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Direct evidence of amine-metal reaction in epoxy systems: an *in situ* calorimetry study of the interphase formation

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Abstract

Epoxy resins are ubiquitously encountered in industrial applications as in adhesives and composites. The properties of epoxy-amine networks are directly impacted by the presence of metal (hydr-oxidized) surfaces, leading to a modification of their glass transition temperature T_g . We propose here an innovative experimental approach, investigating the interaction of DETA amine and DGEBA epoxy with Al and Cu powder substrates (partially (hydr)oxidized). We explored for the first time the formation of the amine-metal interphase by *in situ* mixing calorimetry to evaluate the energetics of interaction. While DGEBA interacted only slightly with Al-based surface, the reaction with DETA was associated with a high exothermic enthalpy of reaction. The enhancing role of surface hydroxylation was also evidenced by comparing boehmited Al to a simply oxidized counterpart. An even larger exothermic effect was measured with copper, which was related to the high chelating power of Cu compared to Al. The possible underlying mechanism of amine-metal interphase formation was discussed with a generalized schematic.

Keywords

Mixing calorimetry, Interphase, Epoxy-amine, Metal, Chelate, Epoxy

1. Introduction

Epoxy resins represent a major family of thermosetting polymer precursors. They are encountered in various strategic industrial sectors, such as ground transportation and aeronautics, building and construction, sports and leisure. They are typically used as adhesives and sealants, coatings (e.g. paints, primers...) and composite matrices. The world market for epoxy resins represented 3.3 million tons per year in 2016 and is in constant expansion [1]. They became commercially available since 1946 [2] and were then extensively studied and used since the 1970s [3].

Epoxy resins are often polymerized with amine hardeners, leading to epoxy networks. Independently of the application, the latter always involve interfaces: between fibers or fillers and the epoxy-amine matrix in composites, or between a (metal) substrate and epoxy-amine coatings or adhesives. Such 2D interfaces in 3D multimaterials can be considered as boundaries between two spatial regions occupied by different components. However, at a microscopic scale, these interfaces should more accurately be considered as extended tri-dimensional domains corresponding to so-called "interphases", which may exhibit physical and/or chemical property gradients.

The occurrence of chemical interphases in epoxy-amine systems involving different kinds of substrates or fillers have been reported in the fields of biomaterials [4], building materials [5, 6], composites [7,8], as well as coatings and adhesives [9-20] leading sometimes to the modeling of epoxy-amine/metal interactions [21-22]. A great deal of epoxy-amine mixtures, especially in the latter domain, involve a metal substrate such as aluminum and titanium (e.g. in aeronautics), steel (e.g. in ground transportation), copper (e.g. in electrical applications), etc. In this case, the interphases arise from the adsorption of monomers (amine and/or epoxy in this case) onto the metallic surface, as was first reported by Kollek *et al.* essentially on the basis of spectroscopy analyses (XPS, FTIR) [23]. Some research shows the variation of the network morphology within the interphase, linked to an enrichment or depletion of amine near the metal surface [17-18]: the segregation of the monomers was then followed by XPS in order to show the amine enrichment within the metal surface [20]. In addition, it was shown by XPS that after contact between an amine and a metallic surface, the amine component can form metal-bound surface complexes and hydrogen-bonded surface complexes [24-27]. Then, when the amine component is mixed with epoxy monomers, the polymerization (i.e., reaction between the amine and the epoxy monomers) and interphase formation (i.e., reaction between amine and metal) are in competition. This chemical sorption was also shown to be concomitant with metal surface dissolution, leading to an organometallic complex or chelate formation [11-13, 24-26]. On the other hand, from the state of the art, the epoxy component of the mixture did not seem to react with metallic surfaces. XPS data also pointed out that the dissolution process of the metal surface upon contact with the amine strongly depended on the (hydr)oxidation of the surface [24-28], leading to direct evidence of metal compound (its state is not evidenced) within the adhesive layer [15,19]. The interphase formation however depends on many other parameters, such as the surface treatment [14], the nature of the amine (hardener) and the curing cycle [11-13], the thickness of the coating and its environment (thin coatings versus thick adhesive joint) [16], or the viscosity of the pre-polymer mixture [28-29]. These interactions at the level of the interphase lead to modifications of the physico-chemical, mechanical and thermal properties typically over a hundred micrometer range. In particular, the glass transition temperature (T_g) was found to decrease significantly – typically of more than 10 °C – compared to the bulk and the Young modulus may increase or decrease depending on the used amine; finally, the adherence between the epoxy-amine coating or adhesive and the substrate may decrease with the formation of the interphase [11-13].

Therefore, the properties of the final epoxy-amine-containing multimaterials are likely to extensively depend on the characteristics of the interphase. However, the formation of epoxy-amine/metal interphase was only examined to-date via indirect analyses (measurement of the final thermal and mechanical properties) or observations made *a posteriori* (XPS, dissolution measurement, FTIR), but was never followed during the chemical reaction. In this article, after investigating by DSC the glass transition temperature (T_g) for epoxy-amine networks in contact

with or without metal (hydr-oxidized) surfaces, the interaction between either amine or epoxy monomers and metal powders was followed *in situ*, for the first time, using a mixing calorimeter. Hence, using industrially-relevant monomers (DETA and DGEBA) and metals (aluminum and copper), the aim of this work is to allow direct assessments of the corresponding interphase formation. As debate continues about a possible reaction between metal surfaces and amine or epoxy groups, this study is intended to shed light on this question.

2. Material and methods

2.1. Material

In order to favor the interaction between the monomers and the metal-based surfaces, metals were used here in the form of powders.

The aluminum sample was a powder 200 mesh (passing through a 74 μm seive) (99% purity from Acros). Prior to use, in order to ensure a reproducible initial oxidized state (native oxide layer of aluminum), the powder was contacted with atmospheric air in a ventilated oven, at 80°C for 14 h. In a second approach, for comparative purposes, the powder was preliminarily immersed in boiling ultrapure water (milliQ system, conductivity verified higher than 18 M Ω) at 100°C for typically 90 min prior to a drying step in the oven at 80°C for 14 h. The BET specific surface area of these Al-based samples, independently of the “low-temperature” treatment undergone, reached 30 m²/g. This was cross-validated by similar values of the surface area moment mean D[3,2] (10.8 and 10.3 μm respectively for boehmited and initial Al powders) as evidenced from particle size distribution assays.

The copper sample was purchased from Prolabo. Prior to calorimetry experiments, in order to ensure a reproducible surface state, the powder was preliminarily immersed in boiling deionized water, at 100°C for 90 min and then dried at 80°C for 14 h. The BET specific surface area of this Cu-based sample reached 1 m²/g.

The monomers used in this study are the main components of most used adhesives and composite matrices in the industry: DGEBA (Bisphenol A diglycidyl ether, DER 332, from Sigma-Aldrich, Molecular Weight: 340.41 g/mol, viscosity at 25°C: 4000-6000 mPa.s and functionality: 2 epoxy groups) was used as epoxy prepolymer and the curing agent was DETA (Diethylenetriamine from Aldrich, Molecular Weight: 103.17 g/mol, viscosity at 20°C: 7.16 mPa.s and functionality: 5 protons from 2 primary amines and 1 secondary amine). In this work, stoichiometric proportion of reactants was used for the preparation of the epoxy-amine networks (poly-epoxy) in view of glass transition temperature measurements. DGEBA and DETA monomers were then mixed at room temperature in order to form bulk samples after the following curing cycle: 3 h at room temperature and 1 h at 150°C. Therefore, the glass transition temperature measured by DSC corresponds to the $T_{g\infty}$, *i.e.* the maximum glass transition temperature that can be achieved at a theoretical infinite molecular weight. For the sake of simplicity, this temperature will be referred to as “ T_g ” in the text.

