo_3O_9}S_r}{\sqrt{2\pi RTM_{Mo_3O_9}}} + \frac{12p_{Mo_4O_{12}}S_r}{\sqrt{2\pi RTM_{Mo_4O_{12}}}} \end{aligned} \quad (15)$$

Table 3. Relations to calculate the total atomic vaporization flows of oxygen F_O as related to different gaseous species vaporizing in the brazing furnace.

Deposit and Solder	$F_O \text{ (tot. evap)} = 2 F(O_2) + F(O) + 3 F(O_3) + F(CuO) + F(AgO)$
Cu-Ag alloys	
Bowls: Cu-Ni alloys	$F_O \text{ (tot. evap)} = 2 F(O_2) + F(O) + 3 F(O_3) + F(CuO) + F(NiO)$
Contacts: Cu-Cr alloys	$F_O \text{ (tot. evap)} = 2 F(O_2) + F(O) + 3 F(O_3) + F(CuO) + F(CrO)$ $+ 2 F(CrO_2) + F(Cr_2O) + 3 F(CrO_3) + 2 F(Cr_2O_2) + 3 F(Cr_2O_3)$
Cu (OFHC) parts	$F_O \text{ (tot. evap)} = 2 F(O_2) + F(O) + 3 F(O_3) + F(CuO)$
Mo resistor	$F_O \text{ (tot. evap)} = 2 F(O_2) + F(O) + 3 F(O_3) + F(MoO) + 2 F(MoO_2) + 3$ $F(MoO_3) + 6 F(Mo_2O_6) + 8 F(Mo_3O_8) + 9 F(Mo_3O_9) + 12 F(Mo_4O_{12})$

1 In this relation the oxygen pressure at the
2 surface (right side of the present equation) is
3 a steady-state surface oxygen pressure. Re-
4 versely, taking into account of the oxygen
5 pressure at the formation of the first solid
6 oxide of molybdenum $MoO_2(s)$, the criti-
7 cal oxygen partial pressure $p_{O_2}(crit)$ at the
8 pumping aperture or cold walls of the fur-
9 nace able to start to oxidize the resistor into
10 $MoO_2(s)$ becomes,

$$p_{O_2}(crit) = \frac{\sqrt{T_{Housing} M_{O_2}}}{2 \sqrt{T_r}} \frac{S_r}{S_{Orif}} \times \left(\frac{2p_{O_2}}{\sqrt{M_{O_2}}} + \frac{p_O}{\sqrt{M_O}} + \frac{p_{MoO}}{\sqrt{M_{MoO}}} + \frac{2p_{MoO_2}}{\sqrt{M_{MoO_2}}} \right. \\ \left. + \frac{3p_{MoO_3}}{\sqrt{M_{MoO_3}}} + \frac{6p_{Mo_2O_6}}{\sqrt{M_{Mo_2O_6}}} + \dots \right) \quad (16)$$

11 The partial pressures quoted at the right side
12 refer to those calculated at equilibrium with
13 the diphasic $Mo-MoO_2(s)$ system. We ob-
14 serve that the critical pressure depends on
15 the surface ratios, the square root of the tem-
16 peratures ratio and of the number of formed
17 gaseous oxides. It is important to note that
18 the small apertures surface of the casing
19 leads to the pressure decrease of the furnace
20 oxygen at the level of all parts inside the
21 casing.

22 The calculated steady-state O_2 pressure
23 at the surface of the resistor for different
24 oxygen pressures in the casing versus the in-
25 verse of the resistor temperature is presented
26 in Figure 13. The curves obtained for dif-
27 ferent set oxygen pressures (calculated from
28 10^{-4} to 10^{-14} bar in the casing) show an ox-
29 idation of the resistor (formation of $MoO_2(s)$)
30 at low temperature.

