In this paper, we briefly review and analyse results of an acoustical investigation of adhesion in metal–ceramic interfaces based on the determination of the slope parameter, which is defined by the linear correlation between the work of adhesion of various liquid metal–ceramic systems and the sound propagation velocity of plate acoustical wave in the corresponding metals. The dependence of values of the work of adhesion slope parameter for several ceramic materials on the acoustic impedances of the corresponding ceramics is examined. The obtained results permit the interpretation of the wave propagation nature in these interfaces according to the existence and the excess of the interfacial bonding.

**Key words:** interface, adhesion, sound velocity, ceramics, liquid metal.
Metalized ceramic are playing a major role in several modern applications [1] such as metal–ceramic joining, metal-matrix composites, thin metal films on ceramic substrates [2], thermal-barrier coatings (TBC) [3], hard TiN coating [4], photovoltaic materials [5] and as functional components in microelectronics [6]. The performance is directly related to the nature of the metal–ceramic interfaces.

The most important characteristics of these materials are their high-impact energy-absorption capacity, dimensional stability, thermal and electrical conductivity, low and controllable density and the large internal surface area. However, they could undergo a severe problem consisting of poor adhesion at metal/ceramic interfaces. This is why an understanding of the adhesion mechanism is needed in order to control the nature of the interfacial bonding and the determination of the reversible work necessary to damage these interfacial bonds [7–12].

Furthermore, the optimization of metal–ceramic interfacial adhesion by non-destructive techniques is crucial to the applications of these materials. In this context, various ultrasonic methods are established for the characterization of the metal–ceramic interfaces [13].

In the liquid metals, the sound propagation is done transversely with a characteristic velocity; there is no matter transfer of but only energy transfer [14, 15]. This acoustic wave does not depend only on the elastic properties of this liquid metal, but it is strongly affected by the properties of the interface with the ceramic substrate. The weakly or strongly adherent regions have different responses. This means that a change in the properties of the adhesion must result in a change of
the velocity of the surface waves in the ceramic [15].

In this paper, a new acoustic approach is suggested to interpret the interfacial adhesion in the non-reactive metal–ceramic systems. Discussions will be made on the relation between sound propagation and the nature of bonding of metals with several ceramic materials.

2. METHODOLOGY

The adhesion of the metal–ceramic system is the most important factor of all metal bonds. It is determined by the change in the free energies of two materials when they come into contact [16] (Fig. 1).

The work of adhesion $W_{\text{ad}}$ between the liquid metal and the ceramic can be expressed using the Young–Dupré equation relating the surface tension of the liquid metal above the melting temperature $\gamma_{LV}$ and the measured equilibrium contact angle $\theta$ formed by the metal on the ceramic substrate [17]:

$$W_{\text{ad}} = \gamma_{LV}(1 + \cos \theta). \quad (1)$$

The work of adhesion $W_{\text{ad}}$ in metal–ceramic contact is generally written as the sum of different contributions of the interfacial interactions between two phases [17]:

$$W_{\text{ad}} = W_{\text{equil}} + W_{\text{non-equil}}. \quad (2)$$

$W_{\text{non-equil}}$ represents the non-equilibrium contribution to the work of adhesion. In the absence of chemical reactions, this term does not appear. $W_{\text{equil}}$ represents the equilibrium contribution, which corresponds to non-reactive systems. This later can be expressed by two distinct terms:

$$W_{\text{equil}} = W_{\text{chem-equil}} + W_{\text{VDW}}, \quad (3)$$

where $W_{\text{chem-equil}}$ is the adhesion energy between the two contact phases, which results from the establishment of the chemical equilibrium

Fig. 1. Schematic profile of a contact angle $\theta$ in a solid–liquid–vapour system in equilibrium [16].
bonds obtained by the mutual saturation of the free valences of the surfaces in contact. The formation of these chemical bonds is not accompanied by the rupture of the interatomic bonds in metal–ceramic interface, which takes place in the chemical non-equilibrium systems.

