Fabrication and Mechanical Properties of Al_2O_3/TiC/Ni Symmetric Functionally Graded Materials Doped with Cu and Cu_2O†

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Abstract

Symmetric functionally graded materials in the system of Al_2O_3/TiC/Ni with three different outer layers of the Al_2O_3-10vol%Cu, Al_2O_3-(5vol%Cu + 5vol%Cu_2O) and Al_2O_3-10vol%Cu_2O were prepared by SHS/HIP process. Highly compressive residual stresses were induced in the Al_2O_3 matrix, resulting in enhancement of both hardness and toughness of the outer layer. Their tribological properties were investigated. A compressive residual stress is found to improve wear resistance of these FGMs.

KEY WORDS : (functionally graded materials) (compressive residual stress) (mechanical properties) (wear resistance)

1. Introduction

Ceramics are expected as a tribological material to be used at high temperatures in corrosive environments and under clean conditions without lubricant because ceramics have high heat, corrosion and wear resistance. However, the friction coefficient of ceramics in the dry condition is relatively high as a tribological material. When metals are applied to the sliding parts of a machine, lubricant oil and grease are often used to decrease the friction and wear of sliding parts. These lubricants not only reduce the friction and wear of sliding parts but also prevent corrosion of metals. In the case of ceramics, water and alcohol can be used as the lubricant.

Ceramics are toughened by inducing compressive stress into the surface. The design of a layered structure is a popular method of inducing such compressive stresses into the surface using the thermal expansion mismatch between the outer and inner layers. For example, SiC/AlN[1], homogeneous/inhomogeneous Al_2O_3+Al_2TiO_5[2], Al_2O_3-containing mullite/ZrO_2-containing alumina[3] and β-Sialon/Si_3N_4[4] are reported to show improvement of strength and indentation toughness. In our previous study, Al_2O_3/TiC/Ni symmetric functionally graded materials (FGMs), one of the layered structure materials, were fabricated by self-propagating high-temperature synthesis-aided hot isostatic pressing (SHS/HIP)[5]. A compressive residual stress was induced in the surface Al_2O_3 layers because the coefficient of thermal expansion of the inner TiC-Ni cermet layer is larger than that of the surface Al_2O_3 layer.

In this study, Cu and Cu_2O were doped in the outer Al_2O_3 layers of the Al_2O_3/TiC/Ni FGM. Cu and Cu_2O were expected to show superior tribological properties of the surface of FGMs because Cu and Cu_2O are relatively soft. The objective of the present study is to investigate mechanical and tribological properties of the Al_2O_3/TiC/Ni FGM doped with Cu and Cu_2O.

2. Experimental Procedure

Specifications of the raw materials used in this study are listed in **Table 1**. The graded structure and composition of green bodies prepared for sintering are shown in **Fig.1**. The powders of each layer were wet-mixed in ethyl alcohol by ball milling. Three kinds of the surface layer were prepared, Al_2O_3-10vol%Cu, Al_2O_3-(5vol%Cu + 5vol%Cu_2O) and Al_2O_3-10vol% Cu_2O. The composi-

† Received on November 29, 1999

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Transactions of JWRI is published by Joining and Welding Research Institute of Osaka University, Ibaraki, Osaka 567-0047, Japan.

Table 1 Characteristics of raw materials

	Purity (%)	Mean Particle Size (μm)	Manufacturer
Al_2O_3	99.99	0.4	Sumitomo Chemicals Co.,Ltd.
Cu	99.99	1.0	Kojundo Chemical Laboratry Co.,Ltd.
Cu_2O	99	3.0	Kojundo Chemical Laboratry Co.,Ltd.
TiC	99.3	1.7	Japan New Metals Co.,Ltd.
Ni	98.6	0.4	Sumitomo Metal Mining Co.,Ltd.
Mo_2C	99.5	1.5	Japan New Metals Co.,Ltd.