31 At high temperature, they show that the
32 surface oxygen pressures decrease from this

diphasic $Mo-MoO_2(s)$ limit meaning that the
33 resistor remains clean from surface oxide
34 and at the same time the total Mo trans-
35 ported to the loaded parts decreases. In the
36 same Figure 13 the pressures of background
37 oxygen – either reduced at room tempera-
38 ture (without surfaces ratio) or with the re-
39 sistor to casing orifice surfaces ratio – are
40 presented and show the background pres-
41 sure of the furnace becomes far above the
42 diphasic $Mo-MoO_2$ limit to be able to oxidize
43 the resistor material. Taking into account of
44 the limiting oxygen pressure reached in the
45 furnace (10^{-10} to 10^{-11} bar), the critical pres-
46 sure in the casing becomes around 10^{-12} to
47 10^{-13} bar and we deduce that the critical tem-
48 perature to oxidize the resistor is ≤ 1300 K.
49

From the above calculation of the steady-
50 state flows at the surface of the resistor,
51 the evaporated Mo quantity is calculated
52 – via its different gaseous species like Mo,
53 $MoO(g)$, $MoO_2(g)$, etc. – and then is con-
54 verted into Mo layers able to condense on
55 the parts. As the ratio between the respec-
56 tive surfaces (parts/resistor) is close to 1, the
57 Mo evaporation rate in micron per hour is a
58 good estimate of probable condensed layers
59 as presented in Figure 14. This figure shows
60 that in our typical conditions the Mo built
61 layers have a negligible thickness whatever
62 is the resistor temperature.
63

However, in case of $O_2(g)$ over pressures
64 i.e. $\approx 10^{-5}$ to 10^{-4} bar, and for higher tem-
65 peratures of the resistor, i.e. ≈ 2000 K, the
66 condensation may build layers of $0.1 \mu m$ for
67 a cycle duration of 1 hour. So, during a braz-
68 ing cycle, the oxygen pressure has to be mon-
69 itored in order to avoid any appreciable Mo
70 transport from the resistor in the casing.
71

Fig. 13. Decimal logarithm of the steady-state $O_2(g)$ pressure at the surface of the Mo resistor as a function of the inverse of temperature of the resistor for different oxygen pressures in the background vacuum of the casing. The critical pressure corresponds to the formation of the first Mo(s) oxide at the surface of the Mo resistor: Mo-MoO₂ line. Other lines correspond to the vacuum in the housing taking into account of the difference of temperatures or adding the conductance of the orifice between the casing and the housing.

Fig. 14. Decimal logarithm of the vaporization (and equivalent) condensation flows – presented as layers – from the Mo resistor under background oxygen pressure in the casing.

3.3 Influence of residual pumping pressure on steady-state formation of surface oxides in the furnace

As already calculated in the case of the resistor, for the [Ag,Cu] deposits, the steady-state oxygen flow equilibrium for instance at the surface S_1 of the deposits on the first thermal shield at temperature T of the casing and taking into account of the formation of gaseous oxides is for instance,

$$\begin{aligned} \frac{2p_{O_2}^{\text{furnace}} S_{\text{Orif}}}{\sqrt{2\pi RT_{\text{Housing}} M_{O_2}}} &= \frac{2p_{O_2} S_1}{\sqrt{2\pi RT M_{O_2}}} \\ &+ \frac{p_O S_1}{\sqrt{2\pi RT M_O}} + \frac{3p_{O_3} S_1}{\sqrt{2\pi RT M_{O_3}}} \\ &+ \frac{p_{CuO} S_1}{\sqrt{2\pi RT M_{CuO}}} + \frac{p_{AgO} S_1}{\sqrt{2\pi RT M_{AgO}}} \quad (17) \end{aligned}$$

