

Formation of growing integrated layer [GIL] between ceramics and metallic materials for improved adhesion performance

Masahiro Yoshimura^{a,*}, Takamasa Onoki^a, Mikio Fukuhara^b,
Xinmin Wang^b, Kazuhiro Nakata^c, Toshio Kuroda^c

^a *Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama, Japan*

^b *Institute of Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai, Japan*

^c *Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka, Japan*

Received 4 September 2007; received in revised form 21 September 2007; accepted 24 September 2007

Abstract

In the ceramic/metal joining and coating, the most difficult problem is how to overcome poor adhesion of ceramic layers by their cracking and/or peeling arising from their intrinsic brittleness. On the basis of accumulated results and discussion, we propose a novel concept and technology of formation “Graded Intermediate Layer” or “Growing Integrated Layer” [GIL] between ceramics and metallic materials to improve the adhesion performance. Those GIL(s) can be prepared from a component of the metallic materials by chemical and/or electrochemical reactions in a solution at low temperatures of RT–200 °C. BaTiO₃ or SrTiO₃/TiO_x GIL films on Ti plates formed by hydrothermal–electrochemical method showed good adhesion. CaTiO₃/Al₂O₃/Ti₂Al GIL films on TiAl exhibited excellent adhesion and anti-oxidation performances. The GIL strategy is effective for metallic alloys and bulk metallic glasses because they generally contain active component(s).

© 2007 Elsevier B.V. All rights reserved.

Keywords: Ceramic; Metal; Joining; Coating; Integration; Adhesion

1. Introduction

Metallic materials including alloys, metallic glasses, etc., have excellent mechanical properties, high machinability, high productibility, high durability, etc., thus they have widely been used in various areas of applications as structural and functional materials. In order to improve their refractory properties, anti-oxidation, anti-wearing, chemical durability and bio-compatibility, ceramics formation and/or coating have been desired for a long time because ceramics materials have higher thermal, chemical and/or bio-chemical durabilities. Various methods for joining [1] of ceramics to metals have been studied (Fig. 1 [A]). Moreover, many methods for coating/deposition of ceramics on metals have been developed for ceramics/metal boundaries as shown in Fig. 1 [B] [1–6]. Particularly, surface modification/alteration treatments have been studied based upon recent development of nano-technologies. Nano-scale bonding between ceramics and metallic materials have been established

in those surface modifications and alterations. However, those surface treatments have rather scarcely succeeded for practical applications in mechanical, structural and thermal bulk materials because interfacial bondings between ceramics coatings and metal substrates are insufficient to overcome the accumulated mechanical and thermal stresses [1–3]. Therefore, cracks occur in the layer of ceramics which are brittle in nature when the accumulated stress exceeds a critical value [7]. In order to improve the adhesion performance without cracking and peeling of ceramic layer, multiple layered, laminated, integrated, graded and diffused coatings have been investigated to decrease the stress accumulation, however, it is not easy particularly when the interface is sharp. Diffused even widely diffused interface(s) of more than micron sizes are rather preferable for joining and coating of bulk ceramics on metallic materials.

2. Proposed novel ceramics/metal joining and its formation process

Based upon the facts and consideration described above, we propose herewith a novel ceramics/metal joining with strong

* Corresponding author. Tel.: +81 45 924 5323; fax: +81 45 924 5358.
E-mail address: yoshimura@msl.titech.a.jp (M. Yoshimura).