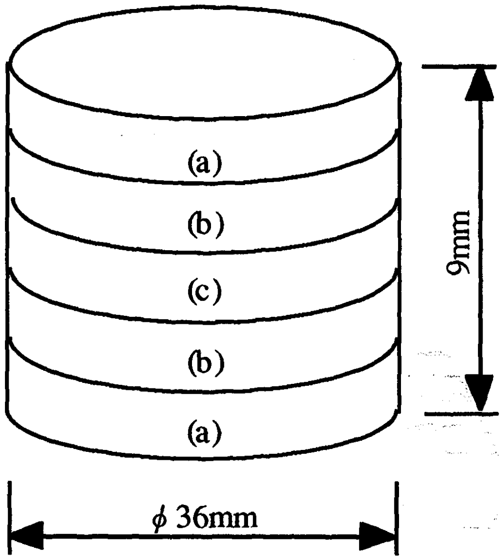

Fig.1 Arrangement of a graded green body.
(a) Al_2O_3 + 10vol%Cu, (5vol%Cu + 5vol%Cu_2O), 10vol% Cu_2O
(b) TiC + 51vol% Al_2O_3 + 2.6vol%Ni
(c) TiC + 20vol%Ni + 6.6vol%Mo_2C

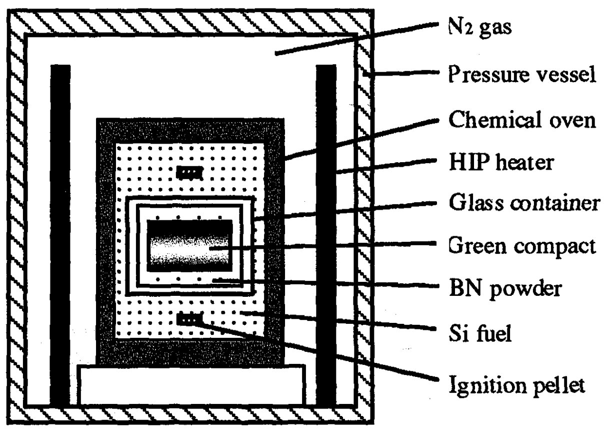

Fig.2 Schematic diagram of the SHS/HIP equipment.

tion of the intermediate layer was fixed as TiC+51vol% Al_2O_3+2.6vol%Ni. The central layer was TiC+20vol%Ni +6.6vol%Mo_2C. The Mo_2C is a popular sintering aid for the TiC-Ni cermet. After drying, the powder mixtures were stacked in a cylindrical die with a symmetrical arrangement of composition and press-formed to a green body, which was vacuum sealed into a borosilicate glass capsule with a BN powder bed. The encapsulated green body was sintered by the SHS/HIP process.

Fig.2 shows a schematic diagram of the SHS/HIP equipment. The chemical oven made of carbon is placed in the HIP apparatus. In the chemical oven, the glass container is placed and surrounded with 40 g waste silicon powder (purity 93%) which is used as a fuel for nitriding combustion of silicon. The ignition pellets of a thermite agent are embedded in the silicon powder. When the glass container is heated to 1030℃ under nitrogen gas pressure, which is applied up to 100MPa in HIP, the silicon fuel is ignited by the exothermic reaction of the thermite agent. The temperature reaches about 2500℃ instantaneously because of the high heat of formation of silicon nitride (748kJ/mol). The sample is kept at 1150℃ for 30 minutes for annealing and then cooled in the HIP.

The sample size was $\phi 32 \times 6$ mm after sintering. The thickness of the outer, intermediate and central layer were 1mm, 1mm and 2mm, respectively. After the sample was lapped with 0.1μm diamond slurry, the residual stress on the surface of the outer layer was measured by an X-ray diffraction method for Al_2O_3. Young's modulus and Poisson's ratio of the Al_2O_3 used for the stress analysis were 400GPa and 0.23, respectively. The Vickers hardness of the surface was measured with a load of 9.8N. Evaluation of the fracture toughness was made using the indentation fracture (IF) method with a load of 9.8N. The radius of the median crack, c, and the length of the half-diagonal of the indent, a, were mesured using an optical microscope. The K_{IC} value can be calculated by the following expression[6].

$$(K_{IC}\,\phi\, H_v a^{1/2})(H_v/E\,\phi)^{2/5} = 0.129(c/a)^{-3/2}$$

where ϕ is a material-independent constant. E is Young's modulus. Hv is Vickers hardness.

