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#### In-detail elaborating the way of titanium in thermite reactions

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#### Abstract

Recently, it has been reported that adding titanium into thermite composites can improve their combustion efficiency and lower their ignition temperature. However, the exact role of Ti reaction in such thermites is still unclear. Here, we put focus on in-depth understanding the reaction mechanism of Ti-based thermite by employing magnetron-sputtering technique to grow high purity and well-defined CuO/Ti nanolaminates. Nanolaminates feature a very well controlled interface and full contact between fuel and oxidizer compared to powered system showing random contact, which is crucial to identify and rationalize the different mechanisms taking place during initiation/propagation. This provides an ideal model-system to quantitatively describe the TiOx interfacial oxide growing using various characterization techniques including microscopy, thermal analysis, spectroscopy and X-ray diffractometric.

#### Introduction

Thermites are energetic systems consisting of a metal fuel and a metal oxide undergoing a rapid redox reaction associated with a high energy of combustion. Nanothermites refer to as thermites with reactants (fuel and oxidizers) size below 500 nm. As energygenerating materials, nanothermites find applications in material synthesis [1], low gas emission heat sources for welding and joining [2], initiation [3,4], and also on chip actuations [5]. Al fuel is by far the most employed metallic fuel because of its high oxidation enthalpy and low cost, despite the negative impact of the native alumina (Al<sub>2</sub>O<sub>3</sub>) coated on aluminum which penalizes the ignitability. As for some applications, is desirable to lower the ignition temperature, much research effort is dedicated to the increase of Al ignitability and decrease of its ignition temperature. Considering other fuels of interest (Boron, Silicon, Titanium) with Al is another effective solution to improve ignitability and combustion performance of nanothermites.

More recently, Zachariah and coworkers added Ti nanoparticles into various thermites (B/CuO [6], Al/I<sub>2</sub>O<sub>5</sub> [7]) and the results demonstrated, in certain conditions, a better combustion efficiency and reactivity, i.e., pressurization and burn rate increased by factor ~3 to 6 when 40% of nanoTi is added in B/CuO. Authors suggested that the performance enhancement upon Ti particle doping is due to the intermixing of both boron and titanium particle shells (namely  $TiO_2$  and melting  $B_2O_3$ ) creating a non-liquid interfacial pathway for a more direct diffusion route for oxygen atoms. In turn, the reaction of oxygen with Ti promotes a higher flame temperature enhancing the melting of boron and volatilization of B2O3. These experimental findings not only point to the complexity of the mechanisms governing ternary thermites reactivity but also raise the question of the exact role of the Ti reaction with CuO in such thermite composites, which is poorly documented from a fundamental standpoint.

The objectives of this study are (1) to confirm the ignitability and combustion performance improvement of a Ti-based thermite compared to its Al-based counterpart, and, (2) to understand the mechanisms driving this improvement by quantitatively analyzing the reaction of oxidation of Ti in contact with CuO.

To do so, we employed magnetron-sputtering to grow high purity and well-defined Ti/CuO nanothermite. Contrary to powdered nanothermites in which a thick titania oxide shell layer separates its pure fuel Ti core from the outer surface oxidizer particle, magnetron-sputtered technique permits a very well controlled interface (in thickness and structure) between the fuel and oxidizer. This provides an ideal model-system to quantitatively describe the TiO<sub>x</sub> interfacial oxide growing using a host of characterization techniques including microscopy, thermal analysis, spectroscopy and X-ray diffraction. CuO was chosen as the oxidizer due to its relative stability in ambient conditions, its ease of sputterdeposition, and its known use as an oxidizing agent/oxygen source for thermite reactions.



**Fig.1.** Burn rate and ignition delay of CuO/Ti compared to CuO/Al. Samples are composed of 5-bilayers of each reactants with a mass ratio of fuel over oxidizer at 2.

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**Fig.1** compare the measured burn rate and ignition delay of CuO/Ti and CuO/Al in ambient condition. The burn rate of CuO/Ti is 3 times faster than CuO/Al. CuO/Ti demonstrated 100% ignition success with a delay of ~ 0.02 ms that is 3 orders of magnitude smaller than CuO/Al (~ 15 ms), giving also 100% of ignition success. Noteworthy the 5-bilayers CuO/Al on glass struggle to sustain continuous propagation, therefore only ~ 10% of the thermite surface area propagates upon ignition, against 100% for 5-bilayers CuO/Ti, which is another indication of the higher reactivity of the CuO/Ti system. Overall, ignition and combustion results clearly indicate that CuO/Ti multilayers are much more reactive than CuO/Al ones.

