

Wetting kinetics and oxidation-induced passivation of copper-nickel and copper-chromium alloys on aluminium oxide substrates

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ABSTRACT

This study examines the wettability and wetting kinetics of Cu-Ni and Cu-Cr alloys on Al₂O₃ substrates using the sessile drop method under high-vacuum and inert-gas conditions. Understanding metal-ceramic wetting behavior is crucial for designing reliable joining processes and metal-ceramic composites based on copper alloys and alumina. Contact angle measurements were performed for Cu-Ni and Cu-Cr alloys using a contact heating approach, complemented by a modified capillary extrusion technique for highly oxidizable alloys. Time-dependent evolution of the contact angle was analyzed to assess wetting kinetics and interfacial stability. The results show that both Cu-Ni and Cu-Cr alloys exhibit poor wettability toward Al₂O₃, with contact angles remaining in the non-wetting regime (>120°) throughout the experiments. Nickel additions did not improve wettability relative to pure copper, and the contact angle remained essentially constant during the holding time. In the case of the Cu-Cr alloy, severe oxidation resulted in the formation of a stable oxide shell, which prevented the use of conventional sessile drop measurements. Although capillary extrusion enabled droplet deposition at the experimental temperature, rapid passivation limited effective wetting, resulting in asymmetric wetting kinetics. These conclusions demonstrate that alloying copper with Ni or Cr alone is insufficient to promote wetting on alumina under the applied conditions. The study offers valuable insights into the kinetic limitations of Cu-based alloy wetting and highlights the critical role of oxide chemistry and experimental methodology in characterizing metal-ceramic interfaces.

Keywords: wettability, wetting kinetics, sessile drop method, Cu-based alloys, Al₂O₃ substrate.

INTRODUCTION

Wetting phenomena at metal-ceramic interfaces play a decisive role in the fabrication and performance of metal-ceramic composites, brazed joints, and electronic packaging systems [1–2]. In particular, the interaction between molten metals or alloys and oxide ceramics governs interfacial bonding, microstructural evolution, and the resulting mechanical and functional properties of the joined or composite materials [3–4].

Among oxide ceramics, alumina remains one of the most widely used substrates due to its high thermal stability, chemical inertness, electrical insulation, and constructive mechanical properties [5–8]. However, its inherently poor wettability by most molten metals presents a persistent challenge in achieving strong and reliable metal-ceramic interfaces [9].

Copper-based alloys are of considerable technological importance owing to their high electrical and thermal conductivity, corrosion

resistance, and widespread use in electronic, thermal management, and structural applications [10–13]. Alloying copper with transition metals such as nickel or chromium is a well-established strategy to tailor its mechanical strength, oxidation resistance, and interfacial reactivity [14]. Cu-Ni alloys are renowned for their exceptional corrosion resistance and thermodynamic stability across a wide range of compositions [12, 14–16]. In contrast, Cu-Cr alloys offer enhanced high-temperature strength and oxidation resistance due to chromium's strong affinity for oxygen. These characteristics make both alloy systems attractive candidates for joining and composite applications involving ceramic substrates, particularly those made of alumina.

Despite their technological relevance, the wetting behavior of Cu-Ni and Cu-Cr alloys on Al_2O_3 substrates remains largely unexplored, particularly with regard to the kinetics of wetting and the mechanisms governing interfacial spreading and adhesion. Wettability is commonly quantified by the equilibrium contact angle formed between a liquid metal droplet and a solid substrate [17–21]. However, the dynamic evolution of the contact angle and triple-line motion provides critical insight into the underlying physicochemical processes [22–23]. These include surface tension-driven spreading, dissolution precipitation phenomena, interfacial reactions, adsorption of alloying elements, and the possible formation of reaction layers or interfacial compounds.

The sessile drop method is one of the most widely employed experimental techniques for investigating wetting phenomena at high temperatures [24–26]. Its advantages include direct observation of droplet shape evolution, precise control of temperature and atmosphere, and the ability to extract both equilibrium wettability parameters and time-dependent wetting kinetics. When combined with high-speed imaging and image analysis, the sessile drop technique enables detailed characterization of spreading behavior, contact angle relaxation, and transient interfacial phenomena. This approach is particularly valuable for multi-component alloys, where selective oxidation or segregation of alloying elements can significantly influence wetting behavior.

In the case of Cu-based alloys on Al_2O_3 , alloying additions such as Ni and Cr are expected to modify wetting behavior through distinct mechanisms. Nickel, which exhibits limited affinity for oxygen compared to chromium, may influence

wetting primarily through changes in surface tension and interfacial energy [27–29]. In contrast, chromium's strong affinity for oxygen may promote interfacial reactions, local reduction of the ceramic surface, or the formation of chromium oxide phases, thereby altering both the thermodynamics and kinetics of wetting [30]. Understanding these effects requires not only equilibrium contact angle measurements but also a systematic analysis of wetting kinetics as a function of time and temperature.

The characteristics of the starting powders play a crucial role in determining the microstructure and properties of metallic materials produced by powder-based technologies. Particle morphology, size distribution, surface development, and the presence of oxide films influence powder packing, consolidation behavior, diffusion processes, and the homogeneity of the final material. Previous studies have demonstrated that powder characteristics significantly affect the microstructural development and performance of metallic systems, including thermally sprayed coatings containing hard phases and powders of different particle sizes. In particular, the use of powders with tailored morphology and particle-size distributions has been shown to influence coating density, porosity, mechanical properties, and resistance to degradation phenomena [31]. Furthermore, the comparison of micro- and nano-sized powders revealed that powder morphology and surface condition can strongly affect the final properties of the processed material [32]. Therefore, characterization of the starting powders constitutes an important step in understanding the behavior of powder-derived Cu-based alloys and their interactions with ceramic substrates.

The present study aims to investigate the wettability and wetting kinetics of Cu-Ni and Cu-Cr alloys on Al_2O_3 substrates using the sessile drop method under controlled high-temperature conditions. Particular emphasis is placed on the time-dependent evolution of the contact angle and spreading behavior, allowing for a comparative assessment of the influence of alloy chemistry on interfacial phenomena. By correlating wetting kinetics with alloy composition and potential interfacial reactions, this work seeks to provide a deeper understanding of metal-ceramic interactions in Cu-based alloy systems, thereby contributing to the optimization of joining processes and composite fabrication involving alumina substrates. Unlike the majority of previous studies on

Cu-based alloy wetting on Al_2O_3 , which primarily report equilibrium contact angle values as a measure of wettability, the present work explicitly focuses on the kinetics of wetting and the time-dependent evolution of the metal-ceramic interface. The central novelty of this study lies in shifting the emphasis from static wettability assessment toward a dynamic, process-oriented interpretation of wetting behavior, which is more representative of real high-temperature joining and composite fabrication conditions. In this context, the work demonstrates that equilibrium contact angles alone are insufficient to describe wetting phenomena in Cu-Ni and Cu-Cr alloy systems. Although both alloys ultimately remain in the non-wetting regime, their interfacial behavior is governed by distinct kinetic pathways. For the Cu-Ni alloy, the contact angle stabilizes rapidly after melting, indicating a kinetically arrested system with negligible interfacial evolution over time.