2.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used for the determination of the glass transition temperature (T_g) of the poly-epoxy under investigation. A DSC 204 Phoenix Series (NETZSCH, Selb, Germany) coupled with a controller (model TASC 414/4) was used. The apparatus was calibrated against melting temperatures of In, Hg, Sn, Bi, CsCl, and Zn, applying two subsequent +10 °C/min temperature ramps, to verify the reproducibility. The samples were placed in aluminum capsules and the mass was measured with the accuracy of ± 0.1 mg.

The presented glass transition temperatures (T_g) are the “onset” ones, *i.e.* the beginning of the

phenomenon (onset being defined at the intersection of the extrapolated baseline in the glassy state and the tangent taken at the point of maximum slope by the Proteus® Software).

2.3. Mixing calorimetry

Monomers/metal (hydr-oxide) reactions were followed isothermally with a mixing calorimeter (C80, Setaram, France). Two-compartment Hastelloy® mixing cells separated by a Teflon® membrane were used in this work. The calorimeter, equipped with two thermopiles connected in opposition (sample cell and reference cell) is based on the 3D Calvet sensor technology allowing us to determine the heat flow accompanying the ongoing chemical reaction. In the present case, the heat effect associated to mixing a liquid/viscous phase composed of pure DETA or DGEBA (1.5 ml placed in the upper compartment of the measuring cell) with metallic powders (10 to 1000 mg placed in the lower compartment) was measured. These proportions were selected so as to have a large excess of monomer with regard to the possible monomer/powder surface reaction. The reactions were carried out under isothermal conditions (40 °C). This temperature was chosen near the room temperature to avoid the evaporation of the monomers, but high enough for an optimized regulation of the calorimeter furnace. After loading the calorimeter and reaching a stabilized temperature and baseline level close to zero mW, the membrane of both cells was ruptured manually by lowering a helix-shaped piercing tool allowing contact between the two compartments of each cell (the reference cell was left empty for these experiments). Completion of the DETA or DGEBA/metal interaction was evidenced by the return of the baseline to a stabilized value, and within a reasonably short amount of time, typically around an hour. The enthalpy of reaction was then obtained by integrating over time the heat flow signal. In order to take into account eventual variations of the heat flow signal due to some asymmetry in the two-cell setup used in the calorimeter, a “blank” experiment was also performed in similar conditions as above (after returning the piercing tools to their upper position) to subtract the eventual effect of an asymmetry of the calorimetry cells. The obtained enthalpy value ΔH_{blank} was subtracted from the raw measured enthalpy value so as to determine the actual interaction enthalpy (ΔH). Prior to these calorimetry experiments, calibration of the calorimeter heat flow signal was verified with the dissolution of dried potassium chloride (KCl, Merck) into water at the same temperature (accuracy of temperature: $\pm 0.1^\circ\text{C}$, heatflow resolution: $0.10 \mu\text{W}$).

2.4. Physico-chemical characterization of metal powders

X-ray diffraction (XRD) was used to examine the metal powder samples. The patterns were recorded using an Equinox 100 diffractometer (INEL) equipped with a cobalt anticathode ($\lambda = 1.78897 \text{ \AA}$). The whole 2θ range was measured simultaneously thanks to a curved detector. Each sample was analyzed for typically 2 h acquisitions.

BET specific surface area measurements were carried out on a BELsorp-mini II (BEL Japan Inc.) by volumetric adsorption of nitrogen (for Al) and krypton (for Cu) at 77 K. Outgassing was done by treating the samples in the apparatus at 150°C for 10 h under vacuum (pressure lower than $5.2 \cdot 10^{-4}$ Pa at the start of the measurements). Surface area moment mean $D[3,2]$ were measured from the particle size distribution determined on a Malvern Mastersizer 3000 laser diffractometer operated with an He-Ne laser (wavelength: 632.8 nm).

3. Results and discussion

3.1. Evidence of glass transition temperature modifications

As mentioned above, the formation of an interphase between the epoxy-amine system and metal-

based surfaces may generate significant modifications of the properties of the final coatings or adhesive layers obtained. This explains in particular the differences of glass transition temperature (T_g) between hundred-micron thick films and bulk for DGEBA/DETA systems, as previously shown [11-13].

In this work, the potential variation of T_g was followed by DSC using metal powders as substrates, so as to increase the surface area in contact with the monomers, and thus to explore further the monomer/metal (hydr)oxide reaction. The bulk sample formed upon reaction between pure epoxy (DGEBA) and pure amine (DETA) monomers, mixed in stoichiometric proportions and cured, was considered as the reference, and led to a T_g value equal to 135 ± 2 °C (**Figure 1**). On the other hand, “modified” DGEBA (denoted DGEBA*) and DETA (denoted DETA*) monomers were prepared by contact for 3 h with previously oxidized aluminum powder, followed by filtration (the filtration step removes the powder particles plus the possibly adsorbed monomer). T_g values were then measured on the cured “modified” bulks obtained by mixing either the modified DGEBA with the same amount of pure DETA as for the stoichiometric mix without contacting the DGEBA with the powder, or the modified DETA with the same amount of pure DGEBA as for the stoichiometric mix without contacting the DETA with the powder, as reported in **Figure 1**. As may be seen, in the case of the polymerized DGEBA*/DETA, our data point out a T_g value of 134 ± 3 °C similar to the reference, therefore suggesting the absence of significant reaction between DGEBA and aluminum. In contrast, the modified DGEBA/DETA* system exhibits a clear decrease in T_g , measured at 111 ± 5 °C, i.e. more than 20 °C below the reference (see **Figure 1**).

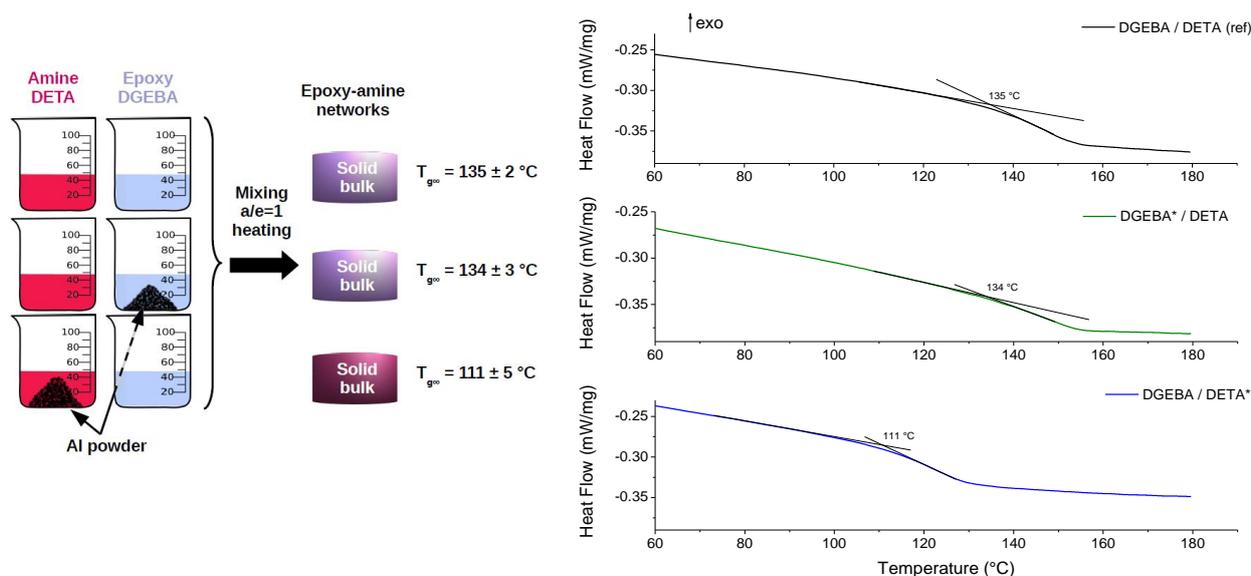


Figure 1: Preparation of epoxy-amine networks, without (reference) and with preliminary contact with aluminum powder, and consequence on glass transition temperature. Typical DSC curves are reported.

