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DIFFUSION KINETICS IN EXPLOSIVE CLADDING OF DISSIMILAR ALLOYS AS DESCRIBED THROUGH THE MIEDEMA MODEL

KINETYKA PROCESU DYFUZJI W UKŁADACH PLATERÓW WYTWARZANYCH Z WYKORZYSTANIEM ENERGII WYBUCHU, NA BAZIE STOPÓW O SILNIE ODMIENNYCH WŁAŚCIWOŚCIACH, OPISANYCH MODELEM MIEDEMA

Explosive cladding of dissimilar plates is achieved by the intensive deformation occurring at high pressure and temperature generated from the detonating explosive at the collision interface. The interface morphology, with its characteristic undulations, is dictated by the extent of kinetic energy spent at the mating interface. Nevertheless, the inter-metallic compound formation at the mating interface weakens the joint. The prediction of the probability of inter-metallic formation at aluminum-SS 304, copper-SS 304 and titanium-SS 304 explosive cladding interfaces is attempted in this study by employing Miedema model. Granular explosives (detonation velocity: 4000 m/s) and parallel plate combination were employed with uni-loading ratio (standoff distance-5 mm). The influence of chemical energy in determining the bond strength of explosive clads is discussed as well.

Keywords: Explosive cladding; dissimilar metals; Miedema model; strength

Zgrzewanie wybuchowe blach z metali o zróżnicowanych właściwościach jest osiągnięte poprzez intensywne odkształcenie pod wysokim ciśnieniem i temperaturze genrowane detonacją ładunku wybuchowego oraz kolizją materiałów łączonych. Morfologia warstwy połączenia scharakteryzowana jest zafalowaniami, które są determinowane przez zewnętrzną energię kinetyczną. Formujące się w strefie połącznia fazy międzymetaliczne prowadza do osłabienia połączenia. W prowadzonych analizach wykorzystano model Miedemy do przewidzenia prawdopodobieństwo formowania się stref przetopień w platerach z aluminium-SS 304, miedź-SS 304 i tytan-SS 304. W modelu obliczeniowym przyjęto układ równoległy płyt (odległość płyt – 5 mm) oraz prędkość detonacji: 4000 m/s. Omówiono również wpływ energii chemicznej na wytrzymałość połączenia układu platerów zgrzewnych wybuchowo.

1. Introduction

Metallic bonding of dissimilar metals is achieved when the atoms are forced to craft a coalescence being affected by the formation of oxides and adsorbed contaminants [1]. When two perfectly clean metal surfaces are forced together in vacuum, some metal combinations mate more willingly than others owing to

(i) Compatibility effects due to non matching crystal structures, lattice parameters, and/or crystallographic orientations at the interface.
(ii) Compatibility effects due to the affinity for chemical bonding and
(iii) Possible interface effects-interface alloying and interface segregation of alloying elements or other diffusion effects [2].

In explosive cladding, fresh new surfaces are cladded as the surface jetting removes the oxides and contaminants present in the mating surface. However, the fundamental chemical effects (i-iii) play a vital role in determining the bond strength which is adversely affected by the formation of continuous molten layer and brittle inter-metallic compounds. The influence of process parameters, geometrical arrangements and the characteristics of participant metals on the nature of explosive clad interface is the subject of discussion for many researchers [3-7]. Recently, Wołczynski et al. [8] thermodynamically detailed the inter-metallic compounds formation while applying Fe-Al coating over steel substrate following non-homogeneous temperature distribution and rapid solidification. Nonetheless, the studies on chemical affinities in dissimilar explosive cladding in determining the formation of inter-metallic compounds is limited and is attempted herein through Miedema model which employs thermodynamic facts.

2. Experimentation

The explosive cladding reported elsewhere [9] is attempted with aluminum, copper and titanium Gr-1 plates (50 mm×90 mm) as flyer plates and stainless steel 304 plates

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of similar dimensions as the base plates respectively. The parallel configuration with a standoff distance 5 mm and a uni-loading ratio is attempted in this study. The mating surfaces of the plates were mechanically polished and thoroughly cleaned prior to experiments. The explosive (detonation velocity 4000 m/s) was packed on the flyer plate and the detonator was positioned on one end. The Al-SS304, Cu-SS 304 and Ti-SS304 explosive clad plates were sectioned parallel to detonation direction for examining the nature of interface and the samples were prepared through standard metallographic practice. Ram tensile tests were conducted in a servo hydraulic testing machine at compression mode and the results are reported.