In contrast, the Cu-Cr alloy exhibits strongly time-dependent behavior dominated by rapid oxidation and passivation, which fundamentally alters the wetting process and prevents the establishment of a stable liquid-solid equilibrium. A further novel aspect of this study is the experimental identification and documentation of kinetic barriers such as oxide-shell formation, triple-line pinning, and asymmetric contact angle evolution that preclude the use of conventional sessile drop analysis. By employing a modified capillary extrusion technique, the work captures the initial transient wetting response of the Cu-Cr

alloy, providing rare insight into the early-stage kinetics of a highly reactive copper-based system. This approach allows the separation of intrinsic wetting tendencies from secondary effects associated with surface passivation. The present results demonstrate that alloying copper with Ni or Cr not only fails to improve equilibrium wettability on Al_2O_3 but also, more fundamentally, imposes kinetic constraints that suppress wetting from the earliest stages of liquid-solid contact. By explicitly addressing wetting as a kinetic process rather than a static outcome, this study provides a new framework for interpreting metal-ceramic interactions in Cu-based systems. It highlights the critical role of time-dependent interfacial phenomena in determining practical wetting behavior.

MATERIALS AND METHODS

Contact angle measurements provide information about possible interactions between components in a composite. Good wettability ensures better interfacial bonding, which influences the properties of the material obtained during the forming process [33]. Contact angle measurements were performed between the metallic phase and the Al_2O_3 ceramic for the following two series: Series I, a Cu-Ni alloy containing 80 vol% Cu and 20 vol% Ni, and Series II, a Cu-Cr alloy containing 95 vol% Cu and 5 vol% Cr. A photo of the materials used for the experiment is shown in Figure 1.

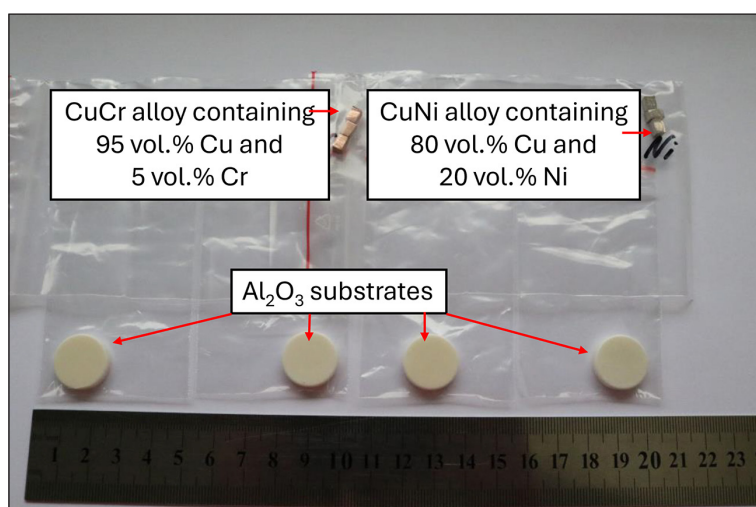


Figure 1. Photo of materials used for wettability investigations. Polished Al_2O_3 substrates and powder-metallurgy-derived Cu-Ni (80 vol.% Cu-20 vol.% Ni) and Cu-Cr (95 vol.% Cu-5 vol.% Cr) alloy specimens were employed in sessile-drop experiments. The alloys were prepared from elemental powders, sintered, and subsequently subjected to plastic deformation prior to contact-angle measurements

The alloy compositions investigated in this study were originally defined in terms of volume fraction (vol.%) because the materials were prepared by powder metallurgy from mechanically mixed elemental powders. In powder-processing routes, volume fraction is often a more relevant parameter than weight fraction, as it directly reflects the relative volume occupied by each constituent in the compact and influences particle packing, densification behavior, and the resulting microstructure. Furthermore, the objective of the present work was to evaluate the effect of alloy composition on wettability using alloys produced from predetermined powder-volume ratios. Nevertheless, for completeness and to facilitate comparison with the broader metallurgical literature, the corresponding weight-percent (wt.%) and atomic-percent (at.%) compositions are provided in Table 1.

The conversion from volume fraction to weight fraction was performed using the theoretical densities of the constituent elements ($\rho_{\text{Cu}} = 8.96 \text{ g/cm}^3$, $\rho_{\text{Ni}} = 8.90 \text{ g/cm}^3$, and $\rho_{\text{Cr}} = 7.19 \text{ g/cm}^3$). Atomic fractions were subsequently calculated from the corresponding elemental masses and atomic weights. As expected, the Cu-Ni alloy exhibits only minor differences between vol.% and wt.% because copper and nickel possess similar densities. In contrast, the lower density of chromium results in a slightly lower chromium content when expressed in weight percent compared with volume percent. The atomic-percent values remain close to the nominal compositions due to the relatively similar atomic masses of the constituent elements.

The alloys were made using powder metallurgy. Photos of the starting powders used to prepare the alloys are shown in Figure 2. The morphology of the starting metallic powders used for alloy preparation is presented in Figure 2. The copper powder (Figure 2a) consists predominantly of irregularly shaped particles with rough surfaces and angular contours, characteristic of water-atomized metallic powders. Such morphology is beneficial for mechanical interlocking during compaction and promotes efficient densification during sintering. The chromium powder (Figure 2b) exhibits a highly

irregular morphology with angular and fractured particles of various sizes, reflecting the brittle nature of chromium and its comminution-based production route. The increased surface roughness and particle angularity may contribute to enhanced mechanical bonding between particles during consolidation, but also increase susceptibility to surface oxidation.

In contrast, the nickel powder (Figure 2c) is composed of relatively fine particles with a dendritic and spongy morphology, resulting in a high specific surface area. This characteristic morphology is typical of electrolytically produced nickel powders and facilitates particle bonding during sintering. The observed differences in particle shape, size distribution, and surface development among the powders are expected to influence powder packing behavior, densification kinetics, and ultimately the microstructural homogeneity of the Cu-Ni and Cu-Cr alloys prepared for wettability investigations.

The powders were mixed in appropriate proportions, pressed, and heated at 950 °C for 5 hours. The sintered were plastically deformed (pressed) by approximately 20% and then heated again at 950 °C for 1 hour. Finally, they were plastically deformed to a height of approximately 5.3 mm, i.e., by approximately 15%. The sample surfaces were mechanically cleaned of any oxides and other contaminants immediately prior to measurement. Cylindrical Al_2O_3 samples were used as substrates and were previously polished. In the present study, the substrates were dense Al_2O_3 plates that were subjected to a standard metallographic polishing procedure prior to use, consisting of sequential grinding with SiC abrasive papers followed by polishing with diamond suspensions down to 1 μm to obtain a mirror-like surface finish. No additional surface modification was applied before the experiments. Direct profilometric measurements of R_a were not performed in this work; however, based on the applied polishing protocol and values reported in the literature for similarly prepared alumina surfaces, the resulting roughness is expected to be in the sub-micrometer to low-nanometer range (typically $R_a \approx 10\text{-}100 \text{ nm}$ for mirror-polished

Table 1. Nominal compositions of the investigated alloys are expressed in volume, weight, and atomic fractions

Alloy	Composition (vol.%)	Composition (wt.%)	Composition (at.%)
Cu-Ni	80 Cu - 20 Ni	80.1 Cu - 19.9 Ni	78.8 Cu - 21.2 Ni
Cu-Cr	95 Cu - 5 Cr	95.9 Cu - 4.1 Cr	95.1 Cu - 4.9 Cr

Al_2O_3). Importantly, all experiments were conducted on substrates prepared using an identical polishing procedure, ensuring consistency across all measurements and minimizing variability arising from surface topography.

