ADVANCED KINETICS FOR EMISSION BY-PRODUCTS OF ABLATING DEBRIS

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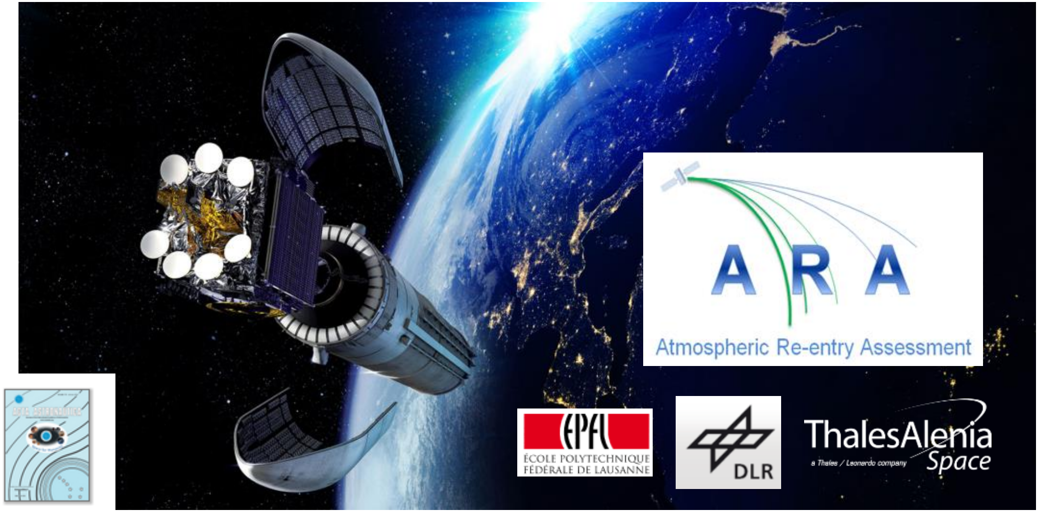
CONTEXT



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Re-entry survival analysis and ground risk assessment of space debris considering by-products generation

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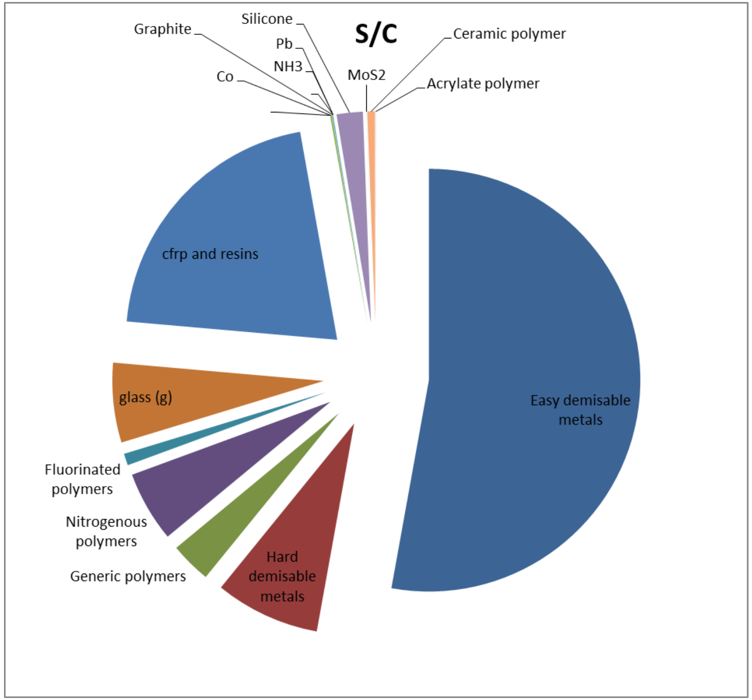
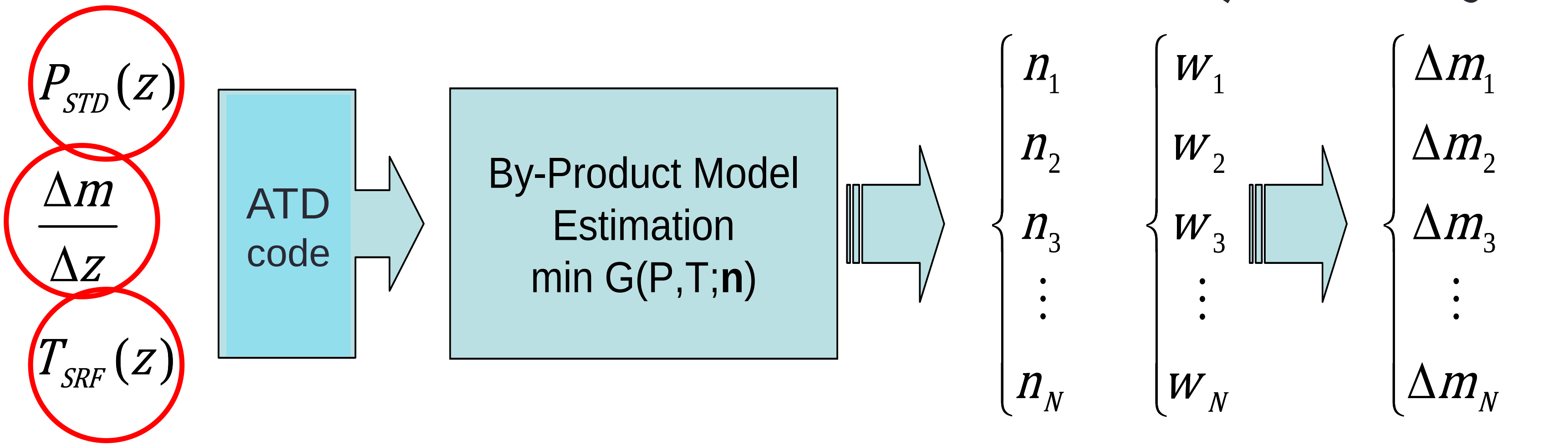
Element / Material	Mass Percentage [%]
Al Alloy	57.46%
Paint	2.44%
PU Foam	2.93%
PET Fibre	2.20%
Vinyl Acetate	0.12%
Ni Alloy	7.09%
Cu	0.12%
Ni	0.49%
Inconel 718	1.34%
Inconel 600	0.98%
Stainless Steel	3.42%
Nextel	0.12%
CFRP	17.11%
Norcoat	0.73%
Electrical Units	2.44%
Graphite	0.98%
Total	*100.00%*