To take advantage of the high reactivity of CuO/Ti material, a thin layer of Ti was incorporated into the first CuO of Al/CuO stacks grown on ignition devices to test its influence. Compared to the commonly used CuO/Al<sub>15BL</sub> [8], the first few bilayers of CuO/Al was replaced by CuO/Ti and referred as  $(CuO/Ti)_{xBL}/(CuO/Al)_{(15-x)BL}$ , x equal to 0, 1, 2 or 3. (CuO/Ti)<sub>1BL</sub>/(CuO/Al)<sub>14BL</sub> means that only one CuO/Ti bilayer is deposited followed by the deposition of 14 bilayers of CuO/Al. For all the samples, the thicknesses of CuO, Ti and Al were set to 200 nm, 170 nm and 200 nm, respectively. The ignition delay of (CuO/Ti)xBL/(CuO/Al)(15-x)BL reduced by almost an order of magnitude, from more than 15 ms to less than 0.3 ms as the number of CuO/Ti bilayer increases from 0 to 3. Interestingly, the beneficial effect of CuO/Ti reaches a plateau as the number of CuO/Ti bilayers is  $\geq$ 2. Only replacing the first 2 CuO/Al bilayers with CuO/Ti can maximumly improve the overall ignition performance.



**Fig. 2**. Ignition delay of  $(CuO/Ti)_{xBL}/(CuO/Al)_{(15-x)BL}$  nanolaminates (x =0, 1, 2, or 3).

In order to investigate the mechanisms of reaction between Ti and CuO responsible of this improvement, thermal behavior of CuO/Ti foils was characterized at slow heating rate and compared to CuO/Al. **Fig. 2** plots the specific heat flow measured by DSC from the ambient temperature to 950 °C for CuO/Ti. DSC plot of CuO/Al multilayers is added to serve as reference.

The most striking feature of DSC analysis is that CuO/Ti reaction features one single major exotherm located at ~ 430 °C, labelled as peak #1 in Fig. 2. This corresponds to the temperature of the first weak and broad exotherm characterizing the CuO/Al reactions in fully dense thermite such as multilayers [9] and attributed to the dual solid phase diffusion of Al and O atoms released from CuO through the naturally grown interface into the adjacent layers. To elucidate details about the processes observed by DSC, a 2-bilayer CuO/Ti on Si-wafer was heated to intermediate temperatures (300, 500 °C) making sense from the DSC exotherms, recovered, and analyzed by XRD. When annealed to 300 °C, Ti, CuO and Cu<sub>2</sub>O are detected, while to 500 °C, TiO<sub>2</sub>, Cu<sub>2</sub>O and Cu were detected (Table 1). This confirms that, upon heating up, CuO decomposes into Cu<sub>2</sub>O. At this stage of annealing, i.e. at 300 °C, the released oxygen atoms may be stored or simply transported through the interface layer to initiate the reaction. As no clear exotherm is seen from the DSC before 300 °C, we can expect slow migration of atoms interacting with Ti in poor quantity that could explain the pre-peak observed at 213 °C.

After thermal treatment at 500 °C, copper oxide continues decomposing into Cu<sub>2</sub>O, but also in Cu, resulting in a continuous oxidation of titanium in this temperature range. The crystallization of a probably thicker TiO<sub>2</sub> layer, as observed from the XRD curve, corroborates the DSC exotherm where reaction stops, which might result from the crystallization/thickening of TiO<sub>2</sub> inhibiting further migration of oxygen atoms.

Table 1. S	Summary of XI	RD analysi:	s results o	of CuO/Ti
at various	temperatures	(diagrams	are prov	ided in SI)

	(	0	4	/
Annealing	Ambiant	300	500	950
temperatures	Ambient	°C	°C	°C
	Ti, CuO	Ti,	Cu <sub>2</sub> O,	Cu <sub>2</sub> O,
Constituents		CuO,	Cu,	Cu,
		Cu <sub>2</sub> O	TiO <sub>2</sub>	TiO <sub>2</sub>

Also, whereas the strongest exothermic reactions in CuO/Al multilayers began just after 550 °C, i.e., just prior to the Al melting (peak # 2 and peak # 3 in **Fig.** 2), CuO/Ti multilayer releases 70% of the total heat of reaction at low temperature (< 500 °C). The high-temperature weak exotherm of CuO/Ti (peak # 2) would be corresponding to a continuation of Ti oxidation due to the higher melting point of titanium (1665 °C, Al being 660 °C).