It should be noted that quantitative measurements of oxygen content in the starting powders were not performed prior to alloy preparation. Nevertheless, both copper- and chromium-containing powders are known to develop thin oxide films during powder production, handling, storage, and consolidation processes. Although the alloy surfaces were mechanically cleaned immediately before wettability testing, oxygen incorporated within the powder particles or present as residual oxide inclusions may remain within the bulk material. During heating to the experimental temperature, this internally stored oxygen can become mobile and participate in oxidation reactions, particularly in the case of chromium-containing alloys, due to the exceptionally high oxygen affinity of chromium. Consequently, the oxidation phenomena observed during the experiments are likely influenced not only by residual oxygen in the testing atmosphere but also by oxygen originating from the initial powder feedstock and processing history. Future studies will include direct oxygen-content measurements to establish a quantitative correlation between internal oxidation and wetting behavior.

Wetting kinetics studies were conducted using the sessile drop method using the contact heating procedure. The procedure involves heating both the Cu-Ni or Cu-Cr alloy sample and the Al_2O_3 substrate to the experimental temperature, holding them at this temperature for a defined period, and subsequently cooling the system. The alloy and substrate remain in constant contact throughout the entire cycle. During the study, images of the test object, the alloy sample placed on a ceramic substrate, were recorded. The recorded images are used to assess changes in the contact angle (θ) as a function of exposure time. The following test procedure was used during the experiment. In the first step, samples from Series I (Cu-Ni/ Al_2O_3) were placed in the device's working chamber, followed by samples from Series II (Cu-Cr/ Al_2O_3). A high vacuum was then achieved using a pump system. In the next step, an inert gas (argon) was introduced into the working chamber. The argon was introduced after reaching a vacuum level of approximately 10^{-6} mbar at room temperature, prior to the heating stage.

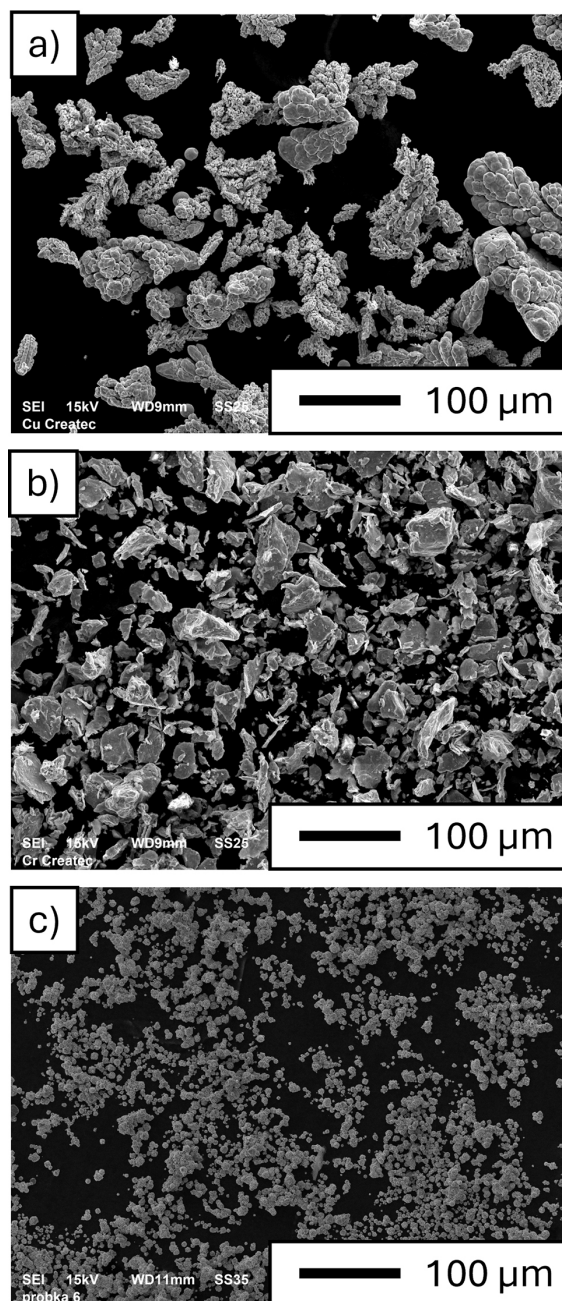


Figure 2. Scanning electron microscopy (SEM) images of the starting metallic powders used for alloy preparation: a) Cu powder exhibiting irregular, angular particles characteristic of water atomization; b) Cr powder composed of fractured particles with pronounced angular morphology resulting from comminution processes; and c) Ni powder showing a dendritic, sponge-like morphology typical of electrolytic production

Heating began at a rate of $15\text{ }^{\circ}\text{C}/\text{min}$ to a temperature above $1200\text{ }^{\circ}\text{C}$ (until the alloy melted and a drop of liquid metal was obtained). The formed drop of liquid metal was then held in contact with the Al_2O_3 substrate for 10 minutes and

subsequently cooled slowly to ambient temperature at a rate of 7 °C/min. During the wetting and spreading kinetics studies (from room temperature through heating and cooling after the tests), the following parameters were recorded: pressure in the test chamber, temperature on the test table, and geometric parameters of the tested samples. Images of the alloy sample on the tested substrate were recorded with a digital camera at 100 frames per second. The obtained images were computer processed to calculate the contact angle using ASTRA software, developed by CNR-Istituto per l'Energetica e le Interfasi U.T. di Genova, Italy.

For the Cu-Cr alloy, conventional sessile-drop measurements proved impractical because the formation of a chromium-rich oxide shell prevented spontaneous droplet formation during heating. To overcome this limitation, a modified capillary-extrusion procedure was employed. In this configuration, the Cu-Cr alloy specimen was placed inside a ceramic capillary positioned vertically above the polished Al_2O_3 substrate. After heating to the experimental temperature (1260 °C), where the alloy was fully molten, a controlled mechanical displacement was applied to force a small volume of liquid alloy through the capillary outlet directly onto the substrate surface. The extrusion process locally disrupted the oxide layer surrounding the molten alloy and enabled fresh liquid metal to contact the ceramic surface. Contact-angle measurements were initiated immediately after droplet deposition. The capillary was positioned sufficiently close to the substrate to minimize droplet free-fall and impact effects, thereby ensuring that the measured droplet geometry was governed primarily by wetting phenomena rather than by hydrodynamic deformation. The method was intended to provide access to the earliest stages of metal-ceramic interaction before extensive reformation of the oxide shell occurred. Although rapid passivation could not be completely prevented, the capillary-extrusion approach allowed reproducible deposition of molten Cu-Cr droplets. It enabled qualitative assessment of the initial wetting kinetics that could not be obtained using the conventional contact-heating sessile-drop configuration.

RESULTS AND DISCUSSION

The wettability of the Al_2O_3 -Cu system has been extensively described in the literature. The contact angle values obtained for copper on an

Al_2O_3 substrate are influenced by several factors, including experimental temperature, atmosphere, contact duration, and the nature of the substrate surface [34]. However, based on an analysis of the literature data, the contact angle for the Cu/ Al_2O_3 system is in the range of 120–160° [33–35]. The measured contact angle values indicate that pure copper is completely non-wetting toward alumina.