Table 2: R/Bs typical material budget (source ESA)



Atmospheric Re-entry Assessment

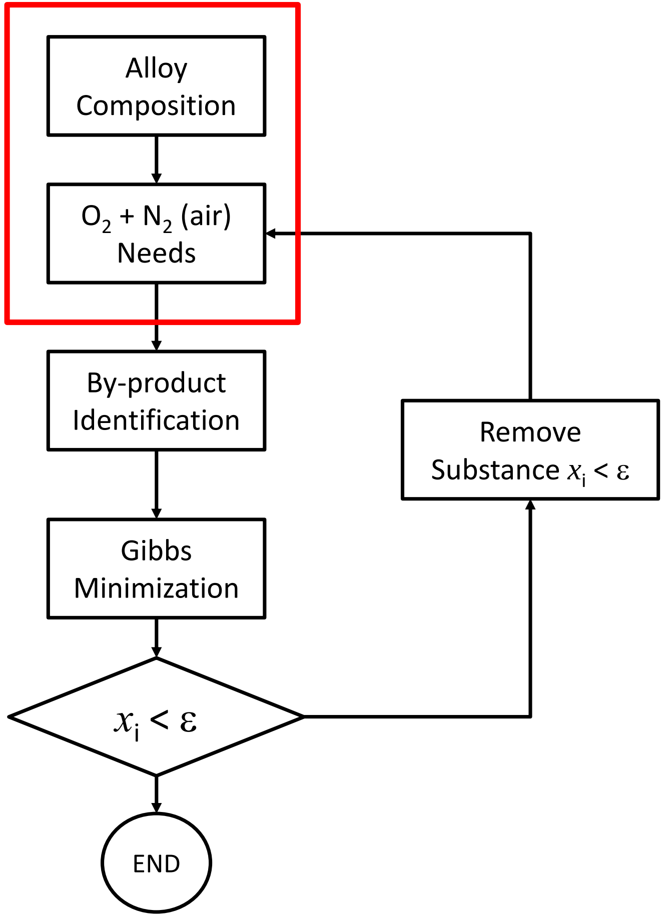
Thermochemical By-Products Estimation
(Chemical Equilibrium)



Burcat's Thermochemical Database

$$\min G(P,T,\mathbf{n}) = \sum_{N_c} n_i \cdot \mu_i(T,\mathbf{n}_c) + \sum_{N_g} n_j \, \mu_j(P,T,\mathbf{n}_g)$$