**Table 2** presents the total heat release, ~1580 and ~1187 J/g, for CuO/Al and CuO/Ti respectively, which are for both roughly 50% of their theoretical values (3300 and 2450 J/g, respectively). The typical lower than expected heat release from the foils are usually attributed to the incomplete reaction as sputtered-deposited as CuO is highly defective, as well as heat losses into the environments. The presence of Cu<sub>2</sub>O in post-DSC products confirms the incompleteness of the Ti+CuO. Indeed, XRD analysis of the (**Table 1 & 2**) shows metallic Cu, TiO<sub>2</sub> and Cu<sub>2</sub>O signatures in the

combustion products. Note that the absence of metallic titanium implies that all Ti has been oxidized to some lower level of oxidation states.



**Fig. 3**. DSC traces of CuO/Al and CuO/Ti foils in Ar. Foils are composed of 5-bilayers of each reactants with a mass ratio of fuel (Al or Ti) over CuO at 2. Heating rate at 10 °C.min<sup>-1</sup>.

**Table 2**. Summary of the heat releases from CuO/Al and CuO/Ti foils composed of 5-bilayers. Mass ratio of fuel (Al and Ti) over CuO is fixed at 2.

	Heat release (J•g <sup>-1</sup> )			
Samples	< 500 °C	Total	Theoretical total	
CuO/Al	179	1580	3300	
CuO/Ti	824	1187	2450	

Thermal analysis suggests that the high reactivity of CuO/Ti multilayers is due to the fast Ti oxidation at low temperature, thus producing a  $TiO_x$  growing interface which appears to be a poor barrier to reactant diffusion when comparing it with the amorphous alumina grown in CuO/Al system [10]. With its crystallization at 500 °C, this layer offers a good barrier to mass transport until temperature above 700-900 °C is reached. However, the question of the nature of diffusing reactants, i.e. both Ti and O or only O, is not answered.

Since no Ti/Cu alloying is observed and as the melting point of the titanium is much higher than aluminum, 1665 °C vs 660 °C, we expect that only atomic oxygen, rather than titanium migrates from CuO to the titanium reservoir. To further analyze the relevance of this conjecture, high resolution microscopy is conducted on CuO/Ti/CuO/Al sample composed of only four nanolayers, to quantitively describe structural and chemical evolution of the TiO<sub>x</sub> interfacial layer upon heating. The target temperatures for annealing were set at 300 °C and 500 °C as a result of the DSC analysis, wherein the first CuO/Ti exotherm are observed just after 300 °C and is completed when reaching 500 °C.

The **Fig. 4a-b** (TEM images and EDX mapping), the CuO/Ti/CuO/Al sample show the four nanolayers: from the bottom to the top, CuO, Ti, CuO, and Al, with thickness of  $194 \pm 1.2$  nm,  $161 \pm 1.9$  nm,  $199 \pm 1.7$  nm,

and  $200 \pm 1.5$  nm, respectively. TiO<sub>x</sub> nanolayer, can be distinguished on both the EDX maps (Fig. 4b) and high magnification TEM images (Fig. 4c-d) of the CuO-Ti and Ti-CuO interfaces. Note that throughout this paper A-B refers to an interface formed upon the deposition of B on A. The CuO-Ti interface formed upon Ti sputtered deposition onto the rough CuO surface is overall ill-defined and inhomogeneous, due to the typical roughness of columnar CuO, with an average thickness of  $9 \pm 2$  nm, more than twice thicker than that of CuO-Al interface (4.2  $\pm$  0.7 nm) formed upon the deposition of Al onto CuO. The interface formed upon the CuO sputter-deposition onto Ti (Ti-CuO) is flat and features a thickness of  $5.1 \pm 0.3$  nm, again thicker than that of Al-CuO,  $3.8 \pm 0.1$  nm. The thicker initial interfacial layers in CuO/Ti system compared to CuO/Al plaids for a higher reactivity of Ti as fuel, which also agrees with the higher Ti-O bond energy compared to Al-O (668 kJ.mol<sup>-1</sup> versus 500 kJ.mol<sup>-1</sup>).



