OVERVIEW

Characterization of Ceramics-Metal Joined Interfaces
by HREM

By Yoichi Ishida*

The role of high resolution electron microscopy in the characterization of ceramic/metal joined interfaces is assessed, taking, as examples, alumina/niobium solid state joining. Both atomic and electronic structures are considered taking into account both the pre and post joining stages as well as where both physical and chemical reactions take place leaving various types of micro to nano structures at or near the joined interface. The major consideration was the mechanism to relax the thermal stress which is generally inevitable when the selection of both ceramic and metal is made a priori to meet the engineering need. Conservative or nonconservative motion of interface structures such as misfit dislocations and atomic ledges at ambient and elevated temperatures respectively and ductility of metal near the interface were considered to be operative to relax the thermal stress. A design of the joined interface must be made to realize the above mechanism. It is stressed that future high resolution electron microscopy should be able to or at least cooperate with other techniques to reveal the nature of bonding at the metal/ceramic interface to characterize the joining fundamentally.

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I. Introduction

Rapidly increasing demand for high performances in materials in recent years has placed no single material in the position to fulfill the rising requirements. The mechanical property called toughness conventional in metals is difficult to meet in most new materials. A combined use is presently considered as the plausible and quick answer to this rather general problem. Ceramic-metal joining has become the pressing subject of research due to this materials strategy.

The ceramic-metal joining in fact is an old technology which dates back even to prehistoric times. Various techniques such as soldering, brazing, enameling, etc. are within the category. They have been in use with the details of the mechanism largely remain unknown, as is generally the case with the old techniques. Steady efforts of European researchers such as Klomp(1) and Nicholas(2) have shed light of modern science on this traditional technique. Wetting angle measurement and the comparison of the work of adhesion with thermochemistry are the examples of the scientific efforts which were considered to combine the joining strength eventually to the interfacial bonding energy.

The majority of the presentations at the metal-ceramic joining session of the Japan Institute of Metals Annual Meeting, however, are more applied: High-tech materials are joined with engineering metals; analytical electron microscopy is used to examine the chemistry of the cross section; and the fracture mechanism is discussed using the Weibull plot and so on. High resolution electron microscopy has come to the stage very recently.

The above trend of research, of course, reflects the pressing demand for the ceramic-metal joining. Recently, however, a still new trend is felt; while the applied research work is advancing further, the initiation of bonding research is felt. The atomic structure of the joined interface is first examined by high resolution electron microscopy(3)(4) and the bonding state is calculated for the observed atomic structure by using the electron orbital theory(5) and the result is checked by photoelectron spectroscopy(6).

The present article intends to assess the recent efforts to characterize the ceramic-metal joined interface from the atomistic bonding point of view taking the alumina-niobium joining system as its example.

II. Mechanisms of Ceramic-Metal Joining

Joining is inherently a complex technique requiring a close examination of each stage from both physical and chemical points of view, referring, of course, to the mechanical problems. The joining stages may be divided generally into a number of stages as shown in Table 1. Careful consideration at each stage is required for a successful design of the joining.

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Table 1  Ceramic-Metal Joining Stages.

1. Surface preparation of ceramic and metal.
2. Processes during joining.
   (1) Wetting of ceramic by metal.
   (2) Removal of ceramic surface layer by metal.
   (3) Solid solution and volume diffusion of ceramic elements into metal.
   (4) Surface and interfacial diffusion and removal of the interfacial cavities.
3. Processes during cooling.
   (1) Precipitation of ceramic from metal by the solid solubility decrease and the growth of ceramics.
   (2) Generation and relaxation of the thermal stress.
4. Processes during the use of joined piece.

![Graph showing the Nb-Al-O ternary diagram at 1873 K. Hatched region is the compositions where direct Al₂O₃/Nb interface should occur.](image)

Fig. 1  A Nb-Al-O ternary diagram at 1873 K. Hatched region is the compositions where direct Al₂O₃/Nb interface should occur.

III. Characterization of the Chemical Reactions

The ternary phase diagram governs the stage at the joining temperature. Figure 1 shows an example of such a phase diagram where alumina/niobium directly bonded interface is expected if the oxygen concentration is kept sufficiently low. Dissolution of alumina into niobium, however, proceeds during the joining process keeping the level of the interface concentrations and the actual dissolution rate controlled by the bulk diffusion of the slowest moving dissolving element, i.e. aluminium. During cooling of the joined specimen, back diffusion of the dissolved elements proceeds by the decrease in the solid solubilities in metal. The precipitation of alumina takes place either in the grain boundary or at other nucleating defects in niobium near the joined interface in the form of $\theta$-Al₂O₃, or it simply returns on to the alumina surface. Equation (1) shows the temperature dependence of the equilibrium:

$$2[Al]_{Nb} + 3[O]_{Nb} \rightarrow Al_2O_3$$

where the maximum concentration of oxygen and aluminium in niobium is of the order of 6%. The precipitation reaction was found to develop a complex concentration gradient in niobium near the joined interface (Fig. 2). An EDX analysis showed a decrease in Al concentration near the joined interface ~2 $\mu$m in thickness. A simple exponential decay would be expected instead if no such precipitation is allowed. A rather ordered alumina lattice and the interface as shown in Fig. 3($^a$) appear to manifest that the alumina layer near the interface precipitated from Nb only during cooling of the joined specimen. Ceramic-metal interface is usually difficult to observe cross-sectionally by high resolution electron microscopy, because the resistance of the two materials against the bombarding ion often differs substantially so that one side thins down more than the other during ion thinning of the specimen. The