3. Miedema model

When two metals collide, the transformation into a new phase occurs and which lowers the energy of a system. If the initial stage is unstable, a transformation to a new more stable state occurs. According to thermodynamics, bond is stable when the Gibbs free energy (G) is low whose change (ΔG) during the process is given by [10]

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

Where H is the enthalpy, T is the atmospheric temperature and S is the entropy. In solid state bonding, change in enthalpy is equal to change in Gibbs free energy as entropy is the order of 0.001 kJ/deg/mol [10] and hence

$$\Delta G \approx \Delta H \qquad (2)$$

Miedema et al. [11] employed a thermodynamic approach and correlated the enthalpy of formation of binary alloy to the difference in work functions of the two metals and the difference in electron density for the specific atoms at the boundaries of Wigner-Seitz cell. Miedema model estimates quantitatively the effects of the change in the Wigner-Seitz cell boundary electron density and is used to determine the enthalpy of formation- the signature of stability in binary liquid and solid phases for various atomic concentrations.

During alloy creation, dissimilar cells, in contact with each other, shift their electron densities to remove the cell boundary discontinuities. Elimination of such discontinuities requires energy; hence the electron density difference (Δn_{ws}) accounts for a positive contribution to the interface energies. The heat of reaction can be calculated if the enthalpy of the products and reactants are known. According to Miedema et al.[12], the energy of an atom A in a metal B,.

$$\Delta H^{AinB}_{Sol} = \frac{2V_A^{2/3}}{(n^A_{ws})^{-1/3} + (n^B_{ws})^{-1/3}} \times [-P(\Delta\varphi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R] \qquad (3)$$

Where V_A is the volume of atom A in the metal, and consequently $V_A^{2/3}$ is a measure of the surface of an individual atom, $\phi^* = \phi^*_A - \phi^*_B$, where ϕ^* is a Miedema electro negativity parameter used to characterize the metals. $\Delta n_{ws}^{1/3}$ is related to the density of valence electron charge at the surface of contact between neighboring atoms. The values of P and Q are dependent on the type of metals forming the alloy/inter-metallic compound. The value of P is 14.2 for metals with valence greater than 2, and 10.7 for metals with valance 1 or 2. The Q/P ratio is maintained at 9.4. The term 'R' in Eqn.1, is due to filling of the Brillouin zones of a particular crystal structure.

Miedema et al. [12] opined that when the enthalpy of formation is positive, solubility of metal A with metal B is slim at higher temperatures and otherwise for a negative enthalpy. They further constructed plots between electro negativity (ΔØ) and density of electrons (Δn_{ws}) and demarcated a parabolic curve between positive and negative enthalpy values for various metals viz., transition-transition metals, transition-non transition metals and non transition-non transition metals. When the enthalpy is negative, chemical energy supports the formation of inter-metallic compounds following higher solubility whereas a positive value denotes negative tendency of alloying due to limited solubility [12].

4. Results and discussion

4.1. Effect of chemical energy

Öberg et al. [13], based on electro negativity difference of metals and Miedema theory plotted interfacial energies of reference metals relative to surface energy (γ_s) to represent the influence of formation energy γ_{AB} found a positive chemical contribution which prevents the formation of inter-metallic compounds. The chemical energy (γ^{chem}_{AB}) may be either positive or negative and, hence, either stabilizes or destabilizes the interface and further opined that a stable bond is possible when the chemical energy is less than the energy reduction owing to elimination of surface area following 'jetting'. The interface between dissimilar metals can be assumed to represent an atomic misfit of a large angle grain boundary and can significantly contribute to the interfacial energy. The Oberg et al. formation energy of an iron–x-metal interface shown in Fig. 1 by thick, continuous line determined by [14]

$$\gamma_{AB} = 0.15(\gamma^s_A + \gamma^S_B) + \gamma^{chem}_{AB} \qquad (4)$$

The metal points in the diagram are evaluated based on their relative positions to Oberg et al. formation energy line and the deviation corresponds to the chemical term γ^{chem}_{AB} is a measure of interface stability. The points prevailing below the Oberg line represent metals exhibiting negative chemical energy and additional solubility with iron supporting inter-metallic compound formation. Points closer to Oberg et al. formation energy line indicate metals whose interface energy is primarily due to grain boundary energy for which the influence of chemical energy is negligible. A point above the Oberg formation energy line has limited solubility with iron, and indicates higher chemical energy which opposes the formation of alloying thereby inhibiting the inter-metallic compound formation.