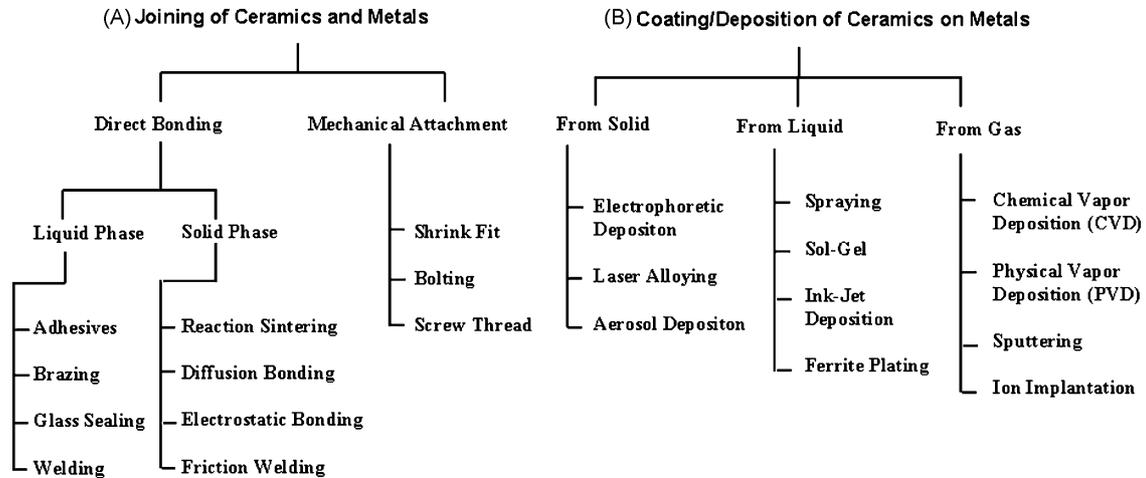


Fig. 1. Various methods of [A] joining of ceramics and metals and [B] coating/deposition of ceramics on metals. This figure was made by modifying the data from Refs. [1–3] and recent data [4–6].

adhesion as shown in Fig. 2. It consists of one compositionally and/or functionally graded intermediate layer [GIL] with two widely diffused interfaces: the first one is between the bulk metallic glass or alloy and the graded intermediate layer [GIL], and the second one is between the ceramics and the graded intermediate layer [GIL]. The first interface can be formed when one of the metal components is changed into other phase(s) by the reaction with another component from the environment like; i.e. $M + 1/2O_2 = MO$. Other components of metallic materials can give a diffused interface because they shift to a M-poor composition when M component diffuses into the MO layer (It is general in the oxide scale formation).

In this process, the metallic materials with multi-components like as bulk metallic glass(es) and alloy(s) are preferable. In particular, if the metallic glass or alloy contains a very reactive component like Ti, it can grow on the bulk metallic materials with its “root” in the bulk. We can give a name, “Growing Integrated Layer or Graded Intermediate Layer [GIL],” for this layer and “Growing Integration Process [GIP]” for its formation process. They are relating to reactive eutectic joining [1,8] and active metal blazing [9] in the point where reacted layer(s) is formed by interfacial reactions, but different in the point where the reactive component exists in the starting metallic materials.

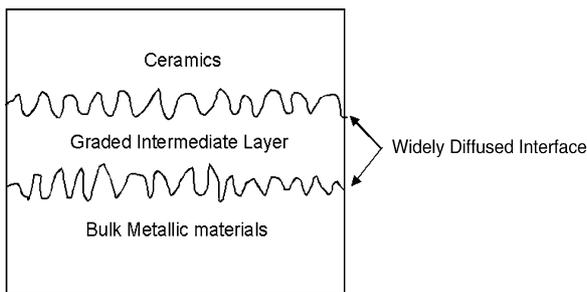


Fig. 2. A novel strategy for strong adhesion between ceramics and metallic materials. [GIL] “Graded Intermediate Layer” or “Growing Integrated Layer” with widely diffused interfaces between it and metallic material or ceramic material.

This type of growing integrated layer [GIL] of oxide films grown from the “seed,” i.e., the most reactive component in the bulk metallic materials is interesting as a novel processing of oxide film formations. Especially, the oxide film can be fabricated in a solution at low temperatures as RT-200 °C when chemical and/or electrochemical potentials can be added. Thermal stress accumulation can be avoided in those low temperature formations of the ceramic film on the metal. We are showing several examples as follows.