By-Products Identification



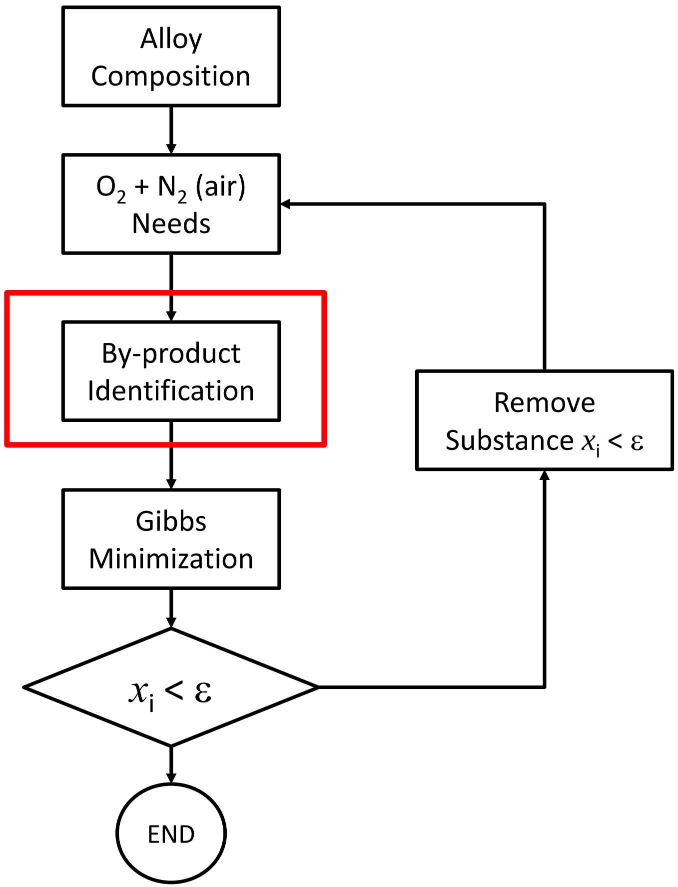
Element	% (w/w)
Al	88.7
Zn	6.1
Mg	2.9
Cu	2.0
Cr	0.3

AA7075 composition

2.5 Excess Air

Compound	Mol Fraction
N_2	0.70503
O_2	0.18414
Al	0.09995
Cr	0.00017
Cu	0.00095
Mg	0.00362
Zn	0.00284

By-Products Identification



Gas	Al, AlN, AlO, AlO2, Al_2, Al_2O, Al_2O_2, Al_2O_3, Cr, CrN, CrO, CrO_2, CrO_3, Cu, CuO, Cu_2, Mg, MgN, MgO, Mg_2, N, NO, NO_2, NOO, N_2O_2,NO_3, N_2, N_2O, N_2O_3, N_2O_4, N_2O_5, N_3, O, O_2, O_3, Zn, CrO, CuO, Cu_2, N_4, N_4, N_4, O*, O_2*, O_3c, O_4, ZnO
Condensed	Al(cr), Al(L), AlN(cr), AlN(L), Al_2O_3(a), Al_2O_3(liq), Cr(cr-a), Cr(cr-b), Cr(liq), CrN(cr), Cr_2N(cr), Cr_2O_3(l'), Cr_2O_3(l), Cr_2O_3(liq), Cu(cr), Cu(liq), CuO(cr), Cu_2O(cr), Cu_2O(liq), Mg(cr), Mg(L), $MgAl_2O_4$(cr), $MgAl_2O_4$(liq), MgO(cr), MgO(liq), Mg_3N_2(cr), Zn(cr), Zn(liq), ZnO
Ion	Al^+, Al^-, AlO^+, AlO^-, AlO_2^-, Al_2O^+, $Al_2O_2^+$, Cr^+, Cr^-, CrO_3^-, Cu^+, Cu^-, Mg^+, N^+, N^-, NO^+, NO_2^-, NO_3^-, N_2^+, N_2^-, N_2O^+, O^+, O^-, O_2^+, O_2^-, $Zn^+CrO_3^-$, NO^-, NO_2^+, NO_2^+, NO_2^-, NOO^+, NOO^-, NO_3^+, NO_3^-, N_2^-, N_2O^+, N_2O^-, N_2O^+, $N_2O_3^+$, $N_2O_3^-$, N_3^+, N_3^-, N_4^-, O_3^+, O_3^-, O_3c^+, O_3c^-, O_4^+, O_4^-