4.2. Microstructural interpretation

The optical microstructure of Al-SS304, Cu-SS304 and Ti-SS304 are superimposed on the Oberg et al. scatter plot for Iron-X-Metal (Fig. 1) which have properties similar to stainless steel. It can be seen from Fig. 1 that, copper falls

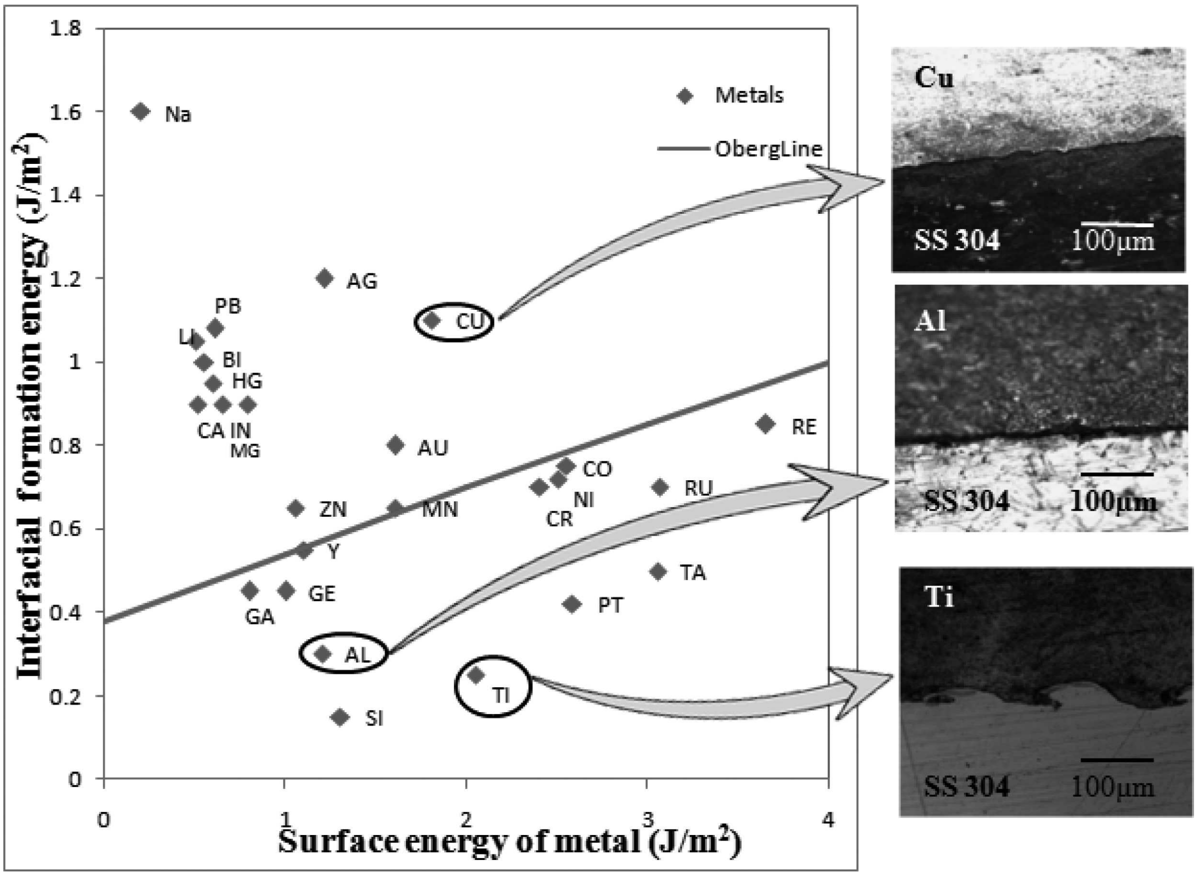

Fig. 1. Oberg et al. interfacial formation energy plot for iron with other metals

above the Oberg et al. line which possess a positive enthalpy (ΔH for Cu-Steel= +60 kJ/mole) denoted in eqn.1 with a high positive chemical potential ($\gamma_{AB}^{chem.}$), whereas, aluminum (ΔH for Al-Fe=-41 kJ/mole) and titanium (ΔH for Ti-Steel= -70 kJ/mole) have negative enthalpy of formation and falls well below the Oberg et al. line indicating high negative chemical energy with respect to iron. The microstructure of Al-SS304, Cu-SS304 and Ti-SS304 explosive clads shown in Fig. 1 reveal a smooth undulating interface to conclude a strong clad. The interfacial waves serve as a reason for better mechanical interlocking between the two participant plates and the nature of wave formation inherently depends on process parameters viz., collision angle, collision velocity, plate velocity and properties of participant metals [15, 16].

In aluminum-SS304 explosive clad, the interfacial waves are larger to resemble a straight interface with a continuous streak of molten layer and is consistent with Acarer and Demir [17], and Saravanan and Raghukandan [18]. In deviation to Al-SS304, the Ti-SS304 explosive clad reveals a sinusoidal wave with a single vortex due to significant difference in densities between participant metals despite the formation enthalpy of titanium is lesser than aluminum (Fig.1). A continuous molten layer is seen at the vortex of Ti-SS304 explosive clad owing to negative chemical potential as reported by Manikandan et al.[15] indicating theoretical results are in accord with experimental findings. In case of copper-steel clads, the formation energy γ_{AB} falls well above the Öberg formation energy line (Fig. 1) having high positive formation energy with strong repulsion for chemical bonding. Durgutlu et al. [16] while cladding Cu-SS304 at varied explosive mass reported smooth wavy interface owing to higher formation energies of these metals.