Table 2 Residual stress at the surface of the monolithic and graded materials

Materials	Residual stress (MPa)
Monolithic Al_2O_3	0±20
Monolithic Al_2O_3-10vol%Cu	60±30
Monolithic Al_2O_3-(5vol%Cu+5vol%Cu_2O)	30±20
Monolithic Al_2O_3-10vol%Cu_2O	40±30
Al_2O_3/TiC/Ni FGM	−220±20
Al_2O_3-10vol%Cu/TiC/Ni FGM	−280±40
Al_2O_3-(5vol%Cu+5vol%Cu_2O) /TiC/Ni FGM	−170±60
Al_2O_3-10vol%Cu_2O/TiC/Ni FGM	−150±50

Tribological tests were carried out on a reciprocal ball-on-block tribometer with an Al_2O_3 ball (3/8 inches in diameter) in water as illustrated in **Fig.3**. The span of the reciprocal sliding motion was 16mm. The test was performed at a sliding velocity of 32mm s^{-1} and a constant applied load of 20N. The accumulated sliding distance was 2500m. The friction coefficient was calculated from the moment of force measured by the test machine just before finishing the test. The specific wear rate was calculated from the volume loss evaluated by stylus surface profilometry. A specific wear rate for the Al_2O_3 ball was calculated from the volume loss determined by optical microscopy.

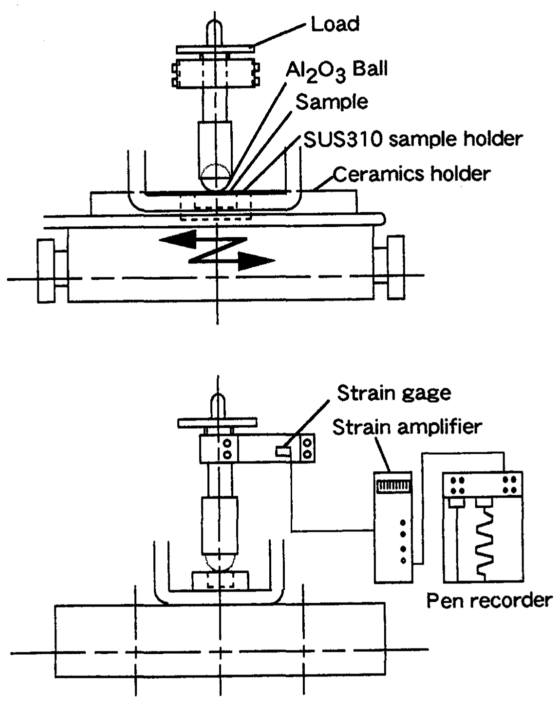

Fig.3 Schematic of reciprocal ball-on-block tribometer.

Monolithic Al_2O_3, monolithic 10vol%Cu-Al_2O_3 and Al_2O_3/TiC/Ni FGM were also fabricated and evaluated in the same way in order to compare with the Al_2O_3/TiC/Ni FGMs doped with Cu and Cu_2O.

3. Results and Discussion

3.1 Residual stress

Table 2 shows the residual stresses for monolithic and graded materials prepared in this study. No stress was induced in the monolithic Al_2O_3. The coefficient of thermal expansion of Al_2O_3 (α=8.2×10^{-6} K^{-1}) is smaller than that of Cu (α=16.2×10^{-6} K^{-1}), but larger than that of Cu_2O (α=1.9×10^{-6} K^{-1}). Therefore, the compressive residual stress of the outer Al_2O_3 layer is expected to be induced by doping with Cu. However, the tensile stress was induced in the Al_2O_3 matrix in all materials by the doping of Cu and Cu_2O into the monolithic Al_2O_3. The tensile stress might be induced because Young's modulus of Cu (E=136 GPa) and Cu_2O (E= 100 GPa~)[7] is significantly smaller than that of Al_2O_3 (E=400 GPa), so that the tensile stress remains in the Al_2O_3 matrix.