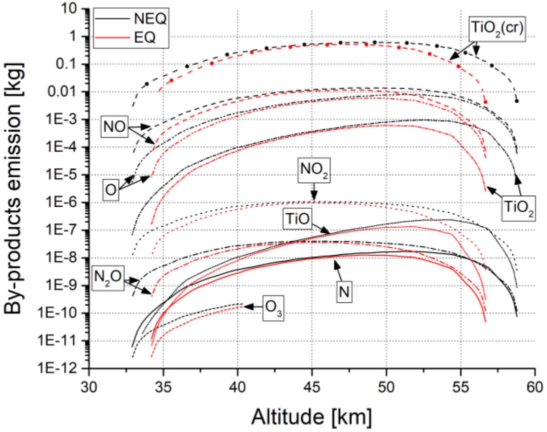
Burcat's Thermochemical Database

By-Products Identification

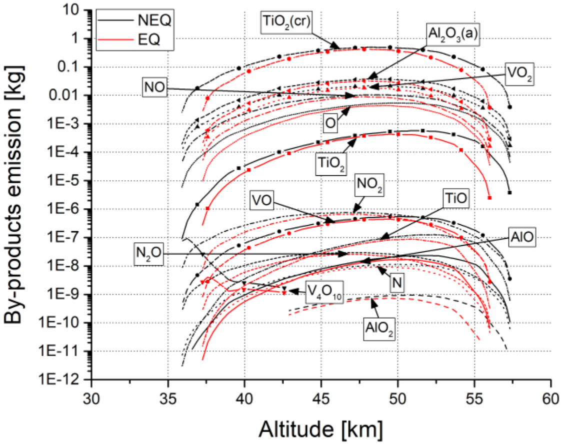
$\varepsilon = 10^{-6}$			$\varepsilon = 10^{-20}$		
Substance	phase	x_i	**Substance**	phase	x_i
NO	gas	$7.23\ 10^{-6}$	**CrO_2**	gas	$2.283\ 10^{-16}$
N_2	gas	0.812717	**CrO_3**	gas	$2.747\ 10^{-11}$
O_2	gas	0.125191	**Cu**	gas	$7.832\ 10^{-12}$
Al_2O_3(a)	Alpha	0.053428	**CuO**	gas	$4.282\ 10^{-14}$
Cr_2O_3(l)	Hexagonal	0.000101	**Cu_2**	gas	$1.829\ 10^{-20}$
CuO(cr)	Crystal	0.001103	**NO**	gas	$7.229\ 10^{-6}$
$MgAl_2O_4$(cr)	Crystal	0.004182	**NO_2**	gas	$9.643\ 10^{-9}$
ZnO	condensed	0.003269	**NO_3**	gas	$7.515\ 10^{-18}$
			N_2	gas	0.812723
			N_2O	gas	$9.987\ 10^{-12}$
			O	gas	$1.294\ 10^{-10}$
			O_2	gas	0.125192
			O_3	gas	$9.609\ 10^{-16}$
			Zn	gas	$2.074\ 10^{-11}$
			Al_2O_3(a)	Alpha	0.053429
			Cr_2O_3(l)	Hexagonal	0.000101
			CuO(cr)	Crystal	0.001103
			$MgAl_2O_4$(cr)	Crystal	0.004182
			CuO	gas	$4.282\ 10^{-14}$
			Cu_2	gas	$1.829\ 10^{-20}$
			O_2*	gas	$2.851\ 10^{-7}$
			ZnO	condensed	0.003269
			ZnO	gas	$1.141\ 10^{-14}$