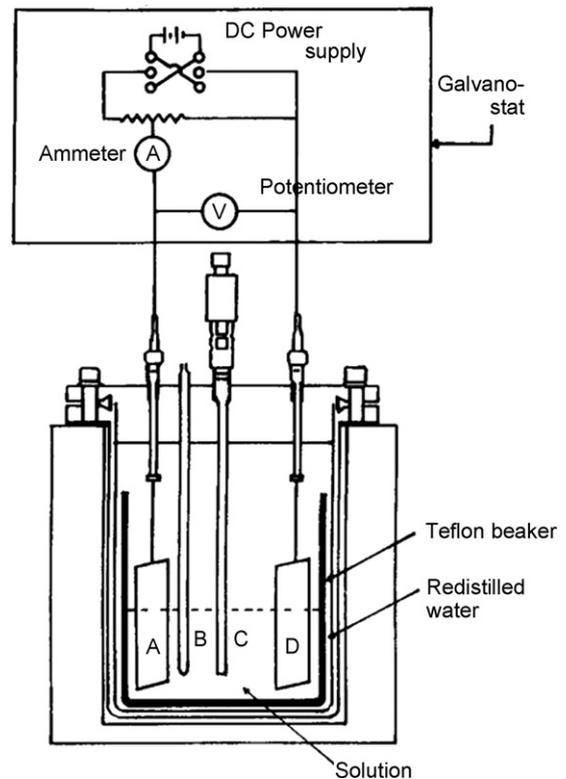


Fig. 3. Schematic illustration of experimental equipment for hydrothermal-electrochemical method. (A) Cathode (Pt plate), (B) thermocouple, (C) stirrer and (D) anode (Ti plate).

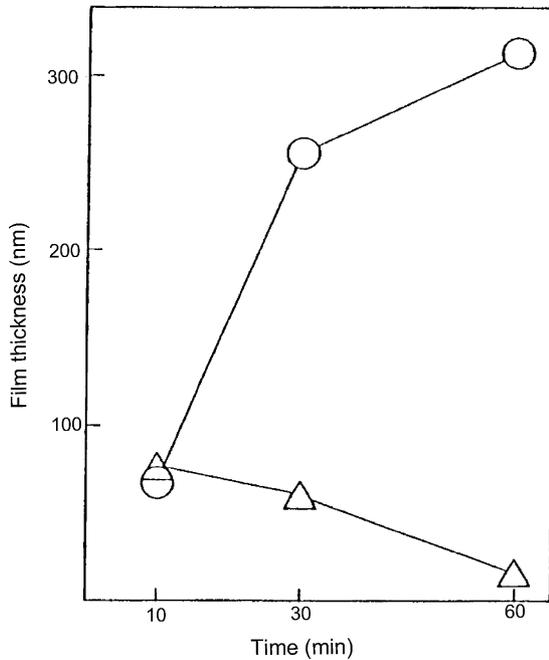


Fig. 4. Change of BaTiO₃ film thickness with current density of 15 mA/cm² (○) and 0 mA/cm² (△) and reaction time, on the Ti-deposited glass substrates at 200 °C in 0.5N-Ba(OH)₂ solution.

3. BaTiO₃ (or SrTiO₃)/TiO_x films on Ti substrate by hydrothermal–electrochemical method [10–15]

In 1989, Yoshimura, et al. reported crystalline BaTiO₃ films could be fabricated on Ti substrate in Ba(OH)₂ solution at 100–200 °C with an electrical current density of 0–15 mA/cm² [10]. Since the anodic oxidation and anodic dissolution of Ti component was observed as illustrated in Fig. 3, this method could be called “Hydrothermal–Electrochemical Method.” [10,11] Fig. 4 demonstrates that the film thickness increases with electrical current and time up to >300 nm [12,13]. The film was lustrous like a mirror and free from any visible defects. Adhesion of the film on the Ti plate was so strong that no exfoliation was observed after bending the specimen as shown in Fig. 5 [12]. A detailed study of such a SrTiO₃ film on Ti plate