This decrease, observed here using metal powder, is in good agreement with data reported on metal alloy plates [11-13], and points out a modification of the formed network, supporting the hypothesis of a chemical reaction between the amine monomers and the metal surfaces. Such T_g decrease can be quantified, and using the Di Benedetto equation modified by Pascault [30]), it is possible to evaluate the conversion degree for the pure DGEBA-Al modified DETA network. With a conversion estimated equal to 1 for the pure DGEBA-DETA network ($T_{g\infty} = 135$ °C), $T_g = 111$ °C for the pure DGEBA-modified DETA network and $T_{g0} = -42$ °C, the conversion of pure DGEBA-modified DETA network was calculated as 0.91. Moreover, in a previous work [13], the T_g was presented as a function of aminohydrogen function/epoxy function (a/e) for pure DGEBA-DETA

and for DGEBA-Al modified DETA systems: the DGEBA-DETA system developed its maximum T_g for the stoichiometric monomer mix, as expected, i.e. an excess of any of the monomers results in a decrease of T_g whereas for the DGEBA-Al modified DETA systems the maximum T_g was observed for a ratio a/e equal to 1.15. The conclusion was that the functionality of the formed organo-metallic complexes was lower than the pure amine one. Here, as the same amount of co-monomer was added to the “modified” monomer as for the stoichiometric mix without monomer-powder contact, it can be concluded that powder contact and filtration do not affect the amount of DGEBA but the amount of DETA is lower. Thus, some relevant part of DETA must have been immobilized somehow by the powder. As a result, the epoxy-amine network made from the “modified” DETA is under-stoichiometric in terms of amine hydrogen, causing the T_g decrease observed, and this decrease (observed here using oxide and/or hydroxide metal powder, without added element) is in good agreement with data reported on oxide and/or hydroxide metal alloy plates, containing 0.5 to 3.5 wt% of added elements [11-13].

At this point, it is not possible to determine the mechanism leading to the modification of the DETA, but the presented results are in good agreement with the literature reporting the chemisorption of DETA onto copper [16-31], or other metals [13]. In the present work, similar T_g decrease observations were also obtained with copper powder (**Figure 2**), and the occurrence of a surface reaction was directly evidenced by the blue coloration of DETA when contacted with copper. This color change points to the transfer of some Cu^{2+} ions from the metal substrate into the solution. It theoretically calls for the formation of copper chelates with the amine or of aquo complexes. However, since the amine is used pure here (non-aqueous medium) and water molecules may only be present in very limited amount (from the partial surface hydration or via the faint inclusion of water vapor into the DETA), then the chelate formation hypothesis appears as the most likely.

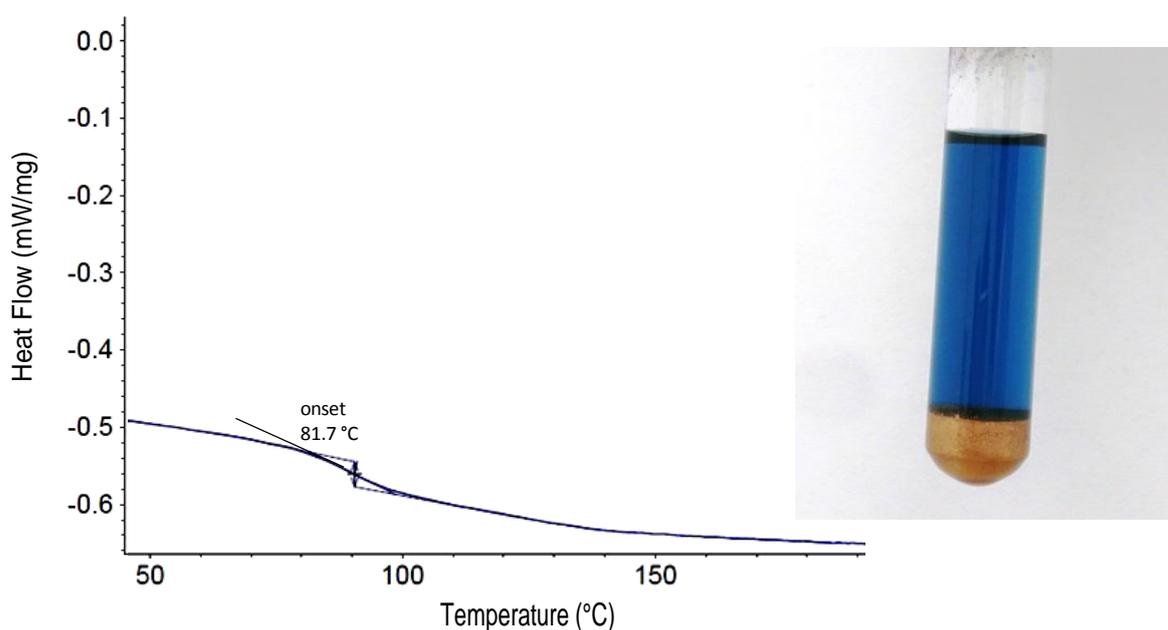


Figure 2: DSC curve for epoxy-amine network, with preliminary contact between copper powder and DETA. The image on the right gives a visual observation of the DETA after contact with Cu powder, evidencing the occurrence of a blue coloration

3.2. *In situ* mixing calorimetry: follow-up of monomer/metal reaction

In order to examine directly the occurrence of such reactions involving metal surfaces, *in situ*

mixing calorimetry experiments were carried out. While a mixing calorimetry approach was used to determine the enthalpy of polymerization of epoxy-amine systems [32-33], it has not been employed so far to explore the monomer interaction with metals or their corresponding (hydro)oxides. The calorimetry experiments were performed isothermally, at 40°C, with two-compartment mixing cells separated by a Teflon® membrane; and consisted of recording over time the heat flow signal upon contacting a pre-supposed excess monomer, DGEBA or DETA respectively, with increasing amounts of metal powder samples (the pre-supposed excess will be verified in the following). This in turn allowed the determination of the corresponding heat of reaction (enthalpy, ΔH_R). A “blank” experiment was systematically done at the end of each run to evaluate the effect of an asymmetry of the calorimeter cells, and thus correct the ΔH_R values. A typical thermogram is depicted in **Figure 3** in the case of DETA contacted with oxidized Al powder.