$W_{\text{VDW}}$ represents the van der Waals interactions.

During the propagation of the ultrasonic waves, the particles undergo a sinusoidal vibratory displacement around their rest position. Consequently, their density varies by making regions appear denser and others less dense than when they are at rest. The ratio of these deletions and depressions by the acoustic velocity defines the notion of

**TABLE 1.** Young’s moduli $E_C$ and densities $\rho_C$ of ceramics and experimental values work of adhesion $W_{\text{ad}}$ in various metal–ceramic systems.

| Ceramic | $E_C$, GPa [14] | $\rho_C$, kg/m$^3$ [14] | Metal | Atmosphere | $W_{\text{ad}}$, mJ/m$^2$ | Refs. |
|---------|-----------------|--------------------------|-------|------------|------------------------|------|
|         | 1               | 2                        | 3     | 4          | 5                      | 6    | 7     |
|        |                 |                          |       |            |                        |      |       |
| AlN    | 350             | 3260                     |       |            |                        |      |       |
|        | Ag              | Vacuum                   | 630   | [19]       |                        |      |       |
|        | Al              | Vacuum                   | 1136  | [19]       |                        |      |       |
|        | Au              | Vacuum                   | 650   | [19]       |                        |      |       |
|        | Co              | Vacuum                   | 1270  | [19]       |                        |      |       |
|        | Cu              | Vacuum                   | 1060  | [20]       |                        |      |       |
|        | Fe              | Vacuum                   | 1320  | [19]       |                        |      |       |
|        | Ga              | Vacuum                   | 750   | [19]       |                        |      |       |
|        | Ge              | Vacuum                   | 811   | [19]       |                        |      |       |
|        | In              | Vacuum                   | 448   | [19]       |                        |      |       |
|        | Ni              | Vacuum                   | 1305  | [19]       |                        |      |       |
|        | Pb              | Vacuum                   | 203   | [19]       |                        |      |       |
|        | Pd              | Vacuum                   | 858   | [19]       |                        |      |       |
|        | Si              | Vacuum                   | 1058  | [19]       |                        |      |       |
|        | Sn              | Vacuum                   | 461   | [20]       |                        |      |       |
|        | Al              | Vacuum                   | 948   | [21]       |                        |      |       |
|        | Au              | Vacuum                   | 577   | [21]       |                        |      |       |
|        | Fe              | Vacuum                   | 1202  | [21]       |                        |      |       |
|        | Ga              | Vacuum                   | 537   | [21]       |                        |      |       |
|        | In              | Vacuum                   | 335   | [21]       |                        |      |       |
|        | Ni              | Vacuum                   | 1191  | [21]       |                        |      |       |
|        | Pb              | Vacuum                   | 218   | [21]       |                        |      |       |
|        | Si              | Vacuum                   | 876   | [21]       |                        |      |       |
|        | Sn              | Vacuum                   | 305   | [21]       |                        |      |       |
|        | Cu              | Ar                       | 600   | [20]       |                        |      |       |
|        | Fe              | He                       | 717   | [20]       |                        |      |       |
|        | Ni              | Vacuum                   | 680   | [20]       |                        |      |       |
|        | Pb              | Vacuum                   | 130   | [17]       |                        |      |       |
|        | Au              | Vacuum                   | 205   | [22]       |                        |      |       |
|        | Cu              | Vacuum                   | 345   | [22]       |                        |      |       |
|        | Si              | Vacuum                   | 364   | [22]       |                        |      |       |
|        | Sn              | Vacuum                   | 128   | [22]       |                        |      |       |
impedance. According to a normal incidence of the acoustic wave on a flat surface, the acoustic impedance $Z$ expressed by:

$$Z = \rho c.$$  \hspace{1cm} (4)