The primary objective of the measurements conducted in this study was to determine whether the addition of a second metal to copper could enhance the wettability of the alloy formed upon contact with Al_2O_3 ceramics. The composition of the alloys to be tested was selected to reflect the solid solutions that can form as a result of metal contact with liquid copper during the sintering process.

Based on the conducted study, it was found that for the Cu-Ni alloy, a complete droplet shape was obtained after heating to 1220°C. Examples of the recorded droplet images for the Series I samples (Cu-Ni alloy / Al_2O_3 substrate) are shown in Figure 3.

It can be seen that the Cu-Ni alloy does not wet the Al_2O_3 substrate surface. The initially calculated contact angle is ~140° (its value did not change significantly during the 10-minute hold at the test temperature – Figure 4). The lack of wettability in the system also translates into very low adhesion strength. The droplet had virtually no adhesion to the substrate and “spontaneously” fell off after cooling to ambient temperature. It is also worth noting the presence of impurities on the droplet surface. These are likely primary oxides that “escaped” to the surface after the alloy was melted (Figure 3).

The experimental results clearly demonstrate that the addition of nickel to copper does not lead to any measurable improvement in wettability toward Al_2O_3 , as evidenced by persistently high contact angle values and the absence of time-dependent spreading. This behavior can be rationalized by considering the combined effects of thermodynamic driving forces, interfacial chemistry, and wetting kinetics. From a thermodynamic perspective, effective wetting of a ceramic substrate by a molten metal requires a reduction in the solid-liquid interfacial energy, often facilitated by interfacial reactions or strong chemical affinity between the liquid metal and the ceramic surface [36–38]. Nickel, however, exhibits a relatively low affinity for oxygen compared to classical active elements such as Ti, Zr, or Cr [39–41].

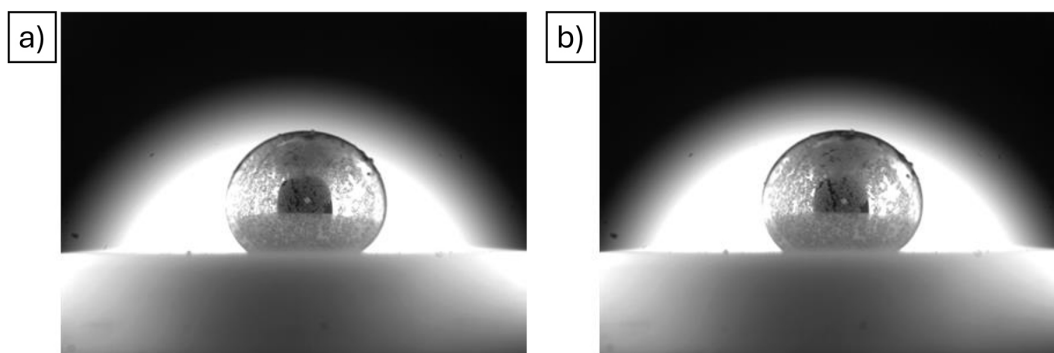


Figure 3. Representative images of a molten Cu-Ni alloy droplet on an Al_2O_3 substrate during sessile-drop testing at 1220 °C: a) immediately after complete melting and droplet formation, and b) after 10 min of isothermal holding. The droplet maintains a nearly spherical geometry throughout the experiment, indicating limited spreading and persistent non-wetting behavior. Surface irregularities visible on the droplet are attributed to oxide inclusions transported to the surface during melting

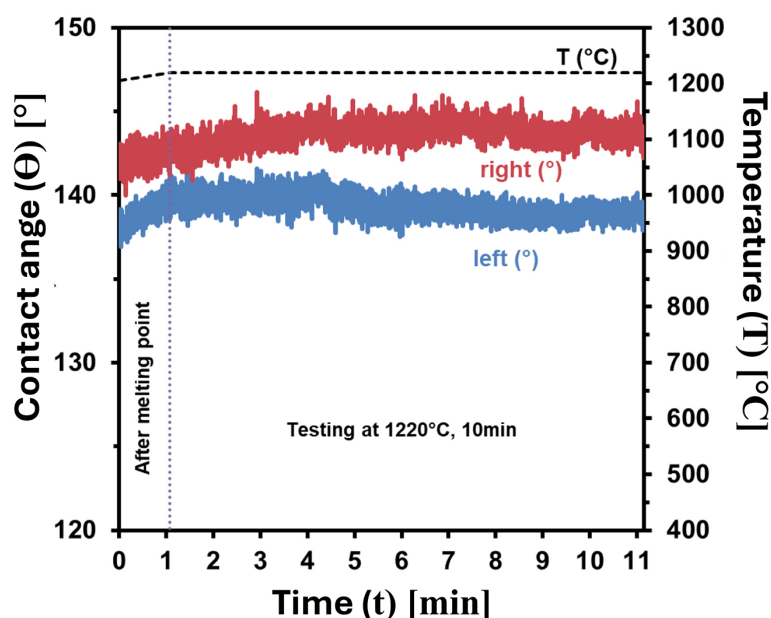


Figure 4. Evolution of the contact angle as a function of holding time for the Cu-Ni/ Al_2O_3 system at 1220 °C. The contact angle remains approximately constant at $\sim 140^\circ$ throughout the 10 min experiment, indicating the absence of significant spreading, interfacial reactions, or time-dependent wetting enhancement. The results confirm that Ni addition does not improve the wettability of copper on alumina under the investigated conditions

As a result, Ni does not promote the chemical reduction of the Al_2O_3 surface, nor does it form stable reaction products (e.g., spinels or interfacial oxides) that could lower the interfacial energy [42–43]. Consequently, the solid-liquid interfacial energy in the Cu-Ni/ Al_2O_3 system remains comparable to that of pure Cu/ Al_2O_3 , leading to similarly poor wettability [44–46].

Additionally, nickel is fully soluble in liquid copper over a wide compositional range, forming a homogeneous metallic solution [47–48]. This complete solubility prevents preferential segregation of Ni to the metal-ceramic interface, which

would otherwise be necessary to modify interfacial chemistry. While Ni addition can slightly modify the surface tension of molten copper, these changes are insufficient to overcome the high interfacial energy between the metallic melt and the Al_2O_3 substrate. Any reduction in liquid vapor surface tension due to alloying is effectively counterbalanced by the unchanged solid-liquid interfacial interactions, resulting in negligible net improvement in contact angle [49]. The rapid stabilization of the contact angle observed for the Cu-Ni alloy indicates that the wetting process becomes kinetically arrested shortly after

the alloy melts [50]. The absence of progressive spreading suggests that no time-dependent interfacial reactions or adsorption processes occur during the holding period.

Furthermore, the presence of residual surface oxides, even under high-vacuum and inert gas conditions, may further inhibit wetting by acting as a diffusion barrier and promoting triple-line pinning. Nickel does not actively disrupt or reduce these oxides and therefore cannot facilitate kinetic wetting enhancement. Taken together, these factors indicate that Ni acts as a non-active alloying element with respect to Al_2O_3 wettability. Its role is limited to modifying bulk alloy properties rather than interfacial chemistry. The present findings confirm that alloying copper with nickel alone is insufficient to alter either the thermodynamic driving force or the kinetic pathway of wetting on alumina. This result underscores the necessity of incorporating chemically active elements or controlling oxygen activity when designing Cu-based alloys for metal-ceramic joining applications.