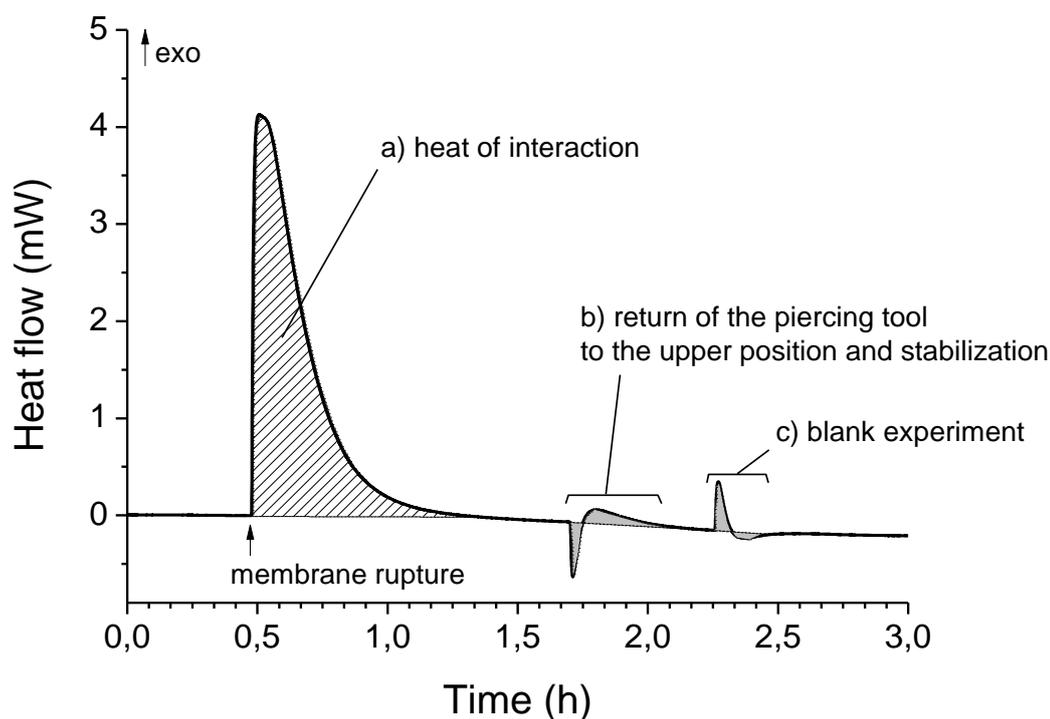


Figure 3: Example of thermogram obtained by *in situ* mixing calorimetry: a) heat flow exothermic peak after contacting DETA (1.5 ml) with Al powder (147 mg) at 40°C upon membrane rupture, b) return of the piercing tool to the upper position and c) blank experiment (to assess thermopiles asymmetry)

In the case of DETA, **Figure 4** reports the measured evolution of ΔH_R (corrected from the blank, with an average $\Delta H_{\text{blank}} \sim 300$ mJ) versus $m_{\text{Al-ox}}$, ranging for oxidized Al between 0 and -7800 ± 600 mJ (value reached for 1.2 g), ΔH_R becoming all the more negative that the mass of Al powder increased. These experiments thus show, for the first time, the occurrence of a very significant exothermic reaction when contacting the DETA monomer to aluminum.

It may be noted that, in contrast to DETA, the interaction between DGEBA and Al was found to be significantly lower in magnitude ($\Delta H_R \cong +2360 \pm 1000$ mJ for 1.2 g). The very high experimental uncertainty on the latter value can be related to the elevated viscosity of DGEBA, initially placed in the upper compartment of the calorimetry cell and partially remaining up despite the rupture of the cell membrane. The lower heat effect measured with DGEBA along with its endothermic character and the very limited modification of T_g (see **Figure 1**) show that the amine is considerably more

reactive than the epoxy monomer on oxidized aluminum surface. While the endothermic character of the DGEBA/metal substrate interaction reveals an interaction that is not favorable from an (enthalpy) energetic viewpoint, the exothermic DETA/metal interaction points in contrast to an energetically favorable event. The rest of this paper will therefore concentrate on amine/metal reactions. Close examination of the $\Delta H_R = f(m_{\text{Al-ox}})$ curve in **Figure 4** points out a linear trend, leading for oxidized Al to a slope of $-6.4 \pm 0.5 \text{ J.g}^{-1}$. This linearity confirms the hypothesis of amine excess in our experimental conditions. Taking into account the specific surface area of this powder evaluated by BET ($30 \text{ m}^2.\text{g}^{-1}$), this value corresponds to $-0.21 \pm 0.02 \text{ J.m}^{-2}$.

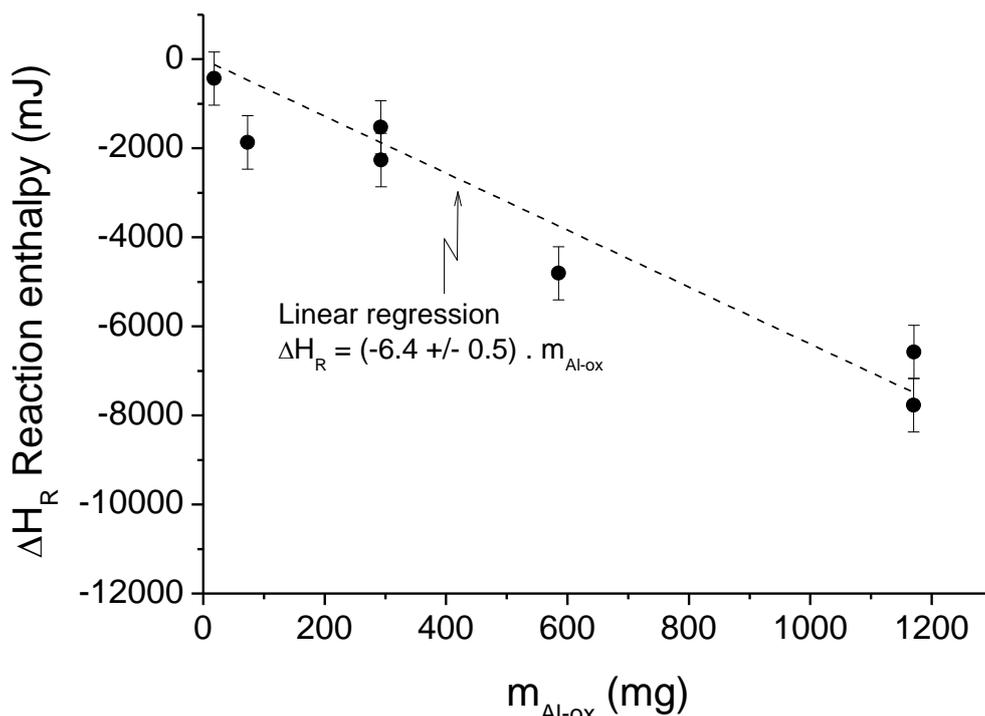


Figure 4: Enthalpy of reaction ΔH_R between DETA and (oxidized) aluminum powder, as a function of powder mass

Such a reactivity of aluminum surfaces with amines could be explained by -OH group ligand exchange and mostly by an acid-base reaction as evidenced by XPS in the case of ethylenediamine [24-26]. In aqueous solution, let us remind that the DETA molecule exhibits three pK_a values: $\text{pK}_1 = 4.42$, $\text{pK}_2 = 9.21$ and $\text{pK}_3 = 10.02$ [34], showing that the different protons of DETA may exhibit different behaviors and evidencing in particular a strong alkaline character; and the presence of (a limited amount of) moisture at the DETA-aluminum interface may locally create an alkaline aqueous environment. Therefore, the strong exothermic effect measured here might be correlated to the amount of -OH groups on the surface of the Al particles, as the amine is present in excess. In this regard, with the objective to confirm this hypothesis, a treatment of the Al powder was undergone to promote for occurrence of surface -OH groups. Numerous reports are available on the formation of boehmite $\text{AlO}(\text{OH})$, that may be seen as hydrated alumina $\text{Al}_2\text{O}_3 \cdot 1\text{H}_2\text{O}$, via immersion in boiling water [35]. The aluminum powder was thus treated in boiling water for 90 min prior to drying so as to favor its transformation into boehmite. Analysis of the treated sample by XRD (**Figure 5**) confirmed the appearance of $\text{AlO}(\text{OH})$ boehmite besides metallic Al, therefore validating this surface hydroxylation protocol.