**Fig. 4**. (a.) *TEM micrographs of the cross section of CuO/Ti/CuO/Al sample.* (b) *corresponding EDX mapping. High magnification TEM micrographs across the two different interfaces (c) CuO-Ti and (d) Ti-CuO. Each color indicates the different elements.* 

**Fig. 5 and 6** present high magnification TEM crosssections and EDX profiles of CuO-Ti, Ti-CuO interfaces and CuO/Ti/CuO/Al stack post the annealing treatment at 300 and 500 °C, with a zoomed-in highangle annular dark field (HAADF) image of Ti-CuO-Ti in **Fig. 6d**. Furthermore, the thicknesses of each layer (metal, fuel and interfaces) measured from the TEM images (precision 1 nm) are reported in **Table 3**. As the annealing temperature increases, both CuO-Ti and Ti-CuO interfaces grow (**Fig. 5**) and, the CuO layers greatly modifies structurally, in thickness and composition (**Fig. 6c** and **Fig. 6d**). Also, delamination was observed at both CuO-Ti and Ti-CuO interfaces (**Fig. 6b-c**) with lots of high contrasted areas in between TiO<sub>x</sub> layers and CuO, attributed to voids. **CuO-Ti interface**: the CuO-Ti interface evolved from hardly distinguishable (as deposited) to over a ~60 nm thick and well-define oxide layer after thermal annealing at 500 °C (**Fig. 5a** and **Fig. 5e**). The atomic percentage ratio between Cu and O increased from 2 (as deposited) to 4 (annealed at 500 °C), which implies the CuO near the CuO-Ti interface has lost three quarters of its oxygen content. Interestingly, the atomic percentage ratio of Ti to O at 500 °C equals to 1 (EDX profile of **Fig. 5f**) thus TiO is the proposed materials that develops in contact to CuO. Due to the low sensitivity of EDX towards oxygen element, the exact oxidation state of titanium in TiO<sub>x</sub> will be further quantified in the EELS section.

Ti-CuO interface: the native titanium oxide layer at the Ti-CuO interface is thickening upon annealing to reach ~ 65 nm thick after thermal treatment at 500 °C (Fig. 5c and Fig. 5g). The atomic percentage ratio of Ti to O at 500 °C (EDX profile of Fig. 5h and Fig. 6f) indicate the composition of TiO<sub>2</sub>, and no more metallic Ti is present as the Ti layer contains ~20% of oxygen (to be further examined by EELS) after thermal treatment at 500 °C. As a summary, from the EDX analysis, confirmation is made that CuO starts to decompose at low temperature (300 °C) to oxidize the adjacent titanium, which leads to the rapid growth of the titanium oxide interfacial layer (more than 60 nm gain in thickness from ambient to 500 °C). Also, even deeper penetration of oxygen atom throughout the initial titanium layer, beyond TiO and TiO<sub>2</sub> that are grown upon annealing in their crystalline form, is consistent with the loss of the titanium XRD peak and oxygen presence from EDX spectra, at 500 °C.

Altogether these results not only support the DSC findings featuring a high exotherm event below 500 °C caused by the titanium oxidation, but also bring an explanation for the superior reactivity of CuO/Ti thermite over CuO/Al [9] linked to the stronger binding affinity of titanium with oxygen originated from CuO decomposition [11] and probable higher diffusion rate of oxygen through titanium oxide compared with aluminum oxide. Indeed, unlike CuO-Ti and Ti-CuO interfaces where oxygen penetrates deep inside the Ti layer after annealing to 500 °C, in CuO-Al and Al-CuO oxygen did not diffuse into the metallic aluminum layer: the oxygen signal drops to almost zero as passing through the alumina layer. In addition, the aluminum oxide layer grows up to ~ 20 nm after annealing at 500 °C, against 60 nm for TiO<sub>2</sub> (Table 3), i.e. only one third.

Interestingly, analyzing the CuO and Ti layer thickness variation upon annealing (**Table 3**), both the Ti and CuO do not vary much in thickness: a reduction of 26% and 10% only after the annealing at 500 °C, respectively, while the interfacial layer grows by 650%. As comparison, the aluminum layer does not change in thickness after annealing at 500 °C. The whole CuO/Ti/CuO/Al stack thickens by 7 %, corresponding to a ~50 nm global increase. This overall increase is consistent with the titanium oxidation: the ratio of

density between pure Ti and rutile  $TiO_2$  gives an estimate of  $\times 1.82$  increase of the titanium layering that is being oxidized, giving birth, in theory, to 74 nm of grown  $TiO_2$ . This reasonably falls in the order of magnitude of the experimentally grown titanium (~100 nm) as the estimate does not account for the lateral titanium over-density when turning titanium into  $TiO_2$ , that should lead to a slightly higher estimate.