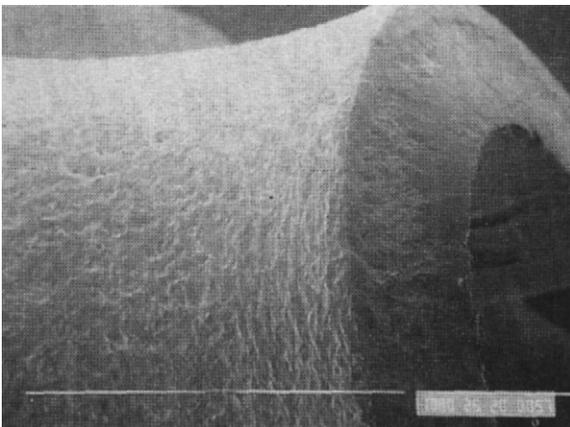


Fig. 5. BaTiO₃ film on Ti plates formed at 200 °C in 0.5N-Ba(OH)₂ solution for 30 min. No exfoliation was observed even after bending the specimen (bar = 1 mm).

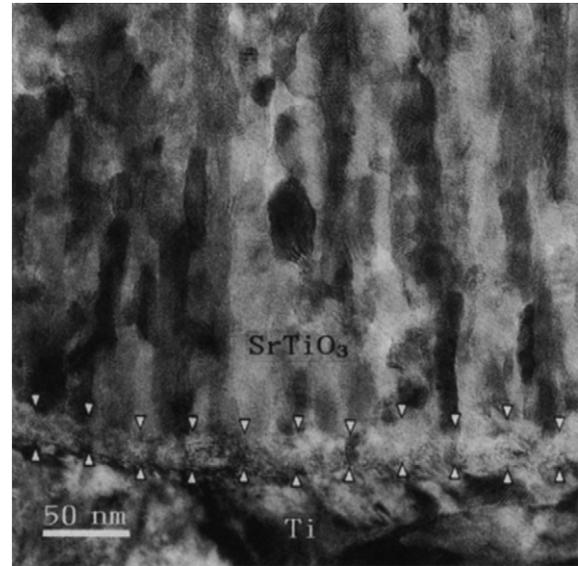


Fig. 6. Magnified TEM image for SrTiO₃ film on Ti substrate grown in 0.5 M gr(OH)₂ solution of pH 14.2 at 150 °C. A polycrystalline intermediate layer of Ti-oxides can be observed between SrTiO₃ and Ti shown by arrows.

revealed the existence of the intermediate layer of Ti-oxides between SrTiO₃ and Ti layers (Fig. 6) [15]. We believe that the intermediate layer could strengthen the adhesion of SrTiO₃ ceramic film.

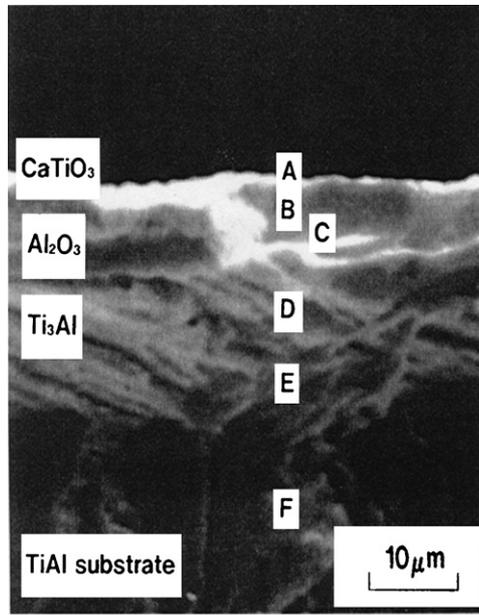
4. CaTiO₃/Al₂O₃/Ti₂Al grown films on TiAl [16,17]