Following the various calculations derived from this equation [18], we will use the general form of the acoustic impedance $Z$ as a function of the density $\rho$ and the Young’s modulus $E$ of the transverse acoustic wave:

$$Z = (\rho E)^{1/2}.$$ \hspace{1cm} (5)

The stresses imposed by a liquid on the surface of the ceramic are mainly due to the viscosity. The liquid metal–ceramic coupling results in radiation in the liquid of a highly damped transverse wave. The acoustic reflection coefficient at the interface is written as follows:

$$R = (Z_{LM} - Z_c)/(Z_{LM} + Z_c),$$ \hspace{1cm} (6)
where \( Z_{LM} \) and \( Z_c \) are the impedances of the liquid metal and ceramic. The reflection coefficient \( R \) makes it possible to determine the transmitted energy as a function of the impedances at the liquid metal–ceramic interface. This energy is determined by its transmission coefficient, which is defined as follows:

\[
T = 1 - R.
\]

3. RESULTS AND QUANTIFICATION

A new acoustic model is proposed to interpret the work of adhesion in non-reactive metal–ceramic systems. In this model, the energy transfer by the sound propagation is assured by the existence and the excess of the interfacial bounds between a metal and a ceramic. The relevant parameters determining the work of adhesion of a metal–ceramic system have been found to be the sound propagation velocity in liquid metal and the acoustic impedance of the solid ceramic.

Detailed experimental results of the work of adhesion for various metal–ceramic systems are summarized in Table 1. It should be noted that the criterion of liquid metals and given ceramics selected in this investigation must have the experimental \( W_{ad} \) values of at least three different contacting metals available in the literature.

From Figure 2, it can be observed that the work of adhesion of different liquid metal–aluminium nitride (AlN) interfaces increases line-

![Fig. 2. Correlation between work of adhesion \( W_{ad} \) for different liquid metal–AlN systems and sound velocities \( c \) of corresponding liquid metals. The sound velocity values of liquid metals are taken from Blairs [27].](image-url)
arly when the sound propagation velocities $c$ of the corresponding metal increases.

Thus, it is important to define a new interfacial characteristic, which defines the energy transfer strength by the interfacial bounds to the ceramic phase, depending on the stability and the strength of the interfacial adhesion between different metals in contact with the ceramic that is the slope parameter of the work of adhesion $\xi = dW_{ad}/dc$. Similar idea was used by Li [26] for the same systems but for the dependence of the work of adhesion and the electron density $n_{ws}$, which is responsible of the electronic transfer between the metallic phases and the ceramics. Therefore, the electron density allows the formation of the interfacial bonds whether in excess or in deficit depending on the type of the ceramic.

The linear correlation of the points presented in Fig. 2 yields a $\xi$ value of 0.312 mJ s/m$^3$ for aluminium nitride. These results, together with the $\xi$ values, obtained for other solid ceramic materials are given in Table 2.

It is important to note that, the $W_{ad}$ values for the selected liquid metal–ceramic systems exhibit a good convergence as a function of the sound velocity of several liquid metals on a ceramic, as indicated by the values of the regression coefficients given in Table 2.

In Figure 3, the slope parameter $\xi$ values for work of adhesion for various ceramics are plotted as a function of the acoustic impedance $Z_C$ of the corresponding ceramics. It can be seen that the slope parameter $\xi$ stabilizes at about 0.185 mJ s/m$^3$; however, then it increases sharply. For $Z_C > 38 \cdot 10^6$ kg/m$^2$ s, $\xi$ seems to stabilize again, but at about 0.600 mJ s/m$^3$.