Reversely, taking into account of the oxygen pressure at the saturation limit of the deposited alloy the critical oxygen partial pressure $p_{O_2}(\text{crit})$ at the casing pumping aperture or cold walls of the furnace able to start to form $\text{Cu}_2\text{O}(\text{s})$ at the deposit surface becomes,

$$\begin{aligned} p_{O_2}(\text{crit}) &= \frac{\sqrt{T_{\text{Housing}} M_{O_2}}}{2\sqrt{T}} \frac{S_1}{S_{\text{Orif}}} \left(\frac{2p_{O_2}}{\sqrt{M_{O_2}}} \right. \\ &\left. + \frac{p_O}{\sqrt{M_O}} + \frac{3p_{O_3}}{\sqrt{M_{O_3}}} + \frac{p_{CuO}}{\sqrt{M_{CuO}}} + \frac{p_{AgO}}{\sqrt{M_{AgO}}} \right). \quad (18) \end{aligned}$$

In this relation the partial pressures in the right parenthesis are those corresponding to the [Cu-Ag-O alloys (O saturated) – $\text{Cu}_2\text{O}(\text{s})$] system equilibrium obtained directly from thermodynamic calculations performed for the deposited alloy composition

The same relation is written for each material of the loaded parts. The different critical furnace oxygen pressures (at the furnace side of the pumping orifice of the casing) as a function of the inverse of temperature T of the load are presented in Figures 15 to 19. For furnace oxygen pressure values above the calculated critical ones the $\text{Cu}_2\text{O}(\text{s})$ oxide will be formed on the deposit or pure Cu parts, $\text{Cr}_2\text{O}_3(\text{s})$ on Cu-Cr contact tips and $\text{NiO}(\text{s})$ on the flanges or on the braze; whereas under this limit, oxygen remains

dissolved in the deposit or parts materials as unsaturated solid solutions

As a conclusion for the critical oxygen pressure at pumping and related to different materials:

- Cu, Ag and Ni components deliver very small $\text{CuO}(\text{g})$, $\text{AgO}(\text{g})$ or $\text{NiO}(\text{g})$ partial pressures whereas the main evaporated species is $\text{O}_2(\text{g})$ meanwhile $\text{O}(\text{g})$ remains lower. Thus the evaporated and incident flows have practically the same composition (pure $\text{O}_2(\text{g})$) and the equilibrium oxygen pressure above (Cu-Ag-O) deposits, Cu-Ni flanges or pure Cu-OFHC parts and the incident oxygen pressures differ from their only emitted temperatures and surfaces according to the simple relation,

$$\begin{aligned} \frac{p_{O_2}^{\text{furnace}}}{p_{O_2}^{\text{parts}}} &= \frac{\sqrt{T_{\text{housing}}}}{\sqrt{T_{\text{parts}}}} \frac{S_{\text{parts}}}{S_{\text{apertures}}} \\ &\approx \sqrt{\frac{300}{1200}} \frac{S_{\text{parts}}}{S_{\text{apertures}}} \approx \frac{1}{2} \frac{S_{\text{parts}}}{S_{\text{apertures}}} \quad (19) \end{aligned}$$

- Cr component has gaseous oxides that participate to the oxygen evaporation more than the oxygen pressure and consequently the critical oxygen furnace pressure becomes higher than the very low equilibrium Cr- Cr_2O_3 pressure at the surface of the contacts.

In Figures 15 to 19 the critical temperatures above which de-oxidation occurs are quoted for the different materials taking into account of the oxygen pressure limit in the furnace. Considering these temperatures and the mean value of the brazing temperature (≈ 116 K) the only Cu-OFHC parts and deposits materials are not oxidized at the brazing temperature, the [CuNi] alloyed flanges slightly oxidize meanwhile the contact tips containing chromium and the brazes containing Ni will probably be sensitive to oxidation. For the contact tips in [Cu-Cr] alloys, the chromium oxides volatility remains not enough efficient to prevent the contact tips from oxidation except if higher temperatures are reached i.e. >1430 K.

These calculations take into account the behaviour of any part in front of the total oxygen flow entering the casing. Really, in the furnace we can consider that the oxygen

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Fig. 15. Decimal logarithm of the partial pressures of $O_2(g)$ as a function of the inverse of temperature for the different $O_2(g)$ pressures existing at the formation of the first oxide $Cu_2O(s)$: (i) at the surface of the OFHC parts in the casing, (ii) after temperature correction for vacuum background, (iii) and in the cold side of the furnace or pumps entrance.