![High resolution electron micrograph of an alumina/niobium joined interface.](image)

Fig. 3  A high resolution electron micrograph of an alumina/niobium joined interface. (1012)$_{Al_2O_3}$/[000]$_{Nb}$, [2301]$_{Al_2O_3}$/[001]$_{Nb}$ (Wang et al.$^b$).
alumina/niobium system is exceptional and gives a relatively good image like that in Fig. 3. The interface micrograph first obtained by Rühle et al.\(^{(3)}\) was highly appreciated, but there arose controversy in our country because the formation of a reaction product layer of NbO\(_x\) has been reported by Morozumi et al.\(^{(9)}\) by conventional EM. The niobium oxide NbO\(_x\), with \(x\) up to 0.15 was \(-2\ \mu\text{m}\) in thickness. A rather unusual linear image was noted in their photograph in the alumina matrix near the interface. The same type of linear image is shown in Fig. 4\(^{(10)}\), which is interpreted as impurity stained layer. The thickness agrees roughly with that of hibonite (CaO·6Al\(_2\)O\(_3\)) \(-0.15\ \mu\text{m}\), which Wang et al.\(^{(4)}\) found in their specimens when contaminated by calcium oxide. The hibonite apparently precipitated instead of alumina and served as a convenient marker of the amount of precipitation. The mechanical property of the precipitate, of course, should differ from that of pure alumina, but the compound structure is similar to alumina with Ca atoms forming a layer on every 6th alumina layer so that one may consider hibonite nearly equal to alumina in thermal expansion coefficients parallel to (0001).

The formation of NbO\(_x\) proposed by Morozumi et al.\(^{(9)}\) is still an issue yet unsettled in spite of the concentration profile of Fig. 2, because the oxygen concentration near the joined interface was not measured. A plateau in aluminium concentration in Fig. 2, however, may suggest the formation of a certain phase such as NbO\(_x\) in this region. A rather extensive image changes in the niobium matrix near the interface in the high resolution image of Fig. 3 may reflect the formation of NbO\(_x\), as suggested by Morozumi et al.\(^{(9)}\). Rühle et al.\(^{(15)}\) has attributed their difference from that of Morozumi et al.\(^{(9)}\) to the initial oxygen concentration in niobium. The oxygen concentration profile should be the clue. Oxygen, however, is a difficult element to analyze with EDX and other techniques. The thermal expansion coefficients differ by only a small amount so that only a limited amount of dislocation is needed in Nb to accommodate the thermal stress. Even if a high density dislocations are produced, the dislocations are likely to align at elevated temperatures and form a small angle boundary. Experimental proof, therefore, may be available in the high resolution image to settle this issue.

The chemical issues described above symbolize, as examples, the largeness of chemical interactions at the ceramic-metal interface even when no reaction product layer forms. The chemical reaction, however, is a phenomenon useful for the relaxation of thermal stress as discussed in the later section.

### IV. Characterization of the Atomic Structure

High resolution electron microscopy has come to the stage to reveal atomic features of the interface as is already shown in Fig. 3.

Various interfaces result by the type and extent of chemical reaction at the joined interface. The classification of the interface is varied depending on the interest of individual researchers. From the structural point of view the macroscopic classification of Kingery\(^{(11)}\) (Table 2) is the simplest and useful to plan experiments. The interface with the reaction product layer\(^{(11)}\), however, consists of a number of cases differing in the structure of the layer, which may be amorphous, nanocrystalline or multilayered consisting of coarse and/or fine crystals. Figure 5 is a case with both fine and coarse grains\(^{(12)}\). A nanocrystalline TiN layer separates ceramic from coarse grained titanium silicide Ti\(_3\)Si. The strength of the interface appears to be strongly affected by the structure. The control of the interface structure, therefore, is considered a key to the strong ceramic-metal joining. Ceramic-metal interfaces\(^{(20-24)}\) in Table 2 are directly jointed and structurally similar in atomic scale, but the strength can vary due to the morphology of the interface and also by the structure and chemistry of both metal and ceramic layers. Both the atomic structure and the morphology of the joined interface are affected since ceramic precipitates from metal during cooling of the joined piece as described in the preceding section. A well-modified ordered interface may be constructed during the chemical process.