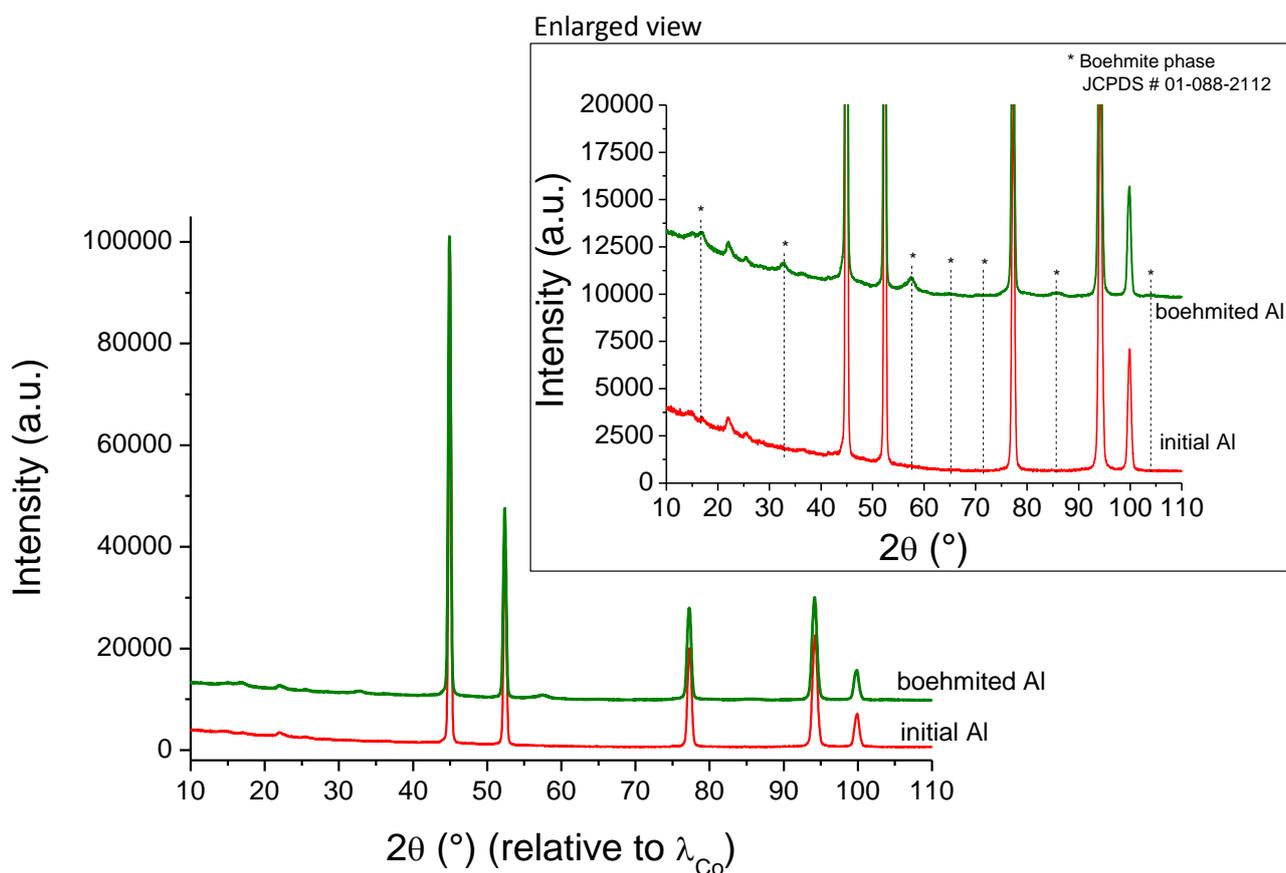


Figure 5: XRD patterns for the initial (i.e. powder contacted with atmospheric air in a ventilated oven, at 80°C for 14 h) and boehmited Al powder (λ_{Co} anticathode), normalized relatively to the most intense Al diffraction line at $2\theta \sim 45^\circ$. The occurrence of additional diffraction lines relating to the formation of boehmite (JCPDS file # 01-088-2112) is indicated by a star (*)

In situ mixing calorimetry was performed, following the same strategy as above, on this boehmited Al powder sample and **Figure 6** reports the corresponding measured enthalpy values. Again, a linear trend was found, confirming that the reaction was still undergone under an excess of amine. As expected from the above discussion, a noticeably more exothermic behavior was evidenced relatively to the oxidized Al previously tested, thus demonstrating that a larger number of surface sites associated to -OH groups have reacted with DETA (see **Figures 4 and 6**). From a quantitative perspective, a linear regression of the $\Delta H_R = f(m_{Al-boeh})$ curve led to a slope of $-9.0 \pm 0.1 \text{ J.g}^{-1}$ to be compared to $-6.4 \pm 0.5 \text{ J.g}^{-1}$ found for oxidized Al. Note that the linearity obtained for boehmited Al is significantly better than for solely oxidized Al, which can likely be explained by a more OH-rich reproducible surface state, and then less dependent on air moisture. This value corresponds, per unit surface area, to $-0.30 \pm 0.01 \text{ J.m}^{-2}$.

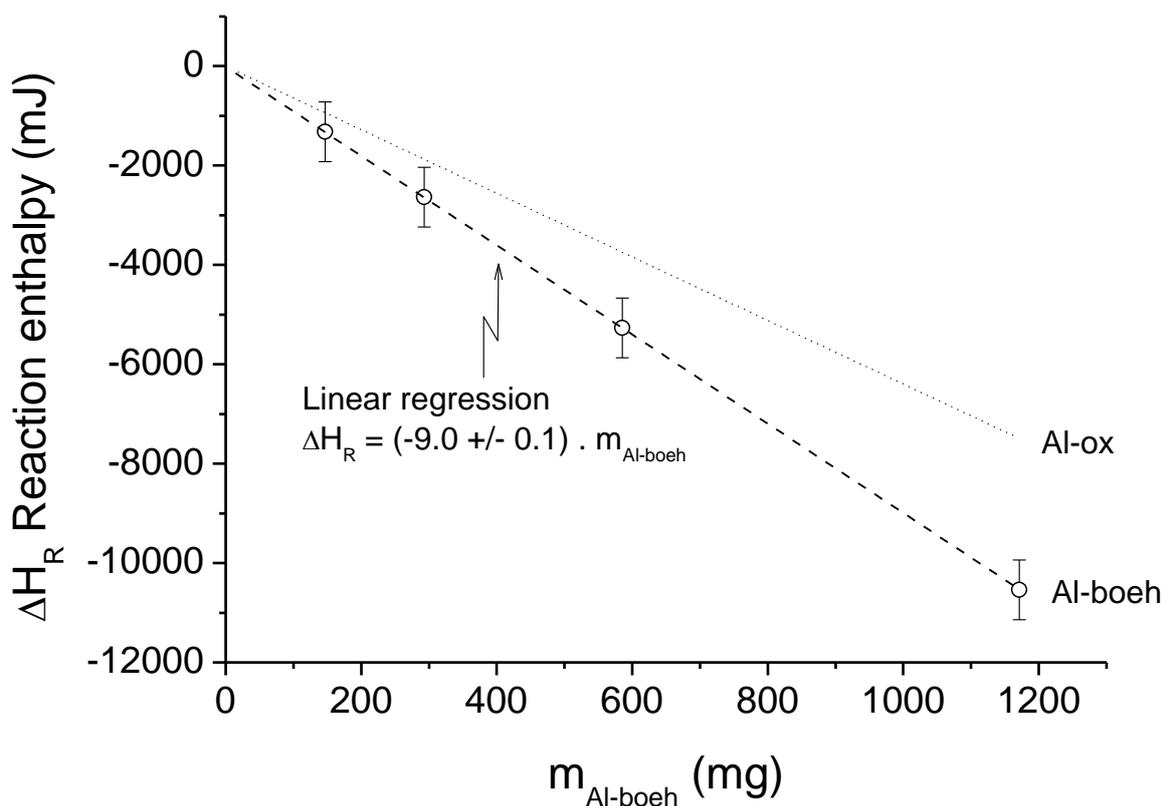


Figure 6: Enthalpy of reaction ΔH_{R} between DETA and boehmited aluminum powder, as a function of powder mass (dashed line, -----). The dotted line (·····) reminds data obtained in Figure 4 on oxidized Al

All of the above findings allowed us to follow, in a direct approach via *in situ* mixing calorimetry, the interaction between DETA and aluminum-based surfaces, evidencing a strong exothermic character and the role of surface hydroxylation. In order to widen this investigation to other metal surfaces, experiments were also carried out on a copper powder, which is another widely encountered metal – as such or in the composition of alloys – in industrial epoxy-amine applications. Indeed, amines are susceptible to react with a large variety of metals, as pointed out by the diminution of the glass transition temperature of epoxy-amine networks [9-13, 28-29]. Another interest of copper is the coloration it gives to most derivatives such as chelates. Upon contact with DETA, a clear blue taint of the liquid amine was indeed evidenced, as shown above in **Figure 2**.