Next, the focus was on Series II testing. In the case of the second alloy (Cu-Cr) (Series II), the strong oxidation of the alloy surface due to the presence of primary oxides did not allow for the formation of the droplet shape necessary to calculate the wettability angle (even after heating to $T = 1273^\circ\text{C}$). It should be emphasized that before testing, all surfaces of the alloy samples were mechanically cleaned (grinding on sandpaper followed by rinsing in isopropanol); hence, the primary source of oxygen forming the oxide “shell”

is internal oxidation of the material (e.g., resulting from powder oxidation during sintering).

Evidence that the alloy had liquefied is the presence of a small droplet (on the right side of the sample in the photos - Figure 5), which formed at a discontinuity in the “shell” at a temperature of approximately 1080°C . According to the Cu-5Cr phase equilibrium system, this temperature corresponds to the eutectic transition upon heating: $\text{Cu} + \text{Cr} = \text{L}$ ($T = 1076^\circ\text{C}$). However, even a relatively strong overheating of the material did not allow for thermal destabilization of the outer “shell” and thus did not enable the collection of data for calculating wetting kinetics.

The experiment reveals that chromium oxidation dominates the interfacial behavior of the Cu-Cr alloy, even under high-vacuum and inert-gas conditions, which is a critical finding of the present study. This behavior can be explained by the exceptional oxygen affinity of chromium, combined with kinetic and microstructural factors inherent to Cu-Cr systems. This behavior highlights the limitations of atmosphere control alone in suppressing oxidation-driven phenomena during high-temperature wetting experiments.

From a thermodynamic standpoint, chromium exhibits one of the strongest affinities for oxygen among transition metals commonly alloyed with copper. The Gibbs free energy of formation of chromium oxides (Cr_2O_3 , CrO) is significantly more negative than that of copper oxides across the entire temperature range investigated [52–54]. Consequently, even at extremely low oxygen partial pressures well below those typically

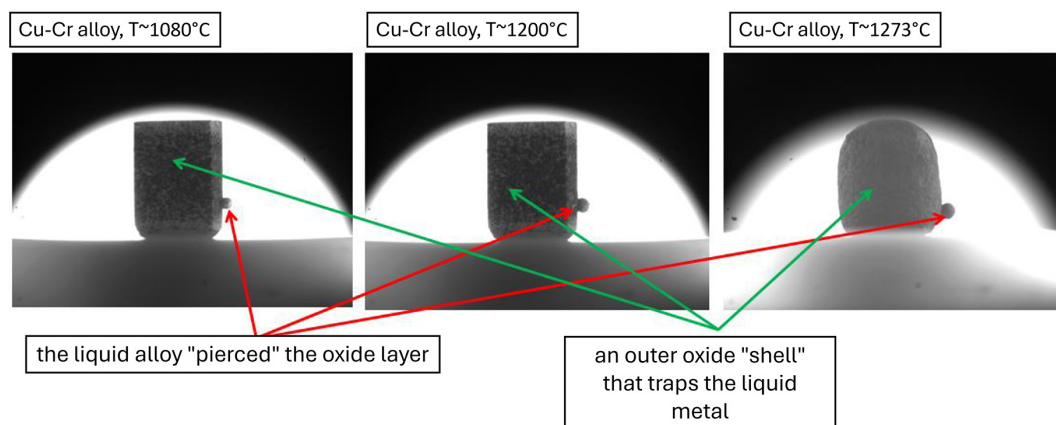


Figure 5. Sequential images recorded during attempted sessile-drop measurements for the Cu-Cr/ Al_2O_3 system.

Despite heating above the alloy melting temperature, the formation of a stable droplet is prevented by the development of a rigid chromium-rich oxide shell. Localized liquid extrusion through discontinuities in the oxide layer provides evidence of melting, while the overall sample geometry remains constrained by oxidation-induced passivation

achievable in high-vacuum or argon-purged environments, chromium oxidation remains thermodynamically favorable. Trace amounts of oxygen originating from residual gases, chamber walls, or desorption from system components are therefore sufficient to trigger chromium oxidation.

A simple thermodynamic estimate further illustrates why chromium oxidation is unavoidable under the present experimental conditions. Considering the oxidation reaction $3\text{Cr} + 3/2\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3$, the standard Gibbs free energy of formation of Cr_2O_3 at temperatures close to the experimental range (approximately 1250–1300 °C) remains strongly negative, typically on the order of -500 to -600 kJ/mol O_2 [52–54]. Using the equilibrium condition $\Delta G = RT \ln(p\text{O}_2, \text{eq3/2})$, the corresponding equilibrium oxygen partial pressure required to suppress Cr oxidation is extremely low, typically in the range of 10^{-18} – 10^{-20} atm. This value is several orders of magnitude lower than the residual oxygen activity commonly encountered even in high-vacuum systems backfilled with high-purity argon. Consequently, chromium oxidation remains thermodynamically favored throughout the experiment. The calculation demonstrates that only trace quantities of oxygen, originating either from residual gases in the chamber or from oxygen stored within the powder-derived alloy itself, are sufficient to promote the formation of chromium-rich oxide layers. Therefore, the observed oxide-shell formation and associated kinetic arrest should be regarded as an intrinsic consequence of the thermodynamic stability of chromium oxides rather than as a result of insufficient atmosphere control.

A more detailed thermodynamic analysis helps explain why chromium does not promote reactive wetting of Al_2O_3 under the present conditions despite its strong oxygen affinity. In principle, a reactive alloying element can improve wetting when it participates in interfacial redox reactions that reduce the ceramic surface or form a thin reaction layer at the metal-ceramic interface. For the Cu-Cr/ Al_2O_3 system, however, the dominant thermodynamic driving force is not interaction with alumina but rather the preferential oxidation of chromium itself. At the experimental temperature (~1260 °C), the standard Gibbs free energy of formation of Cr_2O_3 remains substantially more negative than that of copper oxides and is also more negative than that associated with any reduction of Al_2O_3 by chromium. Consequently, chromium preferentially consumes available

oxygen according to: $4\text{Cr} + 3\text{O}_2 \rightarrow 2\text{Cr}_2\text{O}_3$ rather than participating in interfacial reactions with the ceramic substrate. Furthermore, because Al_2O_3 is thermodynamically more stable than chromium-containing spinel or mixed oxide phases under the present oxygen activities, there is no significant driving force for extensive reduction of the alumina surface. Instead, oxygen originating from residual atmosphere, adsorbed species, or internally stored oxides within the powder-derived alloy is scavenged by chromium, leading to rapid formation of a dense Cr_2O_3 layer. Thus, the competitive redox balance strongly favors chromium oxidation over chromium-mediated modification of the Al_2O_3 interface. The consequence is a transition from the initially expected reactive behavior to oxidation-induced passivation, whereby the thermodynamically stable Cr_2O_3 scale isolates the liquid alloy from the substrate and suppresses further interfacial evolution.