The excellent correlation between $\xi$ and $Z_C$ as presented in Fig. 3 demonstrates that the work of adhesion slope parameter $\xi$ of liquid

| Ceramic | $\xi$ | $R$ |
|---------|-------|-----|
| AlN     | 0.312 | 0.9951 |
| Al$_2$O$_3$ | 0.270 | 0.9780 |
| BeO     | 0.200 | 0.9991 |
| BN      | 0.184 | 0.9846 |
| CoO     | 0.606 | 0.9954 |
| MgO     | 0.203 | 0.9389 |
| NiO     | 0.604 | 0.9526 |
| TiO     | 0.603 | 0.9066 |
| SiO$_2$ | 0.183 | 0.9464 |
| ZnO     | 0.585 | 0.9880 |
| ZrO$_2$ | 0.183 | 0.9764 |
metal–ceramic interfaces depends only on the nature of the ceramic and not on the contacting liquid metals.

From Figure 3, we can distinguish two different cases of the variation of $\xi$ as a function of $Z_C$. The first part of this figure reveals that the reflection mode $R$ of the propagating acoustic wave in liquid metal becomes the most dominant according to the equation (6), for the impedance acoustic values of ceramics lower than that of AlN ($Z_C < Z_{AlN}$). Therefore, the acoustic wave will be reflected in this middle and only a small part of the energy will be transmitted from the metal–ceramic interface because of a low interracial adhesion. The work of adhesion $W_{ad}$, in this part, is only resulting from the van der Waals interactions $W_{VDW}$, and the chemical equilibrium contribution $W_{chem-equil}$ is negligible [20, 22, 23].

The determination of $W_{VDW}$ values for different metal–ceramic systems have been reported in different previous researches. For example, Naidich [17] found a $W_{VDW}$ value of $350 \pm 150$ mJ/m² for metal–oxide ceramic systems.

The second case, which corresponds to the values of ceramic acoustic impedance $Z_C$ greater than that of AlN ($Z_{AlN} < Z_C$), shows that the transmission $T$ becomes the most dominant mode. The energy of the propagating wave in the liquid will be transmitted almost totally to the ceramic from metal–ceramic interface. In this limiting case, the work of adhesion $W_{ad}$ is approximately determined by the surface tension $\gamma_{LV}$ of liquid metals as indicated by equation (1), and the work of adhesion slope parameter $\xi$ is proportional to $d\gamma_{LV}/dc$, that is the linear dependence of the surface tension of liquid metals on the sound propagation.

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**Fig. 3.** Work of adhesion slope parameter $\xi$ values of various ceramic materials as a function of the acoustic impedance $Z_C$ of the corresponding ceramics.
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velocity of corresponding metal.

A linear correlation between \( \gamma_{LV} \) values of various liquid metals against \( c \) is shown in Fig. 4. An important point that can be interpreted from this figure is the possibility of determining the unknown surface tension as function of a known sound velocity of liquid metals and vice versa.

The points presented in Fig. 4 yields a surface tension slope parameter equal to 600 mJ/s/m, which corresponds exactly to the upper limit of Fig. 3. It is noted that this limit of has been already saturated for solid ceramic materials characterized by a dominant transmission energy mode, which explain the good interfacial adhesion.

4. CONCLUSIONS

In this paper, the work of adhesion of different liquid metals on a given ceramic was investigated. A new approach of the interfacial phenomenon was introduced. This novel interfacial phenomenon investigation was deduced after the study of \( W_{ad} \) versus the sound velocity propagation of plate acoustical wave in corresponding metals that shows a linear correlation. Moreover, the work of adhesion slope parameter for several ceramic materials shows a strong dependence on the acoustic impedance of the corresponding ceramics. This result proves that this slope parameter depends only on the ceramic properties. Hence, the determined correlation between the slope parameter values and the

Fig. 4. Correlation between the surface tension \( \gamma_{LV} \) of various liquid metals and the sound velocity \( c \) of the corresponding metals. The surface tensions of liquid metals are taken from Keene [28].
acoustic impedance of various ceramic materials has a deep effect on the nature of the acoustical wave propagation (reflective or transitive) in metal–ceramic interfaces according to the existence and the excess of the interfacial bonding.

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