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Stress corrosion behavior of nickel base titanium carbide cermets prepared by direct consolidation during combustion reaction in 50% aqueous sodium hydroxide solution

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Nickel base titanium carbide cermets are useful engineering materials for turbine blade and electrical brush with abrasive wear resistance [1]. The cermets can be fabricated by direct consolidation during a combustion reaction between titanium, graphite and matrix metals like nickel and molybdenum. Holt and Munir obtained a combustion product with 99% of the theoretical density by rapidly heating a mixture of elemental titanium, carbon, nickel and aluminum powders in a graphite die up to the ignition temperature of about 800 °C, followed by applying mechanical pressure during combustion reaction [2]. The technique is quite simple but has shown problems with undesirable phases due to complex reactions among the initial reactants. Choi *et al.* studied the phase equilibrium during the combustion reaction and showed that densification rate of the combustion products decreased due to the remaining carbon caused by a relatively rapid consolidation [3]. This means that un-reacted carbon existed in the products and the carbon content in the titanium carbide depended on the combustion reaction temperature. Since the mechanical and chemical properties of the titanium carbide cermets depend on the non stoichiometric number of the carbide and composition of the matrix materials, the cermets formed by the combustion reaction will show complicated stress corrosion behavior. Although many studies have been carried out on the stress corrosion behavior of various cermets, little information is available on the stress corrosion mechanism of the materials formed by the combustion reaction [4]. Hence, the objective of this study is to investigate stress corrosion behavior of the cermets formed by the direct consolidation during combustion reaction for their industrial applications.

In this study, titanium, nickel and molybdenum powders (Aesar, NH, USA) with less than 45 μm in size and 99.5, 99.9 and 99.9% in purity, respectively and graphite powders (Aldrich, WI, USA) with less

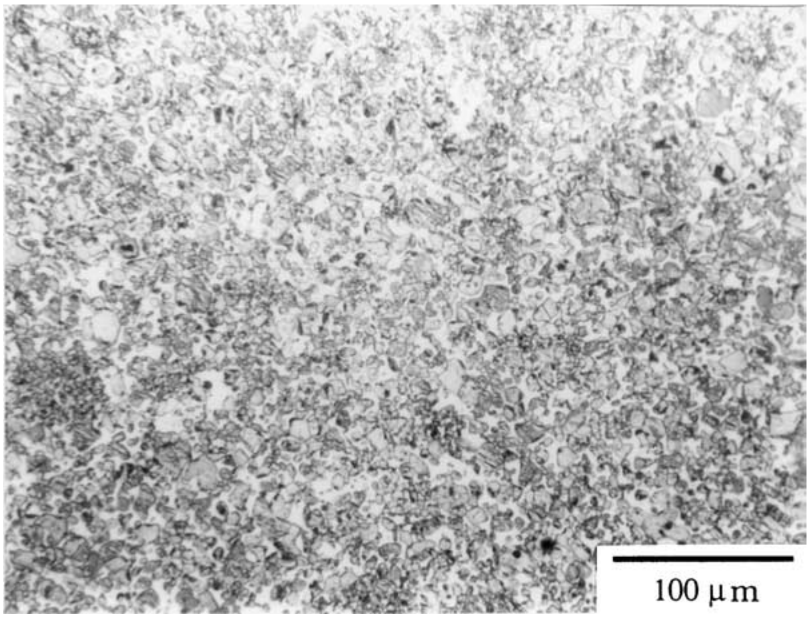

Figure 1 Micrograph of $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo-1.43 wt% C cermet prepared by direct consolidation during combustion reaction.