The residual stress at the surface of Al_2O_3/TiC/Ni FGM was about -220MPa due to the thermal expansion mismatch between the outer Al_2O_3 layer and the inner TiC-Ni layer. Although the Al_2O_3 matrix of the surface layer of Al_2O_3/TiC/Ni FGM was doped with Cu and Cu_2O, higher compressive residual stress as high as 150~280MPa were induced. The interpolation of Cu and Cu_2O could not affect directly the inner stress due to their lower Young's modulus and the higher compressive stress should be induced by the volume reduction of Al_2O_3 to balance of the inner stress between the outer and inner layers.

Table 3 Hardness of monolithic and graded materials

materials	Hardness (GPa)
Monolithic Al_2O_3	17.6
Monolithic Al_2O_3-10vol%Cu	13.7
Al_2O_3/TiC/Ni FGM	19.6
Al_2O_3-10vol%Cu/TiC/Ni FGM	14.5
Al_2O_3-(5vol%Cu+5vol%Cu_2O) /TiC/Ni FGM	15.3
Al_2O_3-10vol%Cu_2O/TiC/Ni FGM	17.1

3.2 Hardness and toughness

Hardness at the surfaces of monolithic and graded materials is shown in **Table 3**. Hardness and toughness of the monolithic Al_2O_3-(5vol%Cu+5vol%Cu_2O) and the Al_2O_3-10vol%Cu_2O could not be measured, because the indentation mark was irregular due to the poor sinterability. Doping of Cu and Cu_2O in the outer Al_2O_3 layer reduced the hardness compared with that of the Al_2O_3/TiC/Ni FGM, because the Cu and Cu_2O are soft materials (Mohs hardness 3~4). The hardness of the Al_2O_3-10vol%Cu/TiC/Ni FGM was higher than that of the monolithic Al_2O_3-10vol%Cu due to the compressive residual stress induced in the Al_2O_3 matrix of the outer layer.

The surface toughness of the monolithic and graded materials is shown in **Fig.4**. The Al_2O_3/TiC/Ni FGM doped with Cu and Cu_2O showed high toughness due to the high residual compressive stress. The hardness of FGMs increased with the increase of the residual compressive stress induced in the Al_2O_3 matrix. In addition, the toughness of the Al_2O_3/TiC/Ni FGM doped with Cu and Cu_2O increased, probably because of the effect of the particle dispersions. Therefore, the toughnesses of the Al_2O_3-(5vol%Cu+5vol%Cu_2O)/TiC/Ni FGM, and the Al_2O_3-10vol%Cu_2O/TiC/Ni FGM were almost the same as that of Al_2O_3/TiC/Ni FGM although their compressive residual were lower.

3.3 Tribological Properties

The friction coefficients of the monolithic, and the graded materials are shown in **Table 4**. Friction coefficients of all materials tested ranged between 0.33 to 0.36. No apparent effect of doping Cu and Cu_2O in the outer Al_2O_3 layer to decrease the friction coefficient of FGMs was observed under this test condition in water.

Specific wear rates of samples and Al_2O_3 balls are

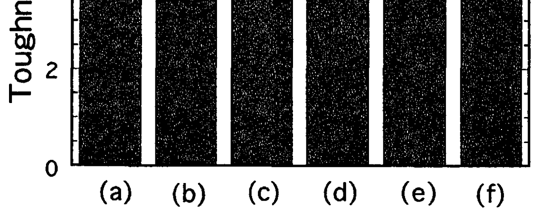

Fig.4 Toughness of (a) monolithic Al_2O_3,
(b) monolithic Al_2O_3-10vol%Cu,
(c) Al_2O_3/TiC/Ni FGM,
(d) Al_2O_3-10vol%Cu/TiC/Ni FGM,
(e) Al_2O_3-(5vol%Cu+5vol%Cu_2O)/TiC/Ni FGM and
(f) Al_2O_3-10vol%Cu_2O/TiC/Ni FGM.