A similar hydrothermal–electrochemical method was applied to the CaTiO₃ coating on TiAl polycrystalline plates. In a Ca(OH)₂ solution at 200 °C for 2 h, crystalline CaTiO₃ films with ~3 μm thickness were fabricated [16]. This CaTiO₃ film could improve the anti-oxidation behavior in air at 900 °C from non-coating sample. We studied extensively to improve anti-oxidation behaviors as well as adhesion behaviors of coated oxide layers. When a CaTiO₃ coated sample was oxidized in a pack of TiO₂ powders at 900 °C for 24 h or in a low vacuum at 1200 °C encapsulated in a quartz tube, an internal Al₂O₃ layer could be formed beneath of the CaTiO₃ coat because an Al-rich layer was prepared by the depression of Ti component due to CaTiO₃ formation. The growing integrated layer (GIL of CaTiO₃/Al₂O₃/Ti₂Al on TiAl as seen in Fig. 7 could outstandingly improve the adhesion and the thermal durability of the sample. Fig. 8 demonstrates that the CaTiO₃ + Al₂O₃ GIL could stop the oxidation even after the cyclic oxidation test of 5 h × 10 times in air at 900 °C [17]. It was almost equivalent to the champion data of anti-oxidation treatments for TiAl samples at that time.

5. Summary

The summary of this work can be given as follows:

- (1) A ceramics layer on metallic materials has a difficult to form a strong adhesion by its cracking and/or peeling arising from its intrinsic brittleness.



	Ti	Al	Ca
A	0. 5 4	0. 0 0	0. 4 6
B	0. 0 6	0. 9 2	0. 0 1
C	0. 0 6	0. 9 4	0. 0 0
D	0. 7 1	0. 2 9	0. 0 0
E	0. 6 5	0. 3 5	0. 0 0
F	0. 5 2	0. 4 8	0. 0 0

Fig. 7. GIL films of CaTiO_3 (A)/ Al_2O_3 (B and C)/ Ti_2Al (D and E) on TiAl (F) formed by heat treatment under encapsulated in a quartz tube at 1200°C for 24 h after CaTiO_3 coating by hydrothermal–electrochemical method in a $\text{Ca}(\text{OH})_2$ solution at 200°C .

(2) To improve the adhesion performance, we propose “Graded Intermediate Layer” or “Growing Intergraded Layer” both can be written as GIL with diffused interface(s) would be preferable between ceramics and metallic materials.

- (3) Those GIL(s) may be grown from a reactive component of the metallic material by chemical and/or electrochemical reaction(s) in a solution at low temperatures of RT– 200°C .
- (4) Such low temperature formation of the ceramic film on metallic material is beneficial to prevent residual thermal stress(s).
- (5) BaTiO_3 or $\text{SrTiO}_3/\text{TiO}_x$ GIL films on Ti plates formed by hydrothermal–electrochemical method showed good adhesion.
- (6) $\text{CaTiO}_3/\text{Al}_2\text{O}_3/\text{Ti}_2\text{Al}$ GIL films on TiAl exhibited excellent adhesion and anti-oxidation performances.
- (7) Metallic alloys or bulk metallic glasses might be rather preferable to form such GIL(s) because they are multi-components and containing active component(s) in most cases.