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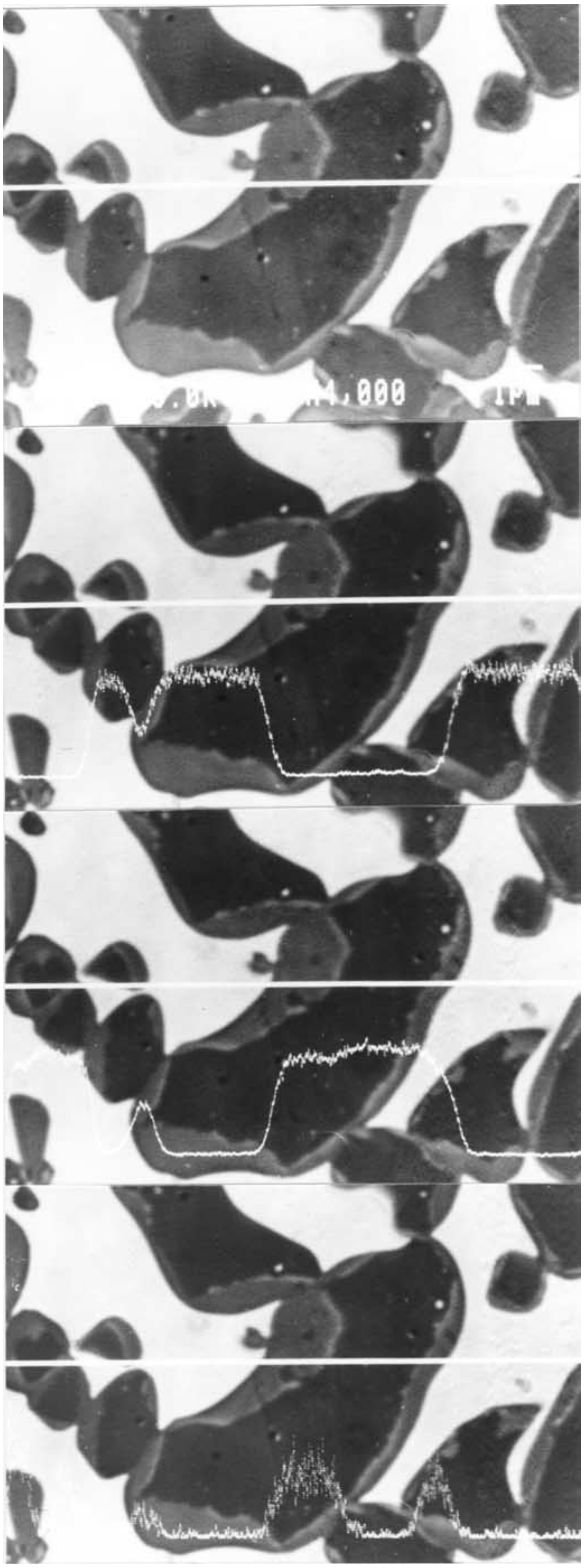

Figure 2 Line analysis profile of Ni, Ti and Mo by EPMA for $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo-1.08 wt% C (top) back-scattered electron image (middle 1) Ni profile (middle 2) Ti profile (bottom) Mo profile.

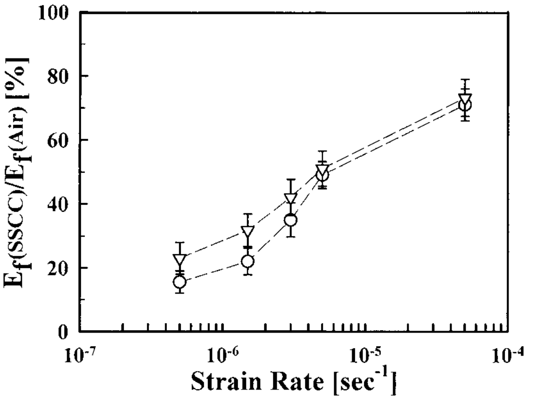

Figure 3 Strain rate dependence of SCC resistance of (∇) $TiC_{0.87}$-49.5 wt% Ni-3.5 wt% Mo-1.08 wt% C and (○) $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo-1.43 wt% C cermets in deaerated aqueous 50% NaOH + 500 ppm of HCl solution at 25 °C.

than 1 μm in average particle size were used for the preparation of specimen. Stoichiometric amounts of titanium and graphite powders were weighed on an electron balance inside a glove box with the exposure of less than 0.1 ppm of hydrogen and 0.2 ppm of oxygen. Each titanium, graphite and matrix powders such as nickel and molybdenum was mechanically blended by a ball mill for 1 h in inert argon atmosphere. The combustion reaction of the reactant mix was ignited by an electrical resistance heater installed at the bottom of the graphite die under hot pressing at 1350 °C. The densities of the materials after the combustion reaction were determined with a helium gas autopycrometer (Micrometrics, autopycrometer 1320). The carbon content in the combustion products was analyzed with a carbon sulfur determinator with the accuracy of 0.002 wt% for carbon contents up to 5.0 wt% (LECO CS 244). Microstructural observation and compositional analysis were performed with an optical microscope (Nikon 1400) and an electron microprobe analyzer (Jeol EPMA C1) after etching the specimen with Murakami's solution ($K_3Fe(CN)_6$:NaOH:H_2O = 10 g: 10 g:100 ml). Corrosion and stress corrosion behavior was determined by electrochemical method with a potentiostat (Gammy 2000) and by constant elongation test method at the strain rates of 5×10^5–$5 \times 10^{-7} s^{-1}$ in de-aerated aqueous 50% NaOH with 500 ppm of HCl solution at 25 °C with a slow strain rate tester (Ahnlab 1500), respectively.