Fig. 16. Decimal logarithm of the partial pressures of $O_2(g)$ as a function of the inverse of temperature for the different $O_2(g)$ pressures existing at the formation of the first oxide $NiO(s)$: (i) at the surface of the [Cu-Ni] flanges in the casing, (ii) after temperature correction for vacuum background, (iii) and in the cold side of the furnace or pumps entrance.

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Fig. 17. Decimal logarithm of the partial pressures of $O_2(g)$ as a function of the inverse of temperature for the different $O_2(g)$ pressures existing at the formation of the first oxide $Cr_2O_3(s)$: (i) at the surface of the [Cu-Cr] contact pads in the casing, (ii) after temperature correction for vacuum background, (iii) and in the cold side of the furnace or pumps entrance.

Fig. 18. Decimal logarithm of the partial pressures of $O_2(g)$ as a function of the inverse of temperature for the different $O_2(g)$ pressures existing at the formation of the first oxide $NiO(s)$: (i) at the surface of the [Ag-Cu-Ni] solder in the casing, (ii) after temperature correction for vacuum background, (iii) and in the cold side of the furnace or pumps entrance.

Fig. 19. Decimal logarithm of the partial pressures of $O_2(g)$ as a function of the inverse of temperature for the different $O_2(g)$ pressures existing at the formation of the first oxide $Cu_2O(s)$: (i) at the surface of the [Ag-Cu] deposits in the casing, (ii) after temperature correction for vacuum background, (iii) and in the cold side of the furnace or pump entrance.

1 flow entering by the casing orifices is dis-
2 tributed among all parts and consequently
3 the critical furnace oxygen pressure must
4 be balanced by the total flow evaporating
5 from all parts in the casing according to the
6 relation

$$p_{O_2}(crit) = \left(\frac{S_{total}}{S_{orif}} \sqrt{\frac{T_{housing}}{T}} \frac{\sqrt{M_{O_2}}}{2} \right) \times \sum_i \frac{S_i}{S_{total}} \left(\frac{2p_{i,O_2}}{\sqrt{M_{O_2}}} + \frac{p_{i,O}}{\sqrt{M_O}} + \frac{3p_{i,O_3}}{\sqrt{M_{O_3}}} + \sum_j v_{i,j} \frac{p_{M_iO_j}}{\sqrt{M_{M_iO_j}}} \right) \quad (20)$$

7 Index i is for each material surface, and in-
8 dex j for the different evaporated molecules
9 from the j material. Figure 20 presents the
10 $O_2(g)$ critical furnace pressure calculated for
11 the whole load in the furnace as a function of
12 temperature. The critical temperature corre-
13 sponding to the pressure limit in the furnace
14 decreases down to 830 K when taking into
15 account the full distribution on all surfaces
16 of the oxygen entrance flow in the casing.

As soon as temperature is decreased be-
low this value, oxides can be formed on the
deposits or at the surfaces of the brazed
parts. At that time the formation and the
growth rate of this oxide will depend on
the balance between the total incident oxy-
gen flow coming from the casing apertures
minus the oxygen released by vaporization
during the cooling and the oxygen diffu-
sion into the bulk materials in view of their
oxygen saturation.

4 Conclusion and perspectives

The brazing at temperatures higher than
1168 K – the eutectic temperature in the [Ag-
Cu-Ni] braze system – induces larger ero-
sion of the parts by vaporization especially
for the braze and consequently a rich sil-
ver deposit is formed on the first thermal
shield of the casing. Thus, better homoge-
neous temperature for the load could allow
a close approach of the needed eutectic tem-
perature for the brazing process that will
reduce these deposits. Indeed, the partial

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Fig. 20. Decimal logarithm of the critical partial pressure of O₂(g) taking into account of the whole assembly of the load reported to the furnace background vacuum as a function of the inverse of temperature compared to the limiting O₂(g) in the furnace cold walls or at pump entrance.