**Figure 5.** *STEM-EDX profile of each interfaces of CuO/Ti/CuO/Al annealed at 300 °C (a-d), and 500 °C (e-h).* 

The fast oxidation of atomic titanium by oxygen released from CuO decomposition leaves voids/delamination along the growing path (green dotted circles in Fig. 6b). EDX-line scans inside these voids (L1 and L2, positions are highlighted in green in Fig. 6d) confirm that there are less materials in these triangle areas, especially with L2 position where the total atomic percentage drops to less than a half. Considering the EDX surface analysis can reach a sampling depth up to 100 nm, thus the line scan profile is in fact an accumulation of each element signals throughout a certain thickness of the examined layer.



**Fig. 6**. STEM image of CuO/Ti/CuO/Al annealed at 300 °C (a) and 500 °C (b); zoomed-in STEM (c) and HAADF (d) images of CuO/Ti/CuO interfaces from sample annealed at 500 °C; EDX line scan profiles of CuO-Ti interface: L1(e) and L2 (f), highlighted in green arrows.

**Table 3**. Layer thickness changes of CuO/Ti/CuO/Al

 at various temperatures.

Temp	Measured thickness (nm)							
(°C)	CuO	TiO <sub>x</sub>	Ti	TiO <sub>x</sub>	CuO	$Al_xO_y$	Al	All
25	$194 ~\pm$	0 + 3	$161\pm$	5 + 0	$199 \pm$	6 + 1	$200 \pm$	$773 \pm$
23	1	9±3	2	$J \pm 0$	2	$0 \pm 1$	2	3
300	$177 \pm$	$15 \pm$	$162 \pm$	10 + 1	$189 \pm$	$11 \pm$	$200 \pm$	$768 \pm$
500	3	3	2	10 ±1	2	2	2	9
500	$177 \pm$	$65 \pm$	$119 \pm$	$63 \pm 4$	$189 \pm$	$18 \pm$	$200 \pm$	$826 \pm$
500	2	2	5	$05 \pm 4$	2	2	2	4

High resolution TEM-EDX analysis revealed that the titania, as Ti+CuO terminal oxide, is grown into the Ti layer from the self-diffusion of oxygens released by CuO decomposition into the growing interfacial layer. As a final experiment STEM-EELS, were performed on both the Ti-CuO and the CuO-Ti interfaces after annealing with the goal to quantify the evolution of the oxidation state of Ti and Cu and therefore validate the single oxygen diffusion. Hence, the energy loss near edge structure (ELNES) of Ti L<sub>2,3</sub>-edges at 456-462 eV, O K-edge at 536 eV and Cu L<sub>2,3</sub>-edges at 931-951 eV were acquired across the various interfaces.

ELNES of the Ti and O are shown in Fig. 7 for both  $TiO_x$  layers annealed at 300° and 500 °C. When annealed at 500 °C (Fig. 7c), the two ELNE Ti L<sub>2.3</sub>edges at 456 - 462 eV are subdivided into four peaks as a result of the strong crystal-field splitting of Ti<sup>4+</sup> from the surrounding oxygen atoms [12], accompany with the same subdivision of oxygen K-edge at 532 eV [13]. Such splitting is not observed in samples annealed at 300 °C (Fig. 7a and Fig. 7b), except for the minor subdivision EELS O-K edge from the upper TiO<sub>x</sub> layer, which might indicate the presence of Ti2+ and/or Ti3+ [14]. Thus, the oxidation state evolution of titanium in upper TiO<sub>x</sub> layer (Ti-CuO interface) confirms the previously discussed EDX line scan results (Fig. 4-6), i.e., as annealing temperate increases, TiOx evolved from TiO to TiO<sub>2</sub>. However, as for the bottom TiO<sub>x</sub> layer (CuO-Ti interface), EELS results indicate the

presence of TiO<sub>2</sub> while EDX results (Fig. 5-6) refers to a Ti to O atomic ratio at 1. Considering the low sensitivity of EDX towards lighter elements [15], EELS is more trusted when it comes to determine oxidation states. Thus, both TiO<sub>x</sub> interfacial layers undergo the same development as annealing temperature increases. Noteworthy, no O-K edge is detected in the Ti layer when annealed at 300 °C as shown in Fig. 7a and Fig. 7b, which proves the ~10% atomic oxygen content detected by EDX in the scans of Fig. 5a and Fig. 5d is a detection error. However, as annealing temperature increases to 500 °C, strong O-K edges are found in all EELS spectra of the Ti layer, in alignment with the EDX result (Fig. 5 indicating 20% of oxygen into the Ti) where atomic oxygen to titanium ratio increases from ~ 0.1 (as deposited and annealed at 300  $^{\circ}$ C) to > 0.25 (annealed at 500 °C).