Fig. 1 shows micrograph of titanium carbide nickel molybdenum cermets prepared by a direct consolidation. The titanium carbide particles were irregularly round and separated by the nickel matrix. Average carbide diameter and contiguity of the cermets determined by statistical treatment were about 2.60 μm and 0.24, respectively. The carbon analysis of carbide revealed that compositions of the cermets prepared by direct consolidation during combustion reaction were $TiC_{0.87}$-49.5 wt% Ni-3.5 wt% Mo-1.08 wt% C and $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo 1.43 wt% C, respectively. In order to know the compositional distribution, chemical analysis was carried across the carbide. Fig. 2 shows a back scattered electron image of $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo-1.43 wt% C and the results of the line analysis by electron microprobe analyzer. There are three regions which have different chemical compositions. According to the line analysis, nickel was not observed in carbide core region. Most of molybdenum atoms exist at the interface between carbide core and nickel matrix, and titanium is concentrated at the core region of carbide, and some of them were found in matrix. From the compositional analysis, the interface phase was identified to be (Ti, Mo)C_x phase. Yamada *et al.* reported that the refinement of carbide was due to the formation of δ-phase, (Ti, Mo)C_x, which would retard the diffusion of nickel from the liquid nickel into the intermetallic phase and the solution of carbide into the nickel binder [5]. Since titanium carbide/nickel molybdenum cermets formed by SHS have excess carbon inside, it is interesting to consider the effect of carbon on the microstructural development. Based on quaternary and ternary phase diagrams of Ti Ni Mo-C [6], the relative amount of δ-phase to β-phase increases with excess carbon content. This means that the TiC_x-Ni-Mo cermet formed by SHS has a larger amount of δ-phase than the cermet produced by other processes due to the excess carbon. Hence, the addition of molybdenum and the existence of excess carbon, which originated from the combustion reaction would result in retardation of the carbide coarsening through the formation of δ-phase around titanium carbide core. Considering the microstructural observation by EPMA in Fig. 2, the addition of molybdenum and the existence of excess carbon, which originated from the combustion reaction result in retarding the carbide coarsening through the formation of δ-phase around titanium carbide core. The δ-phase around titanium carbide slightly increased total volume fraction of carbide, however, the carbide composition is different from the initial carbide composition. Fig. 3 shows the stress corrosion cracking (SCC) resistance of $TiC_{0.87}$-49.5% Ni-3.5% Mo 1.08 wt% C and $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo-1.43 wt% C expressed by fracture energy ratio with strain rate at 25 °C. As shown in this figure, stress corrosion resistance decreased with decreasing strain rate and carbon content in the carbide, however, increased with the carbon content in the matrix. Various mechanisms of stress corrosion considered the dynamic strain processes at the crack tip were proposed [7]. The mechanisms are common to explain the accelerating effects of continuous strain on stress corrosion in which the strain dependence of stress corrosion behavior is related to the formation of slip site at crack tip and anodic dissolution rate of the sites such as pits. Since the mechanical and corrosion effects on the stress corrosion resistance are predominant at higher strain rate and lower strain rate, respectively, stress corrosion resistance showed the minimum value at the strain rate at which corrosion effect is adequately compensated for mechanical effect. In order to evaluate corrosion effect such as anodic dissolution on the stress corrosion resistance, corrosion potential and corrosion rate were electrochemically determined. Table I is the corrosion potential and corrosion rate with carbon and molybdenum contents. The corrosion potential and corrosion rate of the cermet in 50%

TABLE I Mechanical properties and corrosion behaviors of TiC_x-49.5 wt% Ni cermet with molybdenum additions in aqueous 50% NaOH + 500 ppm HCl solution at 25 °C

TiC_x	Mo (wt%)	C (wt%)	Corrosion potential (V_{SHE})	Corrosion rate ($10^6 \times Acm^2$)	Yield strength (MPa)	Ultimate tensile strength (MPa)
$TiC_{0.87}$	0	1.08	−0.9637	3.70	907	1125
$TiC_{0.84}$	0	1.43	−1.9983	4.23	910	1134
$TiC_{0.87}$	3.5	1.08	−1.0574	5.42	1508	1875
$TiC_{0.84}$	3.5	1.43	−1.1678	8.52	1512	1888