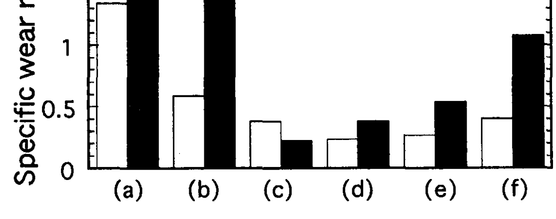

Fig.5 Specific wear rates for an Al_2O_3 ball sliding against (a) monolithic Al_2O_3,
(b) monolithic Al_2O_3-10vol%Cu,
(c) Al_2O_3/TiC/Ni FGM,
(d) Al_2O_3-10vol%Cu/TiC/Ni FGM,
(e) Al_2O_3-(5vol%Cu+5vol%Cu_2O)/TiC/Ni FGM and
(f) Al_2O_3-10vol%Cu_2O/TiC/Ni FGM.

Table 4 Friction coefficient of monolithic and graded materials

materials	Friction Coefficient
Monolithic Al_2O_3	0.36
Monolithic Al_2O_3-10vol%Cu	0.33
Al_2O_3/TiC/Ni FGM	0.33
Al_2O_3-10vol%Cu/TiC/Ni FGM	0.35
Al_2O_3-(5vol%Cu+5vol%Cu_2O) /TiC/Ni FGM	0.33
Al_2O_3-10vol%Cu_2O/TiC/Ni FGM	0.36