Contrary to the high oxygen content in titanium layer, no discernable O-K edge was detected in aluminum layer even at 500 °C (**Fig. S10**) that confirms the higher affinity of Ti towards oxygen than Al as discussed earlier. Only oxygen ions are detected by EELS (**Fig. 7c**) in TiO<sub>x</sub> interfaces regardless of the annealing temperatures, so that it is possible to conclude that the oxidation of titanium is governed by condensed phase mechanism as previous studies argued [7]. Unlike the CuO/Al system, the much faster oxidation of titanium layer impedes the formation and storage of gaseous O<sub>2</sub> inside voids created at the CuO/Ti interfaces.



**Figure 7**. STEM-HAADF-EELS results of Ti-CuO (a) and CuO-Ti (b) annealed at 300 °C, and TiO<sub>x</sub>-Ti-TiO<sub>x</sub> annealed at 500 °C (c), showing Ti  $L_{2,3}$ , Cu  $L_{2,3}$ , and O k-edge.

Interestingly, two Ti oxidation states were observed by STEM-EELS analysis. At 300 °C, the Ti is oxidized into TiO (not detectable in XRD but quantified by STEM-EELS). At 500 °C, the TiO is further oxidized into crystalline TiO<sub>2</sub>, and no more Ti is detected as being oxidized in TiO. Indeed, TiO<sub>2</sub>, Cu<sub>2</sub>O and Cu are detected by XRD without metallic Ti. This is consistent with DSC results featuring one single major exotherm located at ~ 430 °C generating the ~70% of the total heat of reaction. The second broad exotherm at 807 °C may correspond to the second oxidation step.

(1)  $\operatorname{Ti}_{(s)} + \operatorname{O}_{2(g)} \xrightarrow{} \operatorname{TiO}_{2(s)}, \Delta H_R \approx -944 \, kJ \cdot mol^{-1}$ 

(2) 
$$\operatorname{TiO}_{(s)} + \frac{1}{2}\operatorname{O}_{2(g)} \xrightarrow{} \operatorname{TiO}_{2(s)}, \Delta H_R \approx -443 \ kJ \cdot mol^{-1}$$

Importantly, although the Al+CuO redox reaction in CuO/Al dense thermites is controlled by the diffusion of Al and slower counter diffusion of O through the growing alumina layer, only oxygens diffuse through the growing titania layer. In other words, Ti ions do not move which explain why no TiCu alloying was observed by contrast to Al<sub>2</sub>Cu (endotherm at ~ 540 °C in DSC). Hence, the reaction occurs at the Ti/TiO<sub>x</sub> interface, Ti and Cu remains always separated by a layer of TiO<sub>x</sub> preventing formation of the alloys.

#### Conclusions

In this work, as-prepared CuO/Ti nanothermites ignite much sooner (ignition energy reduction by 5) and burn faster (burn rate enhancement  $\times 3$ ) compared to equivalent CuO/Al material. Atomically resolved STEM-HAADF, HRTEM-EDX and STEM-EELS results show that the Ti has a better affinity with oxygen than Al: ~70% of the total heat of reaction of the Ti/CuO system is released within a single exotherm at 430 °C, against only 30% for Al/CuO system. Also, in CuO/Ti, solely oxygen atoms migrate through the titania layer to react with Ti at the TiO<sub>2</sub>/Ti interface, contrary to the dual O and Al migration observed in CuO/Al one. As a consequence, titania grows and propagates into the Ti layer and no Ti/Cu alloying occurs during the reaction, which is another difference with the Al<sub>2</sub>Cu formation seen in CuO/Al system. Finally, Ti+CuO redox reaction undergoes a two-step oxidation process: at 300 °C, Ti is first oxidized into TiO and further oxidized into crystalline  $TiO_2$  at 500 °C. This study confirms that Ti can be of great interest in addition of Al in nanothermites, for applications where it is desirable to lower the ignition temperature. Adding two CuO/Ti bilayers prior to the deposition of CuO/Al multilayers allows reaching ignition delays below the ms regime (ignition time of 200 µs) against 15 ms without CuO/Ti.

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