NaOH-500 ppm HCl solution were $-992.7\ mV_{SHE}$ and $3.8 \times 10^{-6}\ Acm^2$ for $TiC_{0.87}$-49.5 wt% Ni-3.5 wt% Mo-1.08 wt% C and $-1074.8\ mV_{SHE}$ and $8.12 \times 10^{-6}\ Acm^2$ for $TiC_{0.84}$-49.5% Ni-3.5% Mo-1.43 wt% C, respectively. In case of TiC_x 50 wt% Ni cermets without molybdenum addition, the corrosion potential was increased with the carbon content in the titanium carbide, however, corrosion rate was decreased with the carbon content in the carbide. Fig. 4 is the scanning electron micrograph of the corrosion surface, where matrix were selectively attacked. Although nickel base titanium carbide cermet have relatively good corrosion resistance against general attack [8], the corrosion potential of the alloy decreases with small amounts of molybdenum. Nickel matrix on the surface was selectively dissolved at sites where carbides were present. This suggests that δ-phase with less corrosion resistance than the carbide becomes pits at the initial stage of corrosion. This implies that the addition of molybdenum and the existence of excess carbon in matrix reduce corrosion resistance of the cermets. Although it is difficult to verify the corrosion mechanism, we expect that anodic dissolution effect of $TiC_{0.84}$-49.5% Ni-3.5% Mo-1.43 wt% C cermet on stress corrosion resistance was higher than that of $TiC_{0.87}$-49.5 wt% Ni-3.5 wt% Mo-1.08 wt% C because the corrosion resistance of the cermet decreased with molybdenum and carbon contents in matrix and increased with carbon content in carbide. In order to evaluate the mechanical effect on stress corrosion resistance, the yield strength and ultimate tensile strength of the cermets were determined. As shown in Table I, the yield strength and ultimate tensile strength of the cermets without molybdenum addition were 907 MPa, 1125 MPa for $TiC_{0.87}$-50 wt% Ni and 910 and 1134 MPa for $TiC_{0.84}$-50% Ni, respectively. The yield strength and ultimate tensile strength of the cermets with molybdenum addition were 1508 MPa, 1875 MPa for $TiC_{0.87}$-49.5 wt% Ni-3.5 wt% Mo-1.08 wt% C and 1512 MPa, 1888 MPa for $TiC_{0.84}$-49.5% Ni-3.5% Mo 1.43 wt% C, respectively. The strength of the cermet was increased with carbon and molybdenum contents in matrix. The yield strength and ultimate tensile strength differences between $TiC_{0.87}$-49.5% Ni-3.5% Mo-1.08 wt% C cermet and $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo-1.43 wt% C cermet were 0.26 and 0.69%, which were less than about 1%. This implied that the mechanical effect on both TiC_x-Ni-Mo cermets in Fig. 3 was almost similar, especially at higher strain rate. Hence, the stress corrosion resistance of $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo-1.43 wt% C was much lower than that of $TiC_{0.87}$-49.5 wt% Ni-3.5 wt% Mo-1.08 wt% C due to the corrosion effect such as anodic dissolution, especially at slow strain rate. This means that the stress corrosion mechanism of the TiC_x Ni-Mo cermet formed by direct consolidation during combustion reaction is related to the enhanced anodic dissolution due to the phases with carbon and molybdenum in the cermets in the titanium carbide and matrix, respectively.

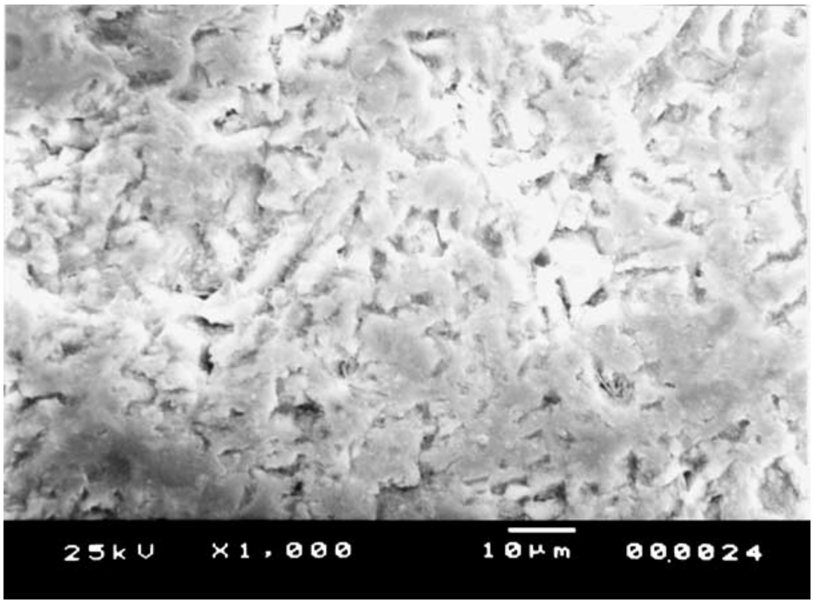

Figure 4 Scanning electron micrograph of the corroded surface of $TiC_{0.84}$-49.5 wt% Ni-3.5 wt% Mo-1.08 wt% C cermet prepared by direct consolidation during combustion reaction.

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