During alloy preparation, powder handling, sintering, or storage, chromium-containing alloys readily absorb oxygen, which becomes incorporated as dissolved oxygen or fine oxide inclusions. Upon heating above the solidus temperature, this oxygen becomes highly mobile and diffuses toward the alloy surface, where it preferentially reacts with chromium due to its superior affinity for oxygen. This process leads to the formation of a continuous or semi-continuous chromium-rich oxide shell, even in environments nominally free of oxygen. Chromium tends to segregate toward surfaces and interfaces during heating due to its lower solubility in copper compared to nickel, and its tendency to form chromium-rich regions [55–57]. Once a thin chromium oxide layer forms, it rapidly thickens due to fast outward diffusion of chromium cations and inward diffusion of oxygen anions, resulting in a mechanically stable and adherent oxide shell [58]. The formation of this oxide layer has profound consequences for wetting behavior. The oxide shell acts as a diffusion barrier, isolating the molten metal from the Al_2O_3 substrate and suppressing direct metal-ceramic contact, thereby preventing interfacial reactions that could otherwise promote wetting. Moreover, the rigid oxide shell constrains droplet deformation, inhibits triple-line motion, and leads to asymmetric contact angle evolution. These effects fundamentally alter the wetting kinetics, rendering conventional sessile drop analysis ineffective.

The inability of inert-gas or vacuum environments to prevent chromium oxidation highlights

a key mechanistic insight: oxidation in Cu-Cr systems is not solely governed by external oxygen partial pressure, but is strongly controlled by internal oxygen transport and chromium surface activity. This finding explains why even significant overheating fails to destabilize the oxide shell and why wetting remains kinetically suppressed throughout the experiment. The dominance of chromium oxidation in the Cu-Cr/ Al_2O_3 system reflects an intrinsic materials limitation rather than an experimental artifact. The present results demonstrate that, without deliberate control of oxygen activity, such as through the use of getter materials, reactive atmospheres, or alternative alloying strategies, chromium-containing copper alloys will inherently favor oxidation-driven passivation over interfacial wetting. This insight is essential for the rational design of Cu-based alloys intended for metal-ceramic joining and high-temperature interfacial applications.

Due to the fact that measurements using the sessile drop method for the Cu-Cr alloy (Series II) were unsuccessful, a modification of this method was employed in the next step for the measurement. A Cu-Cr alloy droplet was deposited on a molten substrate by extrusion from a ceramic capillary. Figure 6 presents sample images of the extruded droplet on the substrate at the experimental temperature. As with the nickel alloy, observations conducted for the Cu-Cr alloy/ Al_2O_3 substrate pair revealed a lack of wettability throughout the experiment. Applying the capillary extrusion modification allowed the droplet to be deposited on the substrate at the experimental temperature ($T = 1260^\circ\text{C}$). However, it rapidly passivated, most

likely due to the dissolution of the oxide substrate in the alloy. Therefore, the wetting kinetics graph in Figure 7 shows asymmetry in the contact angle measurements for both sides of the droplet. Immediately after extrusion, a decrease in droplet contact angle can be observed, followed by a subsequent increase as the oxide film forms. Passivation prevents full contact between the alloy and the substrate, thereby preventing corrosion. Therefore, the contact angle α for this system, which ranged from 128° to 138° , was determined based on the droplet geometry at the initial stage of the experiment. After cooling, no separation of the droplet from the substrate was observed, which may indicate a connection between the tested components.

It should be noted that, in the capillary-extrusion configuration, the initial contact angle measured at $t = 0$ s does not correspond to a perfectly oxide-free liquid surface. During extrusion, the mechanically stressed chromium-rich oxide film covering the molten alloy is locally ruptured, allowing liquid metal to emerge from the capillary and establish contact with the Al_2O_3 substrate. This rupture temporarily exposes fresh liquid alloy and enables the acquisition of an initial contact-angle value before extensive repassivation occurs. However, because oxide fragmentation and rupture are not necessarily uniform over the entire droplet surface, the geometry observed immediately after extrusion may still be influenced by residual oxide fragments attached to the liquid metal. Consequently, the contact angle recorded at $t = 0$ s should be interpreted as an apparent initial wetting angle rather than a true equilibrium or oxide-free contact angle. Nevertheless, the very rapid

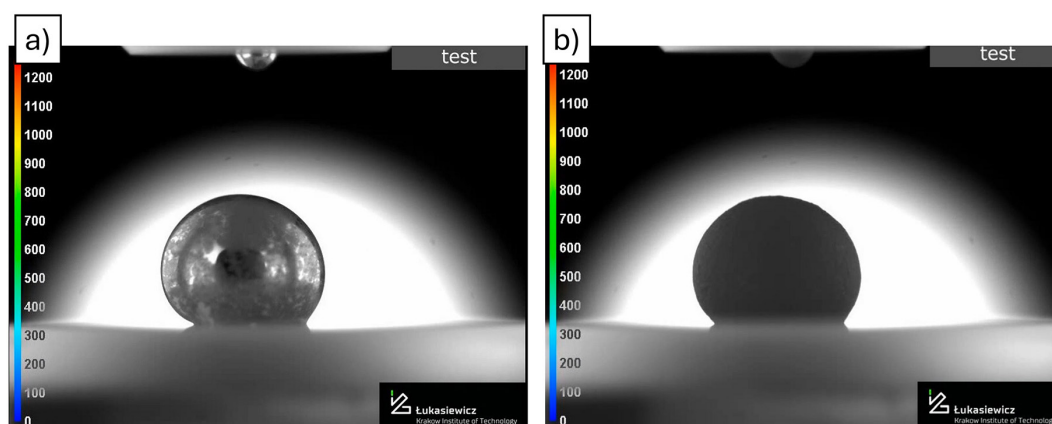


Figure 6. Representative images of a Cu-Cr alloy droplet deposited onto an Al_2O_3 substrate using the capillary-extrusion technique at 1260°C : a) immediately after extrusion from the ceramic capillary and b) after 10 min of holding. However, direct droplet deposition enabled initial contact with the substrate, rapid oxidation and passivation limited spreading, and altered the droplet geometry during the experiment

evolution of the contact angle observed during the first seconds of the experiment demonstrates that oxide reformation occurs almost immediately after extrusion. Therefore, although the absolute value measured at $t = 0$ s may contain a small systematic uncertainty associated with partial oxide retention, it remains representative of the earliest experimentally accessible stage of liquid-metal contact with the substrate and provides a meaningful baseline for assessing the subsequent passivation-controlled wetting kinetics.

Analysis of the obtained results showed that Ni and Cr additions did not improve wettability between the copper-rich metallic phase and the Al_2O_3 substrate. Both the Cu-Ni and Cu-Cr alloys exhibited a complete lack of wettability towards the Al_2O_3 substrate. Despite the use of an inert atmosphere and conducting the measurements in a high-vacuum environment, primary oxides were still present in both alloys after melting. Their presence is likely related to the preparation of the alloys for testing and may have influenced the obtained results. Time is also a factor that can affect the contact angle. Prolonged contact between the alloy and the substrate can improve the wettability of the system. Due to the presence of oxides in the samples, it was decided not to extend the experimental duration in this case. However, the obtained results are consistent with

the available literature. In the work led by H. Matsumoto [59], the addition of nickel to copper did not improve wettability towards the Al_2O_3 substrate. The obtained contact angle values, α , for the experiment conducted at 1150°C for both pure copper and copper with Ni addition, were in the range of 110° to 130° . Their values did not change significantly with increasing holding time.