Burcat's Thermochemical Database

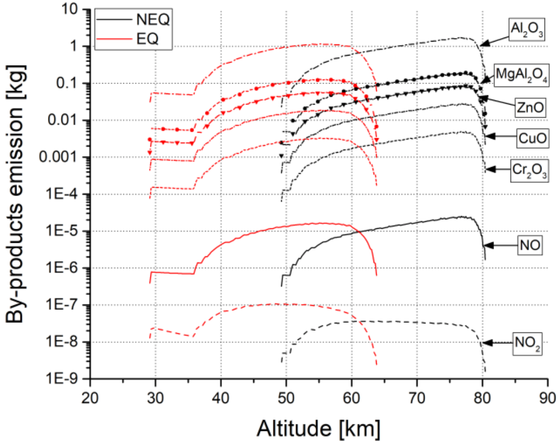
Results



100% Ti

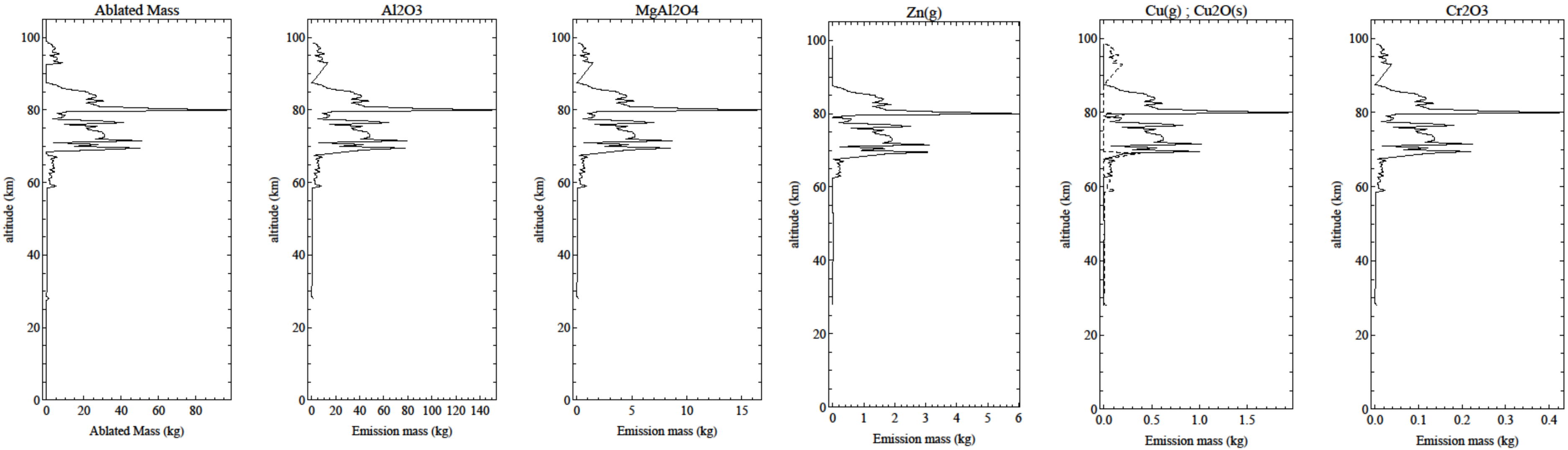


Ti6Al4V alloy



AA7075 alloy

Results. Sentinel-I Simulation



Atmospheric Re-entry Assessment

Partial Conclusions

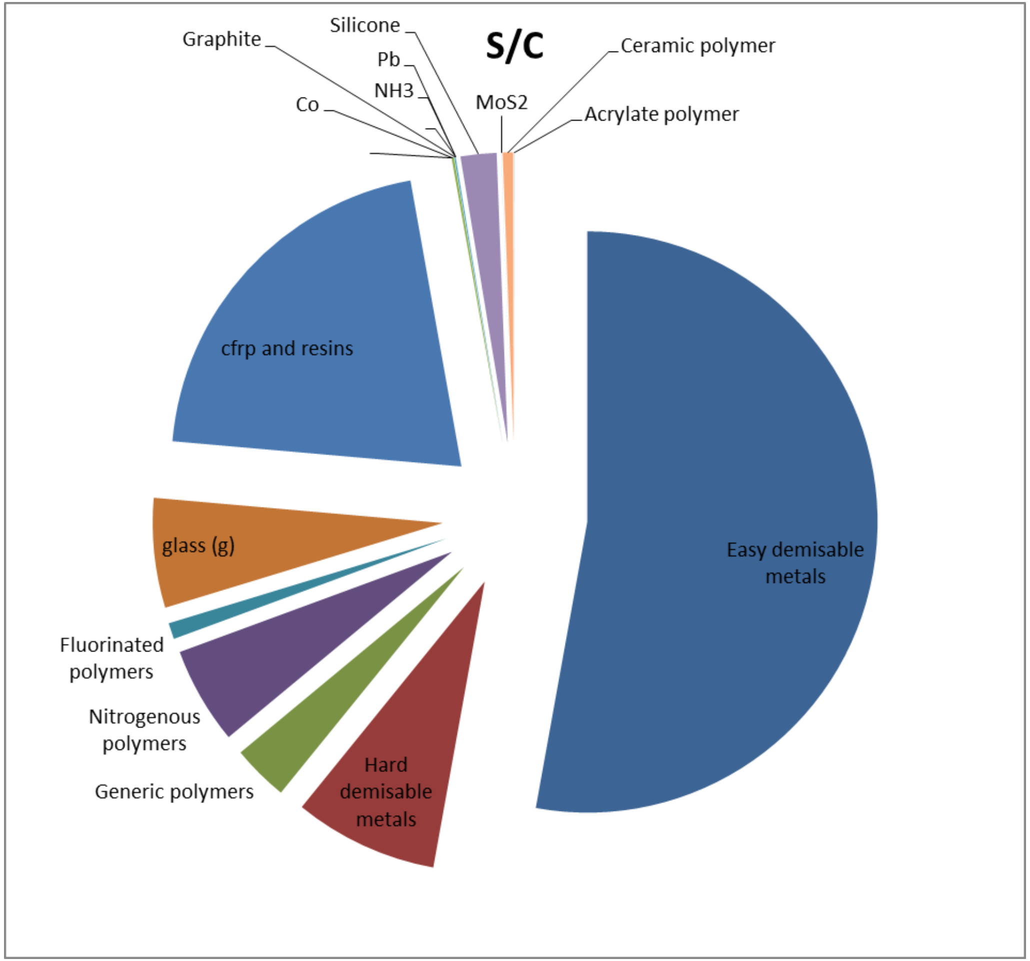
- The emission of the by-products can be evaluated from ATD codes known the total ablated mass (worst case scenario)
- The by-products are mainly stable solid metallic oxides
- The impact on atmospheric chemistry is limited

Open Questions

- What is the size of the emitted particles?
- How is the reactions mechanism for the oxide formation?
- Can be extended the method to other ablating materials?