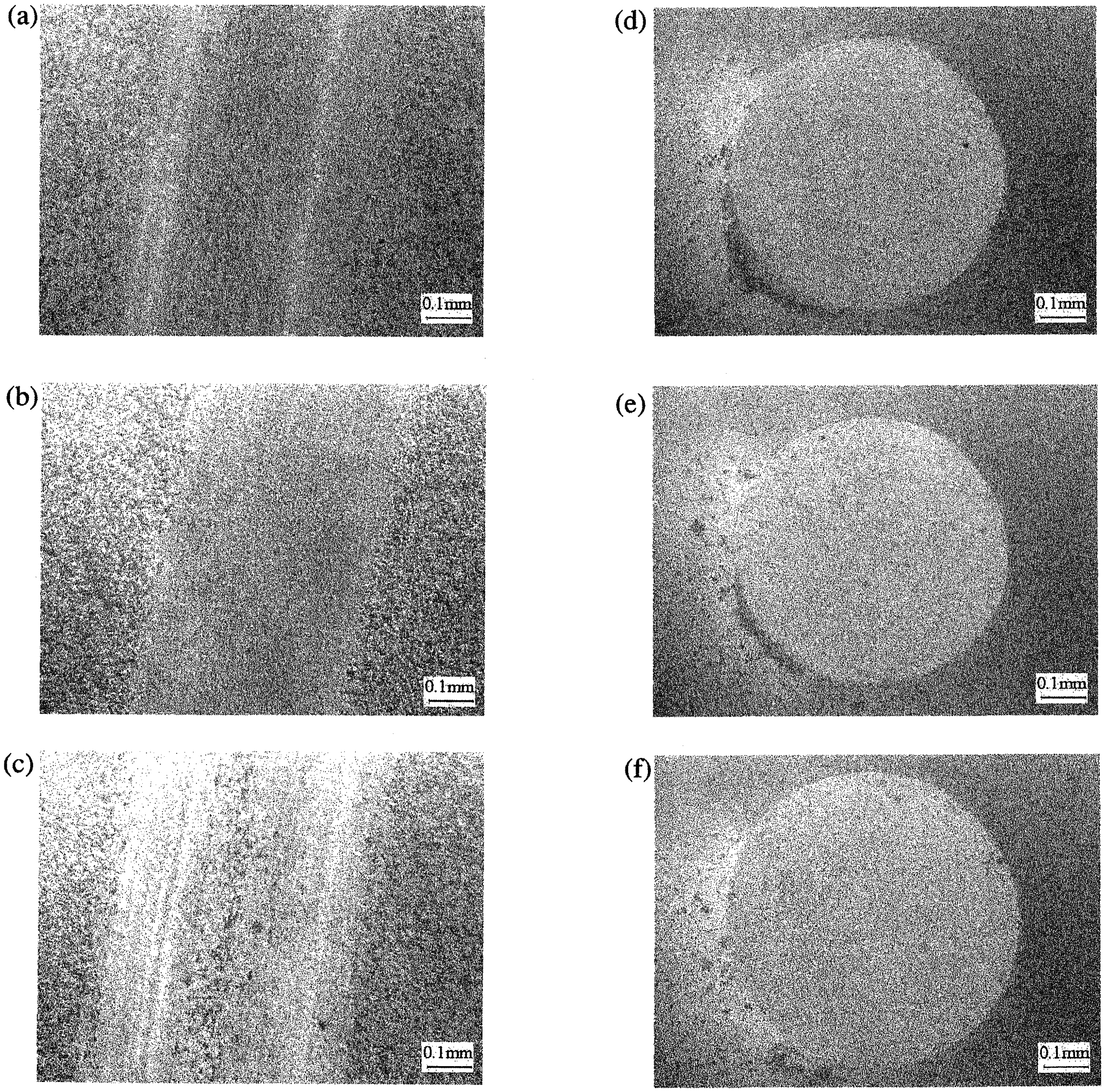

Fig.6 Optical photograghs of worn parts of samples; (a) Al_2O_3-10vol%Cu/TiC/Ni FGM, (b) Al_2O_3-(5vol%Cu+5vol%Cu_2O)/TiC/Ni FGM and (c) Al_2O_3-10vol%Cu_2O/TiC/Ni FGM against (d), (e) and (f) Al_2O_3 balls, respectively.

shown in **Fig.5**. Optical photographs of worn part at the surface of an FGMs and an Al_2O_3 ball after the wearing test are given in **Fig.6**. The specific wear rate of FGMs decreased compared with those of the monolithic Al_2O_3 and the 10vol%Cu-Al_2O_3. The wear rate of the Al_2O_3 ball against FGMs also decreased compared with that of the Al_2O_3 ball against the monolithic Al_2O_3 and the 10vol%Cu-Al_2O_3. Fig.6 shows that the width of worn tracks of the Al_2O_3/TiC/Ni FGM doped with Cu were smaller than those of Al_2O_3/TiC/Ni FGM doped with Cu_2O.

The wear resistance of the 10vol%Cu-Al_2O_3/TiC/Ni FGM showed the best result in the Al_2O_3/TiC/Ni FGMs doped with Cu and Cu_2O. The FGMs had superior wear resistance because the residual compressive stress induced in the Al_2O_3 matrix of FGMs is high. Generally the wear of ceramics starts with the occurrence of microcracks and their propagation. Residual compressive stress can prevent such microcracks effectively.

4. Conclusions

Dense Al_2O_3/TiC/Ni FGMs doped with Cu and Cu_2O were fabricated by SHS/HIP. Their mechanical and tribological properties were evaluated. The obtained results can be summarized as follows.

(1) The high residual compressive stress of 150MPa to 280MPa was induced in the Al_2O_3 matrix of the outer layer because of the thermal expansion mismatch between the surface layer and the inner layer. High residual stress enhanced the surface hardness and toughness of FGMs.

(2) Doping of Cu and Cu_2O into the Al_2O_3/TiC/Ni FGMs could not decrease the friction against Al_2O_3 in water. The wear resistance was improved because of the compressive stress which can prevent the damage of initial wear.

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