However, the addition of chromium to copper, as analyzed in the same study, contributed to a lower contact angle value. The contact angle between the alloy and the substrate decreased with increasing chromium content in the alloy and with increasing holding time on the substrate [59]. After 360 min at 1150°C , the α angle for the chromium systems was in the range of 65 – 90° . Unlike Ni, the Cr addition did not dissolve in copper, and chromium-rich regions tended to accumulate at the surface of the Al_2O_3 substrate. According to the research conducted by P. Krystalis' team, the improvement of wetting for the Cu-Cr alloy on an Al_2O_3 substrate is related to the introduction of additional oxygen into the alloy and the adsorption of CrO clusters at the interface of the copper-rich alloy and the alumina substrate [60].

The wetting behavior observed in the present study cannot be adequately explained by classical thermodynamic considerations alone, such as the minimization of equilibrium contact angle based on surface and interfacial energies. Instead, the results demonstrate that oxide chemistry, both at the alloy surface and within the bulk, plays a dominant and often overriding role in determining wetting kinetics and apparent wettability in Cu-based alloy/ Al_2O_3 systems. From a purely thermodynamic standpoint, wetting is governed by the balance of surface energies at the triple-phase junction, as described by Young's equation [61–62]. Alloying additions are often expected to improve wettability by reducing the solid-liquid interfacial energy through chemical interaction or reaction with the ceramic substrate [63–64]. However, such an approach implicitly assumes direct contact between the liquid metal and the ceramic surface, neglecting the influence of surface films and transient interfacial layers. The present results clearly show that this assumption is not valid for Cu-Ni and, in particular, Cu-Cr alloys. Oxide chemistry introduces a fundamentally different controlling mechanism. Even under high-vacuum and inert-gas conditions, thin but chemically stable oxide layers form on the alloy surface. These oxides are not passive bystanders;

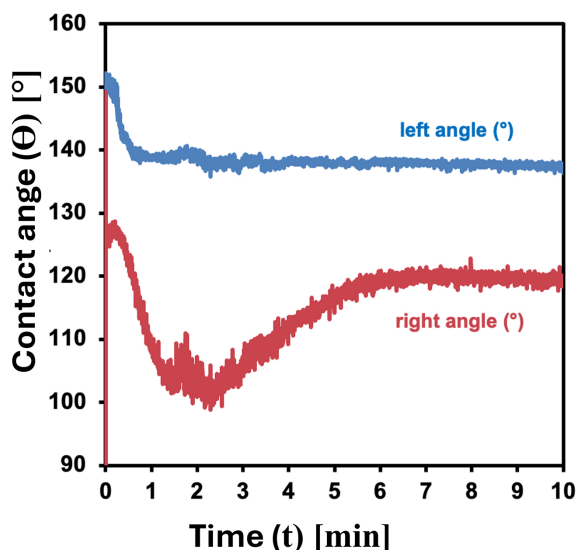


Figure 7. Time-dependent evolution of the left- and right-side contact angles for the Cu-Cr/ Al_2O_3 system measured using the capillary-extrusion technique. The initial contact angle ($t = 0$ s) corresponds to the earliest measurable droplet geometry immediately after mechanical rupture of the oxide shell during extrusion

they actively redefine the interfacial system. Instead of a metal-ceramic interface, the system evolves into an oxide-ceramic interface, whose energetics and kinetics differ substantially from those predicted for metal-ceramic contact. As a result, the effective interfacial energy governing wetting is no longer that of the molten alloy against Al_2O_3 , but that of a complex, often heterogeneous oxide layer against the ceramic substrate. The impact of oxide chemistry is particularly evident in the system's kinetic response. While thermodynamic driving forces may favor spreading at equilibrium, oxide layers impose kinetic barriers that suppress or arrest wetting at very early stages of the process. These barriers include reduced atomic mobility at the interface and the mechanical rigidity of oxide shells. Consequently, the system becomes kinetically trapped in a non-wetting configuration long before it can approach any thermodynamic equilibrium. In Cu-Ni alloys, the oxide layer remains relatively thin and chemically inert, similar to Al_2O_3 , leading to rapid stabilization of the contact angle without significant time-dependent evolution.

In contrast, in Cu-Cr alloys, the formation of chromium-rich oxides fundamentally alters both the chemistry and mechanics of the interface. These oxides possess high thermodynamic stability and strong adhesion, effectively decoupling the liquid metal from the substrate and rendering classical wetting thermodynamics largely irrelevant. In such cases, increasing the temperature or holding time does not enhance wetting because the governing limitation is chemical passivation, rather than an insufficient thermodynamic driving force. These observations highlight a critical distinction between thermodynamic possibility and kinetic accessibility. While thermodynamic calculations may suggest that alloying could reduce interfacial energy and improve wetting, oxide chemistry determines whether such a state can ever be realized in practice. The dominance of oxide-controlled kinetics explains why alloying strategies that appear promising from a thermodynamic perspective often fail experimentally unless accompanied by strict control of oxygen activity or deliberate disruption of surface oxides [65–66]. The present study demonstrates that wetting in Cu-based alloy/ Al_2O_3 systems is governed not only by equilibrium thermodynamic driving forces but also by the dynamic interplay between oxide formation, transport, and stability. Recognizing

oxide chemistry as the primary controlling factor provides a more realistic framework for interpreting wetting experiments and underscores the necessity of integrating chemical kinetics into the design of metal-ceramic joining processes.

Although the present study deliberately emphasizes *wetting kinetics* rather than equilibrium wettability alone, it must be acknowledged that the kinetic interpretation is primarily based on the time-dependent evolution of the contact angle, without recourse to quantitative kinetic modeling frameworks such as spreading regime analysis, triple-line mobility models, or characteristic wetting times [66]. This limitation is not merely methodological, but reflects fundamental constraints imposed by the intrinsic behavior of the systems being investigated. Classical kinetic descriptions of wetting typically assume the continuous spreading of a liquid droplet, driven by a balance between capillary forces and dissipative mechanisms, which allows for the identification of distinct spreading regimes (e.g., inertial, viscous, or diffusion-controlled) and the extraction of kinetic parameters. In the present Cu-Ni/ Al_2O_3 and Cu-Cr/ Al_2O_3 systems, these assumptions are not fulfilled. Instead of progressive spreading, the experiments reveal rapid stabilization, asymmetric evolution, or even complete suppression of droplet deformation due to oxide formation and interfacial passivation. Under these conditions, the wetting process does not evolve toward a regime where classical kinetic models are applicable. Consequently, contact angle evolution plots serve here not as inputs for kinetic fitting, but as *diagnostic indicators* of interfacial activity or, critically, the lack thereof.

In the Cu-Ni system, the near-instantaneous stabilization of the contact angle reflects a kinetically arrested interface, characterized by negligible triple-line mobility and the absence of time-dependent interfacial reactions. In the Cu-Cr system, the transient decrease followed by an increase in contact angle indicates competing kinetic processes, including initial liquid contact and rapid oxide-induced passivation, rather than a monotonic spreading process amenable to quantitative modeling. Triple-line pinning further complicates kinetic interpretation. The presence of oxide films, surface heterogeneities, and mechanically rigid shells leads to strong pinning forces that dominate interfacial dynamics. Under such circumstances, the triple line is not free to advance in response to thermodynamic driving

forces, rendering characteristic spreading times or kinetic exponents physically meaningless. Any attempt to extract quantitative kinetic parameters would therefore risk attributing artificial significance to phenomena that are chemically, rather than hydrodynamically, controlled. From this perspective, the reliance on contact angle evolution plots should be understood as a deliberate and scientifically justified choice. The objective of the kinetic analysis in this study is not to parameterize spreading behavior, but to identify whether wetting kinetics are *active, suppressed, or chemically overridden*. The absence of model-fitting is thus itself a kinetic result, demonstrating that oxide chemistry and passivation dominate the interfacial response from the earliest stages of contact.