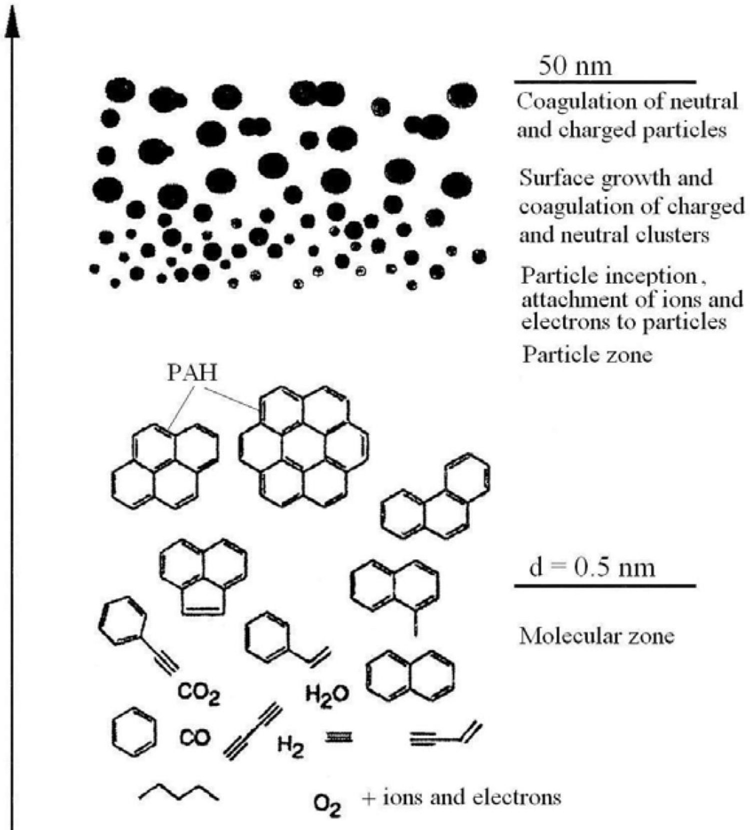
Other Materials

- CFRP
- Polymers
- Batteries
- Glass
- Graphite-based Materials



Polymer combustion and soot formation

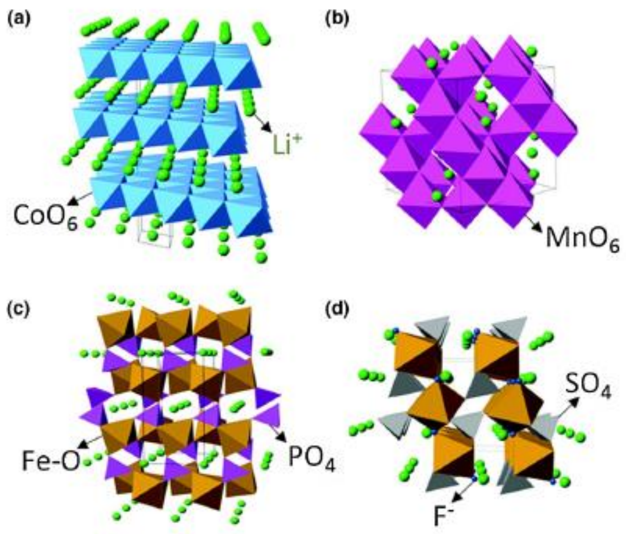
- The detailed chemical mechanism will include thousands of chemical reactions.
- The sensitivity analysis of the reaction scheme will lead to reduced (lumped) models.
- Heterogeneous chemistry modifies reaction rate equations
- Mass-transfer processes inside the material



Formation of Hydrocarbons and soot; J. Warnatz, U. Maas, R.W. Dibble; In **Combustion, 4th Edition**, p. 217, Springer-Verlag, 2006

BATTERIES

Chemical Compounds



Crystal structure	Compound
Layered	$LiTiS_2$
	$LiCoO_2$
	$LiNiO_2$
	$LiMnO_2$
	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
	Li_2MnO_3
Spinel	$LiMn_2O_4$
	$LiCo_2O_4$
Olivine	$LiFePO_4$
	$LiMnPO_4$
	$LiCoPO_4$
Tavorite	$LiFeSO_4F$
	$LiVPO_4F$