1 vapour pressures of metals in the furnace
2 during the brazing process increase by a fac-
3 tor ≈ 10 every 50 K. Same observation works
4 also for Cu vaporization that is sometimes
5 deposited on ceramic parts.

6 The very small thickness of the deposits
7 on the casing as well as their plus or minus
8 fresh surface for each temperature brazing
9 cycle allows asserting that the exposure of
10 the deposited alloy to the residual oxygen
11 in the furnace – coming from the flushing
12 gas and from the pumping system – is going
13 to pull its dissolution in a quasi-immediate
14 time sequence (no limitation by diffusion)
15 compared to room temperature recovering
16 time and the oxygen content will be the one
17 at equilibrium with furnace atmosphere as
18 soon as deposited. The above calculations
19 show that these deposits are at least almost
20 saturated when a new cycle starts. More,
21 during the cooling step, the oxygen impu-
22 rity content of the flushing N₂ gas (less than
23 10 ppm) introduced at about 1000 K is able to
24 totally saturate the deposits and the remain-
25 ing oxygen content can also oxidize the sur-
26 faces of the parts just brazed. An online pu-

rification system for this gas could decrease
at least by a factor 10 to 100 the oxidation
processes occurring in the furnace. This is
valuable also for copper parts since the solu-
bility of oxygen in this material is important
as well as in the braze material.

At the surface of the resistor, of the parts
and of the deposit (inner surface of the cas-
ing) the steady-state reaction with the inci-
dent flow of oxygen coming from the vacu-
um pumps by reverse effusion at pressure
limit into the casing through the casing ori-
fices (front and rear) can form different ox-
ides on these surfaces. At the higher temper-
atures – namely during the brazing – when
good secondary vacuum conditions are es-
tablished ($\approx 10^{-6}$ mbar) these oxides are not
formed and good conditions are established
for the brazing process. It is important to
note that some materials – for instance the
Mo resistor and the Cu-Cr alloys – vapor-
ize oxide molecules that delay the formation
of oxides at their surface. For Mo – besides
the vaporization of Mo that can occur if the
resistor is overheated – the presence of oxy-
gen may increase drastically the transport

1 of Mo via its gaseous volatile oxides and
2 this process may explain the Mo detection
3 by EDX analysis in the deposits on the ce-
4 ramic parts during some standard brazing
5 runs.

6 Note that when some "boiling like phe-
7 nomenon or material projections" are visu-
8 ally observed on the braze surface, these
9 features are in fact a sign of high oxygen par-
10 tial pressure that changes drastically the sur-
11 face tension, generates surface tension gra-
12 dients and creates some vortex in the liquid
13 braze (Marangoni effect).

14 After brazing, as soon as the tempera-
15 ture decreases inside the furnace the exter-
16 nal oxygen pressure – that also decreases as
17 measured with vacuum gauges – cannot be
18 low enough to prevent oxide formation be-
19 low 830 K as calculated. The quantity of ox-
20 ide formed at that time is related to tempera-
21 ture to the residual pumping pressure, to the
22 casing orifice sections and to the diffusion
23 of oxygen in the bulk of the parts. Probably
24 the kinetics of oxidation will slow down also
25 the dissolution process with temperature de-
26 crease. In order to avoid excessive oxide for-
27 mation at surfaces of the parts it is preferable
28 to decrease the back flow from the housings
29 and pumps by these four steps: (i) use puri-
30 fied nitrogen for flushing the furnace; (ii) de-
31 creasing the temperature threshold level for
32 nitrogen flushing; (iii) decreasing the nom-
33 inal pressure limit related to the pumping
34 capacities, and, finally; (iv) decreasing the
35 casing apertures size when cooling.

36 Further some special "degassing" pro-
37 cedures must be planned to eliminate pe-
38 riodically the accumulated deposits along
39 brazing cycles that are a source of oxygen
40 storage. Oxygen gauges could help under-
41 standing the "role" of oxygen as a function
42 of time along successive brazing cycles.

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