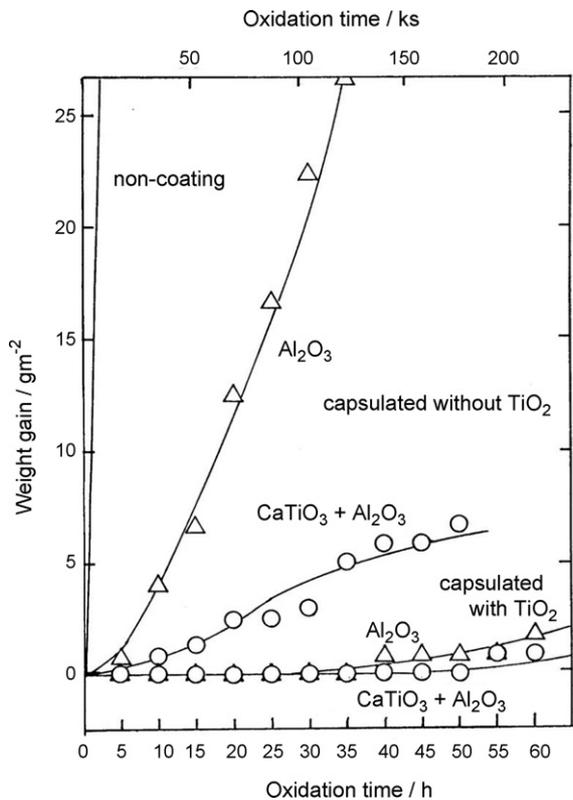


Fig. 8. Cyclic oxidation tests for various TiAl specimens, at 900°C in air for 5 h for every cycle. GIL films of $\text{CaTiO}_3/\text{Al}_2\text{O}_3/\text{Ti}_2\text{Al}$ on TiAl formed by TiO_2 pack oxidation in a quartz tube at 900°C demonstrate excellent adhesion and anti-oxidation performances.

Acknowledgements

The authors are thankful for our colleagues studied in experiments to form the GIL films.

References

- [1] For example K. Sugauma, T. Okamoto, M. Koizumi, M. Shimada, Am. Ceram. Soc. Bull. 65 (1986) 1060–1064.
- [2] Y. Yunzhi, K. Kyo-Han, L. Joo, Ong. Biomater. 26 (2005) 327–337.
- [3] L. Xuanyong, K.C. Paul, D. Chuanxian, Mater. Sci. Eng., R 47 (2004) 49–121.
- [4] M. Yoshimura, J. Mater. Sci. 41 (2006) 1299–1306.
- [5] M. Yoshimura, J. Ceram. Soc. Japan 114 (2006) 888–895.
- [6] A. Matsuo, R. Gallage, T. Fujiwara, T. Watanabe, M. Yoshimura, J. Electroceram. 16 (2006) 533–536.
- [7] S.R. Radin, P. Ducheyne, J. Mater. Sci. Med. 3 (1992) 33–42.
- [8] A.H. Carim, J. Am. Ceram. Soc. 73 (1990) 2764.
- [9] M. Singh, T. Shpargel, G.N. Morscher, R. Asthana, Mater. Sci. Eng. 412/413 (2005) 123–128.

- [10] M. Yoshimura, S.-E. Yoo, M. Hayashi, N. Ishizawa, *Jpn. J. Appl. Phys.* 28 (1989) L2007–L2009.
- [11] S.-E. Yoo, M. Hayashi, N. Ishizawa, M. Yoshimura, *J. Am. Ceram. Soc.* 73 (1990) 2561–2563.
- [12] N. Ishizawa, S.-E. Yoo, M. Hayashi, M. Yoshimura, *MRS Symp. Proc.*, 200, 1990, pp. 57–62.
- [13] N. Ishizawa, H. Banno, M. Hayashi, S.-E. Yoo, M. Yoshimura, *Jpn. J. Appl. Phys.* 29 (1990) 2467–2472.
- [14] K. Kajiyoshi, K. Tomono, Y. Hamaji, T. Kasanami, M. Yoshimura, *J. Am. Ceram. Soc.* 77 (1994) 2773–2776.
- [15] K. Kajiyoshi, Y. Hamaji, K. Tomono, T. Kasanami, M. Yoshimura, *J. Am. Ceram. Soc.* 79 (1996) 613–619.
- [16] M. Yoshimura, W. Urushihara, M. Yashima, M. Kakihana, *Intermetallics* 3 (1995) 125–128.
- [17] M. Yoshimura, W. Urushihara, M. Yashima, M. Kakihana, *Proceedings of 3rd SAMPE Symposium*, 1993, pp. 1471–1475.