4.3. Formation of inter-metallic compounds

Formation and properties of inter-metallic compounds in dissimilar explosive cladding is the subject of interest for many researchers [2, 3, 9, 15, 16, 18] who reported that inter-metallic compounds have a negative influence in the strength of the clad. The inter-metallic phase consists of more are less thermodynamically stable compounds resulting from melting or diffusion. When the surface energy of mating metals is located below the Öberg formation energy line (Fig. 1), the chemical affinity supports the formation of inter-metallic compounds and which is detrimental to weldability. Further, at elevated temperatures, diffusion of carbon into the interface supports the formation of a thin layer of brittle inter-metallic compounds [19]. When the enthalpy of formation of the mating metals is high and negative, the average number of intermediate phases likely to be formed at the interface increases. Raghukandan et al. [20] confirmed FeTi and Fe_2Ti inter-metallic compounds through XRD analysis in their trails of explosive cladding of titanium and steel. From the microstructure shown in Fig.1 (Al-SS 304, Ti-SS304 and Cu-SS304) it is observed that the atoms of lower melting participant metals diffuse into the weaker location in the higher melting point metal to create a strong bond or inter-metallic compounds. Abe [21] estimated, from their numerical simulation that concentration of lower melting point metal is 70% while the higher melting point metal contributes the remaining in the vortex region of an explosively cladded interface. The molar concentration of flyer and base plate depends on the mass diffusion coefficient (D_{fb}) of two metals is given by

$$D_{fb} = 0.0043\frac{T^{3/2}}{p(V_f^{1/3} + V_b^{1/3})^2} + [\frac{1}{M_f} + \frac{1}{M_b}]^{1/2} \tag{5}$$

Where 'p' is the atmospheric pressure in bar, 'T' is the temperature at the collision front in K. V_f, V_b, M_f and M_b are the molecular volume and the molecular weight of flyer and base plate respectively. The mass flux of flyer plate in the interface is given by

$$N_f = \frac{M_f}{A} = -D_{fb}\frac{dC_f}{dx} \tag{6}$$

While the mass flux of base plate in the interface is estimated by

$$N_b = \frac{M_b}{A} = -D_{fb}\frac{dC_b}{dx} \tag{7}$$

Where, dC_f/dx and dC_b/dx is the concentration gradient of flyer and base plate respectively.

4.4. Bond strength

The strength of bond is influenced adversely by the formation of inter-metallic compounds and by the kinetic energy spent at the interface of the impacting metals. In an explosive clad having higher strength devoid of molten regions, the fundamental effects viz., interface alloying, segregation, diffusion effects, compatibility effects due to non-matching crystal structure, crystallographic misorientation and affinity to chemical bonding play a critical role in dictating the strength of interfacial bonding. Ram tensile tests (specimen size-25 mm×25 mm) were performed in a 10T servo hydraulic testing machine, in the compression mode with 0.5 mm/min cross head speed. The ram tensile strengths of the explosive clads are shown in Table.1. The separation into two different components creates two new free surfaces which in turn increase the system energy equal to the sum of two new surface energies ($\gamma_A^s r \gamma_B^s$). The energy spent is more than the energy gained during separation. The interfacial bond strength as a negative energy per unit area can be expressed in terms of

$$\gamma_{AB}^{bond} = -0.85(\gamma_A^s + \gamma_B^s) + \gamma_{AB}^{chem} \tag{8}$$

The interfacial bond strength consists of large negative surface energies ($\gamma_A^s r \gamma_B^s$) term and one smaller term which may be attractive or repulsive ($\gamma_{AB}^{chem.}$). The failure in the ram tensile specimens occurs in the weaker metal indicating the interface has greater tensile strength than weaker of the participant metals as reported by Wronka [22].

TABLE 1

Bond strength of explosive clads

S.No	Combination	Tensile strength (MPa)
1	Al-SS 304	120
2.	Cu-SS 304	250
3.	Ti-SS 304	275

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5. Conclusion

The bond energy, though significantly smaller in magnitude, contributes to the formation and stability of explosive clad. The estimation of atomic concentration at the collision interface provides an initiative for predicting the composition of inter-metallic compounds at the interface. The following conclusions were drawn from this study.

1. Miedema theory can be employed for predicting the weldability and possible formation of inter-metallic compounds at the explosive clad interface.
2. When the enthalpy of formation is negative, solubility of one metal over other increases and supports the formation of intermetallic compounds.
3. The metals falling above the Oberg formation energy line restricts the solubility of metals and restrains the formation of inter-metallic compounds as the enthalpy of formation is positive.
4. The prediction of Miedema model for bond strength is in accordance with the experimental results.

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