Nevertheless, this limitation necessarily weakens claims related to universal wetting kinetics and restricts the scope of interpretation to system-specific behavior. The present results should therefore be interpreted as defining kinetic *constraints* rather than kinetic *laws*. They highlight the conditions under which wetting kinetics cease to be governed by classical spreading mechanisms and become controlled by chemical and mechanical barriers at the interface. By explicitly acknowledging this distinction, the study provides a more rigorous and honest kinetic interpretation. It clarifies that, for Cu-based alloys on Al_2O_3 , the critical scientific insight lies not in extracting kinetic parameters, but in demonstrating why such parameters cannot be meaningfully defined under realistic experimental conditions. This recognition is essential for guiding future work toward experimental strategies and modeling approaches that can overcome, rather than obscure, chemically dominated wetting behavior.

The poor wettability observed for both Cu-Ni and Cu-Cr alloys contrasts markedly with the behavior of active-metal brazing systems containing elements such as Ti or Zr. These elements exhibit a strong chemical affinity for oxygen and readily react with oxide ceramics, including Al_2O_3 , forming stable reaction layers at the metal-ceramic interface. Such interfacial reactions reduce the solid-liquid interfacial energy and promote spreading [37], often resulting in contact angles below 90° under comparable high-temperature conditions [24, 63]. In contrast, nickel acts as a relatively non-reactive alloying element toward alumina, while chromium, despite its high oxygen affinity, preferentially forms surface oxide layers that promote

passivation rather than direct interfacial interaction with the ceramic [37]. Consequently, the wetting enhancement mechanisms characteristic of active-metal brazes are absent in the Cu-Ni and Cu-Cr systems investigated in the present study, explaining their persistent non-wetting behavior.

Moreover, in wetting and interfacial studies, there is a strong tendency to emphasize systems that exhibit improved wettability or favorable interfacial reactions. At the same time, non-wetting results and experimental failures are often under-reported. The present study deliberately addresses this imbalance by providing a detailed and transparent account of non-wetting behavior and the experimental constraints encountered in Cu-Ni/ Al_2O_3 and Cu-Cr/ Al_2O_3 systems. This approach constitutes a significant contribution, as it clarifies the fundamental limitations of alloying strategies that are often assumed to be effective based solely on thermodynamic considerations. Reporting non-wetting behavior is scientifically essential because it defines the *boundaries of applicability* for alloy design concepts. In the present case, both Ni and Cr additions fail to induce wetting under conditions commonly used in high-temperature processing, despite their widespread use as alloying elements in copper-based systems.

By demonstrating that these elements not only lead to suboptimal wetting but also actively impose kinetic or chemical barriers, such as interfacial passivation and oxide-shell formation, the study provides critical evidence that certain alloying routes are intrinsically ineffective for improving Cu- Al_2O_3 wettability. Without such negative results, future studies risk repeatedly exploring the same unproductive compositional space, resulting in redundant experimentation and an inefficient use of research resources. Equally important is the explicit documentation of experimental failure modes, particularly in the Cu-Cr system, where conventional sessile drop measurements are rendered impossible by rapid oxidation and shell formation. Rather than treating this outcome as an experimental artifact, the present work interprets it as a physically meaningful result that reflects the true interfacial chemistry of the system. This distinction is crucial: experimental failure here is not a limitation of the method, but a manifestation of dominant oxidation-driven kinetics that override wetting processes. Recognizing this shifts the interpretation from “insufficient experimental control” to “intrinsic materials behavior,” thereby providing a more accurate

understanding of metal–ceramic interactions. The findings also offer practical guidance for future research by identifying alloying strategies that are unlikely to yield progress without additional interventions. The lack of wetting improvement through Ni addition confirms that non-reactive, fully soluble alloying elements cannot modify interfacial chemistry in oxide-based systems. Similarly, the dominant oxidation of Cr highlights that reactive elements, while thermodynamically promising, may be counterproductive unless oxygen activity is rigorously controlled. This insight directs future efforts away from simple compositional modification toward more effective approaches, such as the use of active elements with controlled oxidation behavior, atmosphere engineering, interfacial coatings, or transient liquid-phase techniques. By clearly articulating why wetting does not occur and under what conditions it cannot occur, the present study contributes to a more rational and predictive framework for alloy selection in metal-ceramic joining and composite fabrication. The explicit reporting of non-wetting and experimental limitations thus serves not as a negative outcome, but as a valuable scientific filter that helps the community avoid unproductive alloying strategies and focus on pathways with genuine potential for interfacial optimization.

CONCLUSIONS

This article presents a systematic experimental investigation of the wettability and wetting kinetics of Cu-Ni and Cu-Cr alloys on Al_2O_3 substrates using the sessile drop method under high-vacuum and inert-gas conditions. By combining conventional contact heating with a modified capillary extrusion approach, the study provides a detailed assessment of both equilibrium contact angles and time-dependent wetting behavior for copper-rich alloys containing nickel and chromium additions.

A key novelty of the work lies in its explicit analysis of wetting phenomena in Cu-Ni/ Al_2O_3 and Cu-Cr/ Al_2O_3 systems, which are scarcely addressed in the existing literature. While previous studies have primarily focused on equilibrium wettability or long-term interfacial reactions, this article emphasizes the dynamic evolution of contact angles and the practical limitations encountered during real-time measurements, including oxide formation, passivation, and droplet instability. The documentation of experimental failure modes, such

as oxide-shell formation, which prevents droplet development in Cu-Cr alloys, constitutes an important and rarely reported contribution, offering valuable insight into the intrinsic challenges of wetting measurements for reactive copper alloys.

The study demonstrates that, contrary to some expectations derived from thermodynamic considerations, nickel additions do not improve the wettability of copper on alumina. Additionally, chromium additions, under the applied experimental conditions, also fail to induce effective wetting, despite their strong affinity for oxygen. The measured contact angles for both alloy systems remain in the non-wetting regime ($>120^\circ$), and wetting kinetics show no significant improvement with holding time. These findings critically complement global data by confirming that alloying effects alone, without controlled oxygen activity or interfacial engineering, are insufficient to achieve wetting in Cu- Al_2O_3 systems.

Another important contribution is the comparative methodological evaluation of standard sessile drop testing versus capillary extrusion for highly oxidizable alloys. The successful deposition of molten Cu-Cr droplets via extrusion, despite rapid passivation, highlights the utility and limitations of alternative wetting measurement strategies, providing practical guidance for future experimental designs.

The scientific value of this article lies in its realistic, process-oriented perspective on metal–ceramic wetting. Rather than reporting idealized improvements, the study delineates the boundaries of wettability enhancement achievable through alloying and underscores the dominant role of oxide chemistry and surface condition. These insights are highly relevant for researchers and engineers working on brazing, infiltration, and composite fabrication involving copper-based alloys and alumina substrates. By clarifying why certain alloying strategies fail under practical conditions, the article contributes to a more rational design of metal–ceramic joining systems. It highlights the need for complementary approaches such as atmosphere control, active elements, or interfacial coatings.

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