TABLE 2 Material Inventories for HEV, PHEV, and BEV Batteries

	Percent Mass		
Component	HEV (%)	PHEV (%)	EV (%)
$LiMn_2O_4$	27	28	33
Graphite/carbon	12	12	15
Binder	2.1	2.1	2.5
Copper	13	15	11
Wrought aluminum	24	23	19
$LiPF_6$	1.5	1.7	1.8
EC	4.4	4.9	5.3
DMC	4.4	4.9	5.3
PP	2.0	2.2	1.7
PE	0.26	0.40	0.29
PET	2.2	1.7	1.2
Steel	2.8	1.9	1.4
Thermal insulation	0.43	0.33	0.34
Glycol	2.3	1.3	1.0
Electronic parts	1.5	0.9	1.1
Total battery mass (lb)	41	196	463
(kg)	18.6	89.0	210.0

Source: N. Nitta, F.Wu, J.T. Lee, G. Yushin
Materials Today 18(2015) 252-264

Source: J.B.Dunn, L.Gaines, M.Barnes, J.Sullivan and M.Wang
Nat. Argonne Lab. (2012) Rep. ANL/ESD/12-3

Metal-oxides Hypothesis

///The Enthalpy of Formation of metal oxides is very high

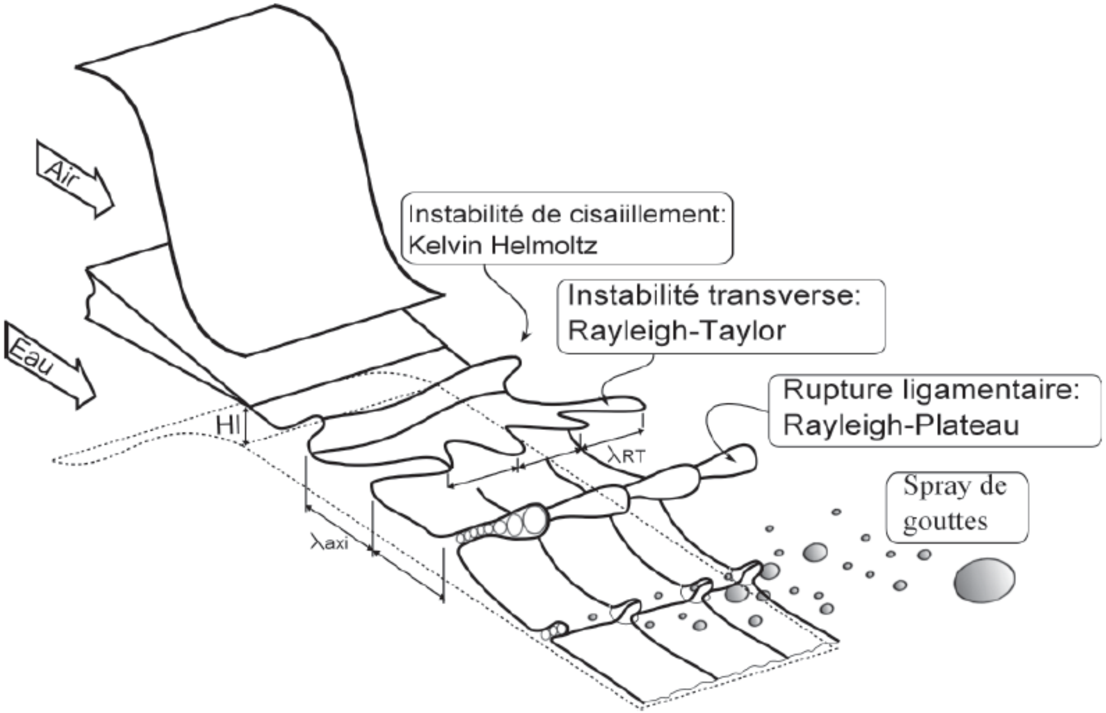
Material	Heat released oxidation (kJ/g)	Mass in Sentinel-I (ablated kg)
$Al \rightarrow Al_2O_3$	31.02	1041.0
$Ti \rightarrow TiO_2$	19.72	4.60
$C \rightarrow CO_2$ (for comparison)	32.80	158.0 (all polymers+CFRP)

///The metal oxides are very active against ozone decomposition. Although there are minoritary in quantity, they are very reactive with the O3.

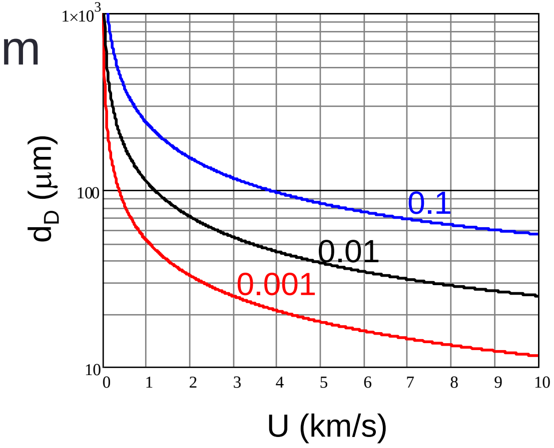
Reaction	Uptake Coefficient
O3 + ice	$10^{-10} – 10^{-8}$
O3 + Al2O3	$10^{-8} – 10^{-4}$
O3 + TiO2	10^{-6}

