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Microstructure evolution of in-situ (Ti,W)C-Al_2O_3 particle-reinforced alloy fabricated by gas tungsten arc cladding

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ABSTRACT

This paper reports the fabrication of TiC-Al_2O_3 or (Ti,W)C-Al_2O_3 ceramic reinforced metal matrix composites (MMC) using gas tungsten arc cladding. For fabrication of the MMC, an in-situ reaction was used to reduce oxides by employing C and Al as reducing materials during the cladding process, and the strengthened particles formed on the surface by solid state reaction were then grown through interaction in the metal matrix. The reactions forming phases in this system were subsequently examined through thermodynamic calculations. Results showed that TiC and Al_2O_3 peaks were observed in XRD for the reduction of TiO_2 and WO_3 by Al and C. The cladded hardfacings were covered by a composite slag zone, which consisted of Al_2O_3 particles embedded in Al and Ti based ceramic matrix, and that carbide particles such as TiC and (Ti,W)C were distributed intensively inside the MMC zone. Most of the TiC particles in the MMC zone had a slow growth rate because the interface controlled the growth; however, some particles that highly interacted with metals exhibited a dendrite structure. (Ti,W)C particles without dendrite growth formed a spherical shape, and the size of the particles was controlled by diffusion of the solute. Following the dissolution and precipitation process, (Ti,W)C-strengthened particles were found to have a sintering-like core/rim structure. Furthermore, the microhardness of the clad obtained was 600–900 $HV_{0.2}$, which is significantly better than that obtained with commercial TiC powder.

1. Introduction

Ceramic-reinforced metal matrix composites (MMC) provide multi-functionality using the advantages of both metals and ceramics, and as such are the focus of many scientific studies. Tungsten carbide (WC) reinforced MMCs were first used as a military material during World War I [1], and research has since been conducted to replace WC carbides with ceramics such as TiC, due to the scarcity of tungsten resources. MMCs are most widely applied in the coating market industry, where they are used in processes such as cutting, rolling, piercing, drawing, and milling [2]. In addition, MMCs have been studied as promising candidates in a variety of fields, such as the aerospace industry, the military, and in 3-D printing [3,4]. In particular, TiC and Al_2O_3 reinforced MMCs have been studied because they are cost-effective materials with high melting points, excellent hardness, superior wearing properties, and outstanding chemical resistance [5].

The traditional and simple method used to incorporate ceramic particles in the metal matrix involves mechanical mixing. However, no phase change occurs between the metal and ceramic particles when using this method [6]; it is also limited cohesion between matrix and hard phase particles [7]. On the other hand, in-situ reaction method of fabricating coatings or specimens simultaneously with the formation of reinforced particles by chemical reactions have been studied [8]. For example, carbide particles can be produced through a reduction reaction using oxides and metals as raw materials, where the sizes and shapes of particles fabricated using this method are considerably changed [9], and mechanical properties are also improved due to the reduction of particle size and the strengthening of the interface between the metal and the ceramic.

In manufacturing processes such as self-propagating high temperature synthesis (SHS) and conventional vacuum sintering, reduction reactions between low-cost oxide materials and reducing materials (such as C and Al) have been applied [10–13]. Research using the SHS process has shown that the formation reaction between WC and TiC generates a large amount of heat that propagates the formation spontaneously, even under adiabatic conditions [14]. However, the process proceeds at a very high speed and a heterogeneous microstructure and pores are easily developed. In contrast, the particles synthesized from vacuum sintering become homogeneous through growth over a relatively longer time. For example, solid solution carbide particles develop complex

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microstructures, and a variety of compositions and shapes have been observed during the growth process due to the driving force of thermodynamic stability differences. Although this improves the mechanical properties [15,16], entire sample including substrate as well as coating part should be heated in furnace. Therefore, the size is also limited. In contrast, gas tungsten arc cladding (GTAC) can increase the temperature locally on the surface, and the heat input can be precisely controlled by various parameters such as position, speed, current, and voltage [17].

Several recent studies have been conducted to fabricate MMC on Fe-based alloys using GTAC processes. According to Sharifitabar, a TiC-Al_2O_3-Fe composite was prepared using a TiO_2-Al-C-Fe system [18]. The Fe content plays an important role in the formation of nano-sized TiC, and the formation mechanism is suggested to be related to the reinforcement of particles when using the SHS process. In addition, the effects of using multiple carbides in MMCs have been reported for TiC-WC [14], TiC-TiB_2 [5,19], and (Ti,V)C solid solution carbides [20], and raw materials used in the reduction reaction have also been varied as $FeTiO_3$ [21] or FeTi [22,23] in addition to TiO_2. Most previous studies using GTAC have focused on reporting improved mechanical properties, such as hardness and wear resistance, whereas mechanism studies based on microstructure changes are rather limited [24]. The effect of TiC rim - Al_2O_3 core structure on properties [5,18] and the deterioration of mechanical properties due to dendritic structure of TiC [25,26] has been reported by others.

This study analyzes ceramic-reinforced MMCs fabricated using an in-situ reduction reaction via a GTAC process. In this study, TiO_2-WO_3-C-Al-Fe-Ni is used as a raw material on a 304 stainless-steel substrate. The microstructure is controlled via process variables and metallurgical changes, and formation and growth of reinforcing phases are discussed. Mechanical properties are also evaluated using hardness measurements, and microstructure and phase analysis are conducted using a scanning electron microscope (SEM) and X-ray diffraction (XRD), respectively.

2. Experimental procedure

2.1. Materials and clads preparation

The experimental procedure involved powder paste preparation and the cladding process. Table 1 shows specifications of the raw powders used in powder paste mixtures. All powders were sieved with a 125 mesh to remove any amounts of hugely agglomerated powder. Table 2 lists the four kinds of systems according to composition and method employed in mixing powder to fabricate a TiC-Al_2O_3 or (Ti,W)C-Al_2O_3 strengthened clad zone. Powder-mixing was conducted using a conventional mixing method that employed simple mechanical mixing and high energy milling (HEM) with a planetary mill (Fritsch, Pulverisette 5, Germany). In the HEM process, oxides and carbon only were pre-placed in a jar with a ball and rotated at 250 rpm for 10 h without solvent. WC-Co balls were used at a ball-to-powder ratio of 30: 1. A conventional ball mill mixing process