The low energy structure of the modified hetero-interface is different in its nature from that of the grain boundary because no perfect lattice matching is expected in the hetero-interface. Alignment of one or two pairs of densely packed low index atomic planes with orientations parallel to each other is the major possible type of the

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<tr>
<th>Table 2 Types of Ceramic-Metal Interface Structures(^{(11)}).</th>
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<tr>
<td>1. Multi-layered interface with reaction product phase(^{(9)}).</td>
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<td>2. Simple interface with evidence of ceramic surface layer eroded by metal.</td>
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<tr>
<td>3. Simple interface with only ceramic boundaries selectively eroded by metal.</td>
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<td>4. Simple interface without evidence of ceramic erosion by metal.</td>
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Fig. 5 A cross-sectional transmission electron micrograph of Si₃N₄/Cu–Ti brazed interface with nanocrystalline TiN next to silicon nitride (Wang[19]).

Fig. 7 Three dimensional representation of an alumina/niobium joined interface by matching two high resolution electron micrographs sliced out of the same specimen (Wang et al.[19]).

Fig. 6 Schematic representation of (a) an array of misfit dislocations and (b) a ledge structure in epitaxial heterointerfaces.

Fig. 8 Orientation relationship of Al₂O₃ and Nb single crystals[19]. The electron beam (marked by e⁻) was aligned parallel to (a) and (b) to obtain high resolution electron micrographs of Fig. 7.

low energy structure. In such an epitaxial interface rather loosely defined line structures such as misfit dislocations or ledges prevail (Fig. 6). The former is the region of poor fit in the atomically planar interface, while the latter is the end of an outer most atom plane of one of the crystalline which is often the beginning of the outer most atom plane of the other crystal when the two plane spacings are comparable in size. Figure 6 explains two such structures schematically. Neither is as rigorously defined as the boundary dislocation. The Burgers vector of the boundary dislocation is defined three-dimensionally by the lattice site matching, while the misfit dislocations and ledge structures are defined at most two-dimensionally and no precise values available because no standard structure may be defined in the epitaxial interface.

The misfit dislocation can glide conservatively and relax the shear stress of the interface while the ledge structure can move only nonconservatively by the atomic diffusion but can relax both the shear and the tensile stresses. The mechanical properties of the interface are governed by these atomic structures as will be discussed in the later section.

The observation of the atomic structure is mostly done by high resolution electron microscopy. Figure 7 is again the observation of alumina-niobium interface[19]. Two micrographs were obtained from thin foil specimens sliced out of the same specimen as shown in Fig. 8, made into thin foils by mechanical polishing and finally ion thinned. The two micrographs were placed on two
surfaces of a box and photographed again at a distance to show three-dimensional impression. The combined photograph (Fig. 7) shows the atomic ledge aligned parallel to (0001)_{Al_2O_3} and [111]_{Nb}. This type of ledge alignment is understood by a close matching of atomic spacings [1120]_{Al_2O_3} in Al_2O_3 and [110]_{Nb} in Nb, which is only 2% as shown in Fig. 9(a). The Fig. 9(a) and (b) correspond to front and right hand side micrographs of Fig. 7. The ledge alignment parallel to the designed direction is a fundamental structural problem of the hetero-interface. A misfit dislocation is not easy to observe by high resolution electron micrograph, because the dislocation core tends to spread out along the interface. Conventional bright field micrograph is better fitted for the observation. After all, the misfit dislocation image is visible only when the spacing is large. The average spacing of the vertical stain lines in Al_2O_3 side shown in Fig. 4 agrees with the spacing of an array of misfit dislocations corresponding to the 2% misfit of the (0001)_{Al_2O_3} // [111]_{Nb} interface.

V. Characterization of the Electronic Structure

Although the bonding state is not analysed by the present high resolution electron microscope, by a further increase in both the resolution and electron beam coherency of the microscope, the information could be made explicit in future. From the point of view of materials science, the atomic structure is significant only indirectly; The structure is only means to assess the bonding state which in principle directly governs the properties of the materials. Electron microscopy of the electronic structure is a dream but is indispensable for ceramic-metal joining because the principal question is the nature of bonding when metal and ceramic bondings face to each other. The present author must confess this naive question has been his major thrust to initiate this study.

Recent photoelectron spectroscopic investigation by Ohuchi[60] gives certain bonding information although it is the averaged information over the thin niobium atomic layers which have been deposited on the (0001) plane of alumina. The spectrum changes with increase in the deposition as shown in Fig. 10 indicated that niobium atom make Nb–O bonding first. It was concluded by Ohuchi[60] that oxygen exposed on the surface of alumina forms partly ionic and partly covalent bonding with
microscopy with certain bonding information would be revolutionary to this scene.
Characterization of atomic and electronic structures of the ceramic-metal interface is geared at present primarily to improve the mechanical properties, especially the embrittlement by the thermal stress which is unavoidable when two parties have to be chosen by the engineering need. The design of the interface with structural mechanism to relax the thermal stress is currently most pressing. High resolution electron microscopy is regarded as an indispensable tool to characterize the interface structures such as misfit dislocations and atomic ledges which should play a crucial role at both elevated and ambient temperatures by either nonconservative or conservative motions in spite of other modern techniques such as STM constantly coming up to the stage. Analysis of the bonding state by HREM is a dream but a pressing one in order to characterize the ceramic-metal joining most directly and fundamentally.

REFERENCES