← Photochemically active

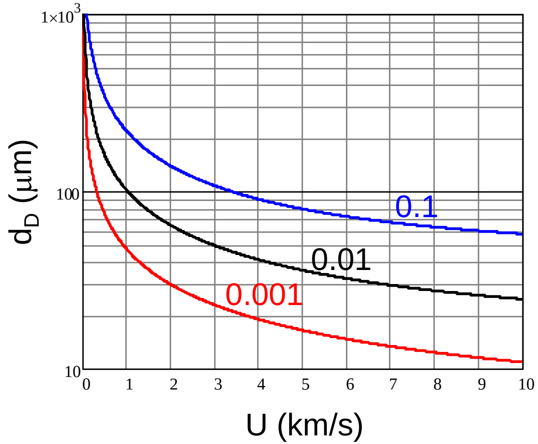
Metal-particles Formation



Titanium



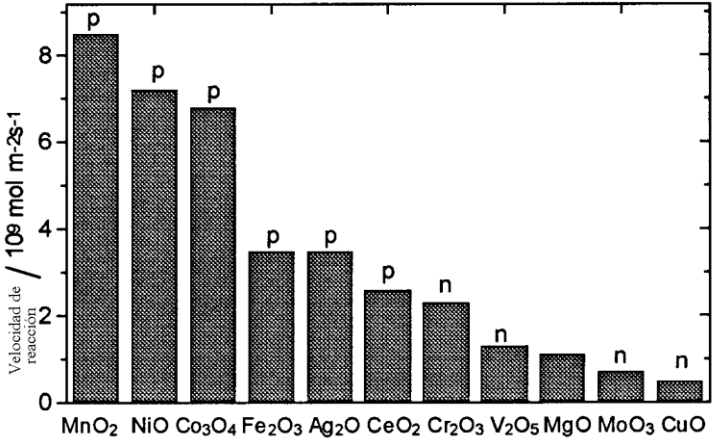
Aluminium



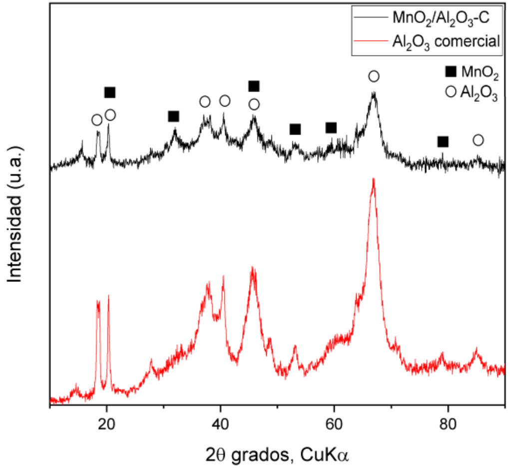
From *Atomisation d'un film liquide mince par action combinée des instabilities de Kelvin-Helmholtz et de Faraday*. Marie LALO, Université de Grenoble, 2006

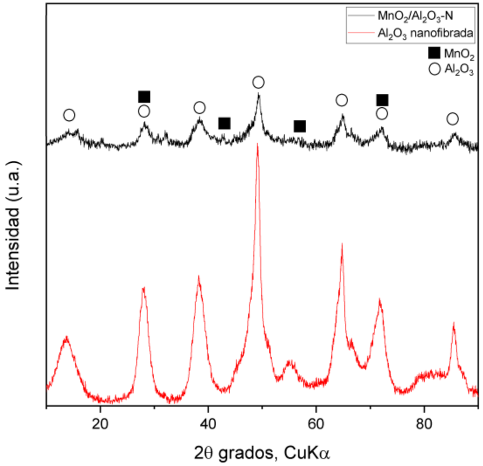
Heterogeneous Chemistry. Ozone Decomposition

Metal oxides activity



RDX of supported MnO_2





Oyama's catalytic ozone decomposition model

Irreversible

$$O_3 + * \xrightarrow{k_1} O_2 + O^*$$

$$O_3 + O^* \xrightarrow{k_2} O_2^* + O_2$$

$$O_2^* \xrightarrow{k_3} O_2 + *$$

Reversible

$$O_3 + * \overset{K_1}{\leftrightarrow} O_2 + O^*$$

$$O_3 + O^* \xrightarrow{k_2} O_2^* + O_2$$

$$O_2^* \overset{K_{O_2}}{\longleftrightarrow} O_2 + *$$

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THANK YOU FOR YOUR ATTENTION!!