Prior to calorimetry experiments, the copper powder was treated in boiling water in similar conditions as for Al so as to obtain a reproducible initial state; and the XRD analysis pointed out the presence of cuprite Cu_2O besides metal Cu (**Figure 7**). While this phase was already present in the initial powder, the related diffraction lines are slightly intensified after the treatment.

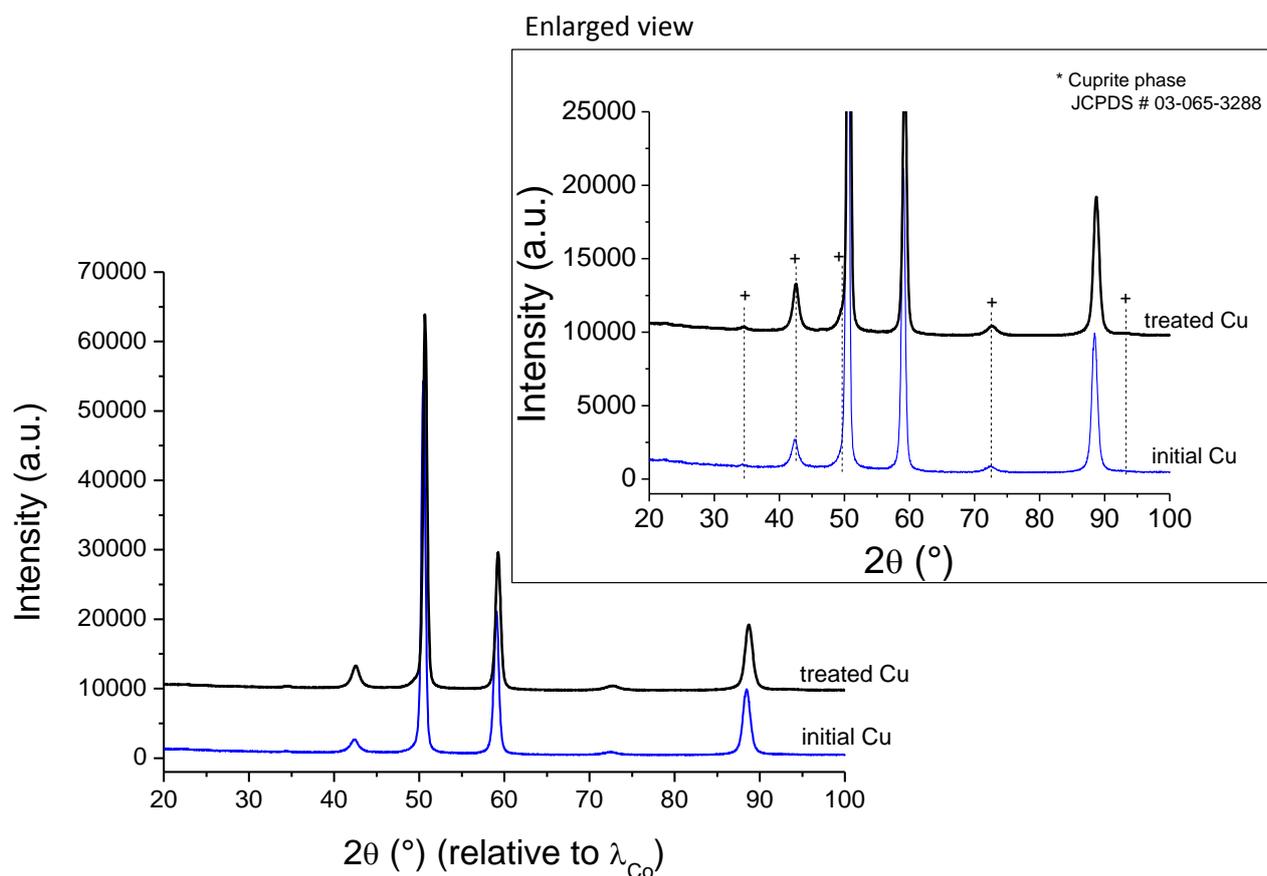


Figure 7: XRD patterns for initial and treated Cu powder (λ_{Co} anticathode), normalized relatively to the most intense Cu diffraction line at $2\theta \sim 50.7^\circ$. No additional diffraction lines are evidenced but an increased intensity of lines related to cuprite Cu_2O (JCPDS file # 03-065-3288) is seen as indicated by a plus sign (+)

The enthalpy values measured upon contacting this oxidized Cu powder with DETA are reported in **Figure 8**. As previously observed in the case of aluminum, a strong exothermic effect was again evidenced. Despite the scatter of the datapoints, the $\Delta H_R = f(m_{Cu-ox})$ curve obtained in the mass range 0-600 mg might be roughly considered as linear in a first approximation, leading to a slope of $-37.8 \pm 6.7 \text{ J.g}^{-1}$. Considering the specific surface area of this powder ($1 \text{ m}^2.\text{g}^{-1}$), this value is then equivalent to $-37.8 \pm 6.7 \text{ J.m}^{-2}$. The last datapoint obtained for $\sim 1.2 \text{ g}$ (see **Figure 8**), in contrast, shows a departure from this linear tendency, with a lower exothermic effect as could be expected. This observation might be related, in turn, to a departure from the “stoichiometry hypothesis” between DETA and the copper surface, unveiling a limitation in the amount of accessible DETA molecules. In any case, these data thus demonstrate, from direct observation, the occurrence of a surface chemical reaction between (treated) copper surface sites and DETA, as for aluminum, suggesting i) that this reaction is not limited to the case of aluminum as expected [11, 13] and ii) that mixing calorimetry is indeed a convenient tool for inspecting DETA/metal interphases *in situ*.

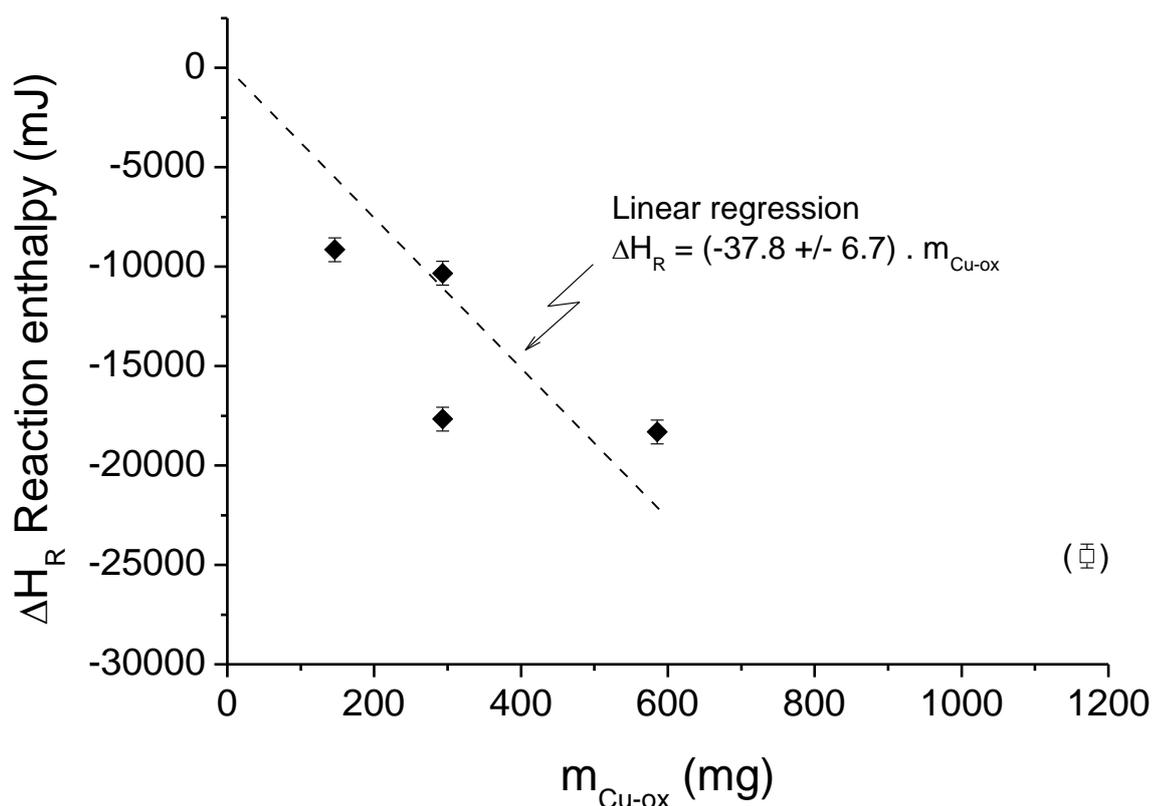


Figure 8: Enthalpy of reaction ΔH_{R} between DETA and (oxidized) copper powder, as a function of powder mass. The square datapoint (\square) appears particularly off the linear regression curve, suggesting a possible departure from the stoichiometry hypothesis between DETA and the copper surface

4. Discussion.

All the above findings allowed us to follow *in situ* the interphase formation between the DETA amine and Al- and Cu-based metal surfaces, and to quantify the corresponding enthalpy of interaction. A clear exothermic response was evidenced, depending on the nature of the metal and its oxy/hydroxylation state. These results establish the energetic background for such amine/metal surface reactions that was previously indirectly or subsequently reported in the literature. One macroscopic manifestation of the existence of these interphases lays in the clear decrease of the infinite glass transition temperature for the final epoxy-amine networks. This decreasing tendency of T_g can be linked to the amine/epoxy stoichiometry ratio of the mixture: upon contact with metal surfaces, the proton functionality of the amine decreases, leading to a less reticulated network [13]. At this point, it is interesting to wonder about the possible mechanisms involved in the formation of amine-metal chelates (e.g. as evidenced in **Figure 2** by the blue color of the amine after contacting copper). The role of surface hydroxyl groups was also demonstrated, at least in the case of aluminum, and needs to be taken into account. Potentially also, the degree of humidity may have some effect. The DETA amine, for example, exhibits three pK_a (4.42, 9.21 and 10.02 [34]) showing a strong basicity, especially in the air with moisture: the presence of moisture at the DETA-metal (hydr)oxide interface can locally create an alkaline aqueous environment that might also affect in some way the formation and/or detachment of the chelated complex. This potential effect is however to-date still unclear; for example Kosmulski discussed the degree of hydration *vs.* the point

of zero charge (PZC) of Al oxide and hydroxide and showed that Al compounds did not show a clear correlation between these two parameters [36].

A possible mechanistic scheme has been proposed on aluminum surfaces by Barthés-Labrousse *et al.* [24-26], based on the acido-basic character of the metal-amine reaction, and supposed to involve both Lewis basicity (nucleophilic attack of nitrogens doublets on surface metal atoms) and Brønsted acidity (release of proton(s) from the metal surface). It involves tweezer-like chelation from the folded polyamine molecule, reaching for Al and OH/H surface sites, followed by a detachment of the chelate from the surface. According to this group [24-26], this last step does not seem possible for the simple amines, and surface dissolution can only be induced by bidentate metal bond surface complexes (chelates) resulting from ligand exchange between hydroxyl sites of the surface and the amino terminations of the molecule. This overall suggested mechanism appears to explain well all experimental data at our disposal to-date, whether from pre-existing literature or from the present paper: Aoki *et al.* [20] worked on these experimental aspects, and Yamamoto *et al.* [21] used these previous results for molecular dynamics calculations. It is also likely to be applicable to most other metal surfaces, which often exhibit at least some degree of surface (hydr)oxidation, as in the example of cuprite [37-38]. On (hydr)oxidized surfaces, coordination to the metal cations through the nitrogen lone pair electrons (Lewis-like interaction) [24-25,39-41] and Brønsted-like interactions with protonation of the amine end-groups by surface acidic hydroxyl groups [24-25, 41] appear possible. A more generalized schematic, inspired by refs. [24-26] and adapted to DETA, is redrawn in **Figure 9** in the case of metal “M”: in the case of DETA, three amine sites can be potentially adsorbed, therefore several types of chelates might be *a priori* envisioned.

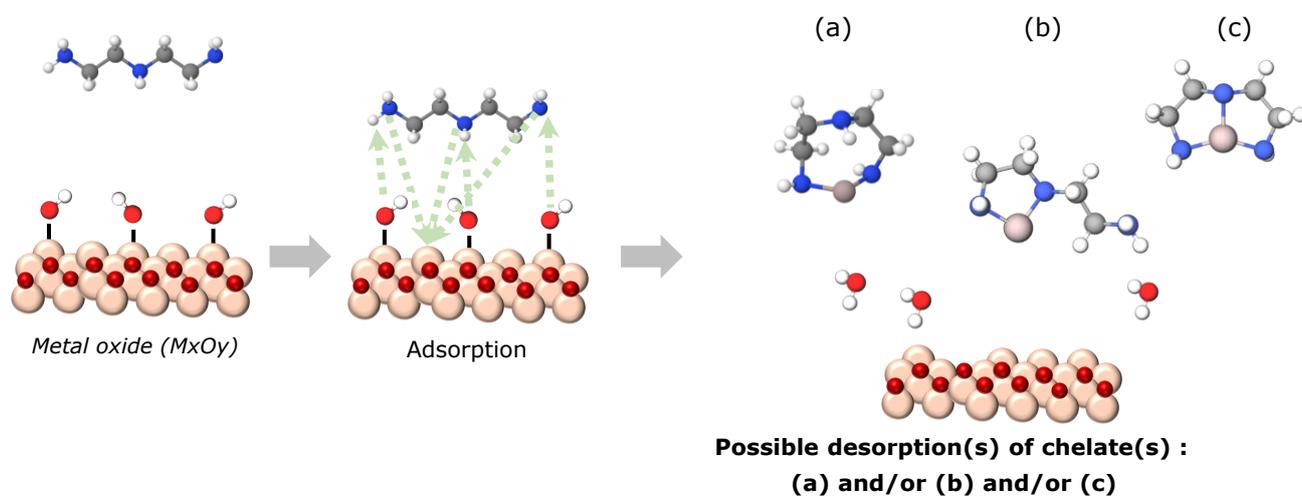


Figure 9: Proposed mechanistic schemes for the DETA-metal interaction. (a), (b) and (c) are potential chelates that may be envisioned

Considering, on the one hand, this mechanistic sequence of amine approach-chelation-detachment and, on the other hand, the enthalpies of interaction measured in the present work on aluminum and copper-based surfaces, it becomes interesting to compare from a quantitative viewpoint the behaviors of these metals. As already mentioned, after contact with the atmosphere, both Al and Cu exhibit on their surface a (hydro)oxidized state. Considering the formation of boehmite $\text{AlO}(\text{OH})$ on Al and cuprite Cu_2O on Cu, as evidenced by XRD, our data allowed us to evaluate the enthalpy of reaction with DETA, ΔH_R , per unit surface area, leading respectively to the values $-0.30 \pm 0.01 \text{ J.m}^{-2}$ for boehmited Al and $-37.8 \pm 6.7 \text{ J.m}^{-2}$ for oxidized Cu (see previous section).

However, comparing different substrates is delicate, as they do not exhibit the same surface densities of metal atoms (which are considered to be the “active” sites in the amine-metal

(hydr)oxide reactions). It is thus necessary to first determine these surface densities, and in a second step to recalculate the global interaction enthalpies per metal ion exposed on the surface.

In order to compare more accurately their behavior, the crystallography of each phase has to be taken into account in order to estimate the amount of surface Al or Cu atoms accessible per unit surface area. These compounds have been largely investigated from a structural point of view. Boehmite crystallizes in the orthorhombic system with typical unit cell parameters $a = 2.876 \text{ \AA}$, $b = 12.24 \text{ \AA}$ and $c = 3.709 \text{ \AA}$ (JCPDS file # 01-088-2112). It is a layered structure involving layers stacked along the b -axis and these layers interact by hydrogen bonds via their external OH groups: the (010) crystal face stands as the most likely to be exposed on the surface of boehmite crystals and to interact with the surroundings via their Al-OH surface sites [42]. The boehmite crystalline structure has been drawn (CaRIne Crystallography 3.1 software) in **Figure 10**. The illustrated (010) face exhibits a surface area of $a \times c \cong 10.67 \text{ \AA}^2$ and counts $1 + 2 \times \frac{1}{2} = 2$ Al “surface” atoms (2 Al atoms shown being shared in half with the adjacent unit cells). On the other hand, cuprite crystallizes in a cubic structure with $a = 4.26 \text{ \AA}$ (JCPDS file # 03-065-3288) and each face is equivalent in terms of Cu atom exposure, counting $1 + 4 \times \frac{1}{4} = 2$ Cu “surface” atoms in a surface area of $a^2 \cong 18.15 \text{ \AA}^2$ (see **Figure 10**).

Combining these data leads to densities of “surface” metal ions of $2 / 10.67 = 0.187_5$ Al surface atoms/ \AA^2 for boehmite and $2 / 18.15 = 0.110_2$ Cu surface atoms/ \AA^2 for cuprite. Converting these numbers in m^2 and in moles of metal surface atoms by introducing the Avogadro number, and considering the above reminded ΔH_R values measured per m^2 when contacted with DETA, this leads to enthalpies of reaction with this amine of respectively $\Delta H_{R,Al} \cong -10 \pm 1 \text{ kJ/mole}$ of surface Al for boehmited Al and $\Delta H_{R,Cu} \cong -2066 \pm 400 \text{ kJ/mole}$ of surface Cu for oxidized Cu. Despite the non-negligible uncertainty on this latter value, these calculations, averaged for one single surface metal ion, strongly suggest that amine interaction with copper metallic centers is significantly more energetic (accompanied by a greater exothermic effect) than on aluminum. This allows ranking the metals according to their reactivity toward the amine. Care should, on the other hand, be taken when trying to compare these absolute values to usual values obtained for example in the case of the physisorption or chemisorption of molecular species on a solid surface. Indeed, the more the metal will be reactive, the more its surface will be “dissolved” by the amine for chelate formation. Thus, the more the metal is reactive, the larger the number of metal ions that will be involved in the reaction and corresponding enthalpy value (i.e. ions corresponding also to the involvement of subsurface metal ions becoming available for interaction with the amine). However, these $\Delta H_{R,M}$ values (with metal “M”) calculated by considering only the first row of surface metal ions can be seen as a “relative reactivity parameter” allowing to rank the metals among themselves, relatively to their interaction with the amine.

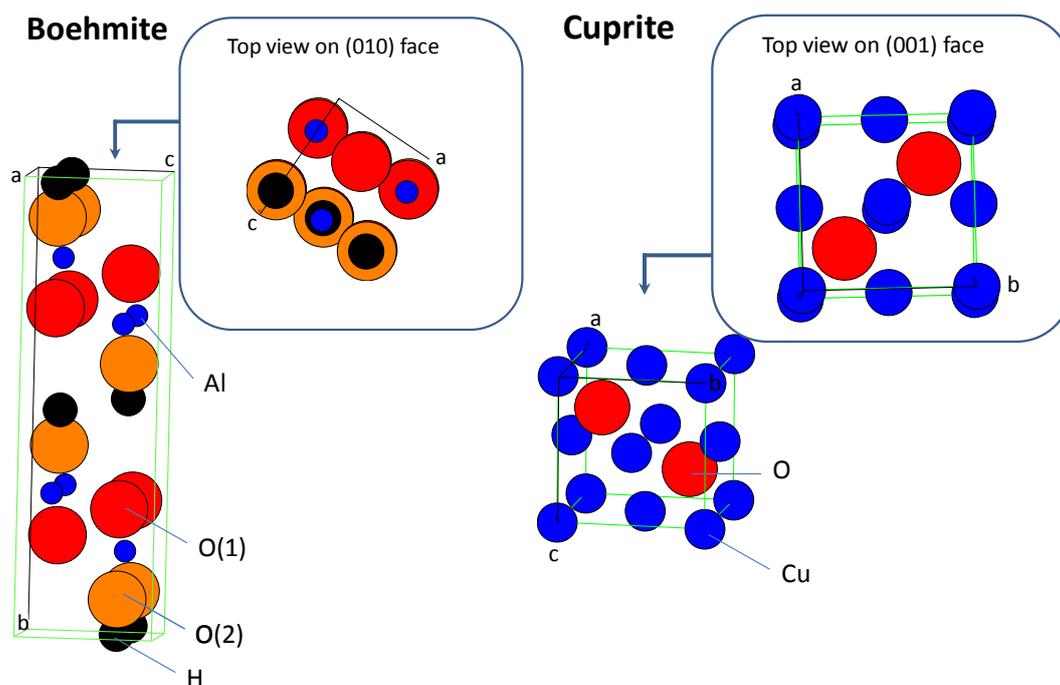


Figure 10: Crystallographic structures of boehmite and cuprite

Considering these data and the chelation step involved in the above-discussed mechanism (see **Figure 9**), it is then interesting to compare the chelation power and/or chelate stability in the cases of aluminum and copper. Literature data indicate that, for a variety of aminated compounds, copper forms more stable chelates than aluminum [43] and that, generally speaking, copper easily forms complexes including with amines such as ethylene diamine (DAE) and DETA [44]: these results can be correlated to Meiser *et al.* work [15] who compared the behaviors of Al and Cu after ageing: the Cu layer was strongly corroded during ageing compared to Al. The presence of water during ageing could be comparable to our surface treatment in boiling water. Even if our drying treatment (80°C) avoids any water physisorption, we can imagine that our surface hydroxide layer could be equivalent to the ageing in Meiser *et al.* [15] work, leading to important metal corrosion and diffusion of Cu compared to Al. The more energetic trend found in the present work for Cu over Al may, in our opinion, be reasonably linked to these different chelation powers, allowing correspondingly easier surface interaction in the (poly)amine-metal system. Future works will be dedicated to enlarging this study with other metals exhibiting diverse chelation powers toward amines.

4. Conclusion

In this paper, we report the first direct investigation by *in situ* mixing calorimetry of amine-metal reactions involved in any amine-metal-containing system. The linearity domain of the ΔH_R versus mass of metal powder allowed us to confirm the non-limitation of amine diffusion in our setup, and thus to compare the averaged enthalpy effect per m^2 as well as per mole of surface metal ion. Copper is shown to exhibit a significantly more exothermic reaction with DETA than aluminum, which was quantified and tentatively associated to its greater chelation power. The mechanistic scheme for this metal-amine reaction was discussed based on literature reports and in the light of these new findings. *In situ* mixing calorimetry is therefore an appropriate technique for investigating amine-metal interactions and obtaining quantitative energetic data with the view of better understanding underlying reaction mechanism(s) and draw comparative conclusions about the

relative reactivity of the various metals used in applicative fields involving epoxy-amine networks as in adhesives and sealants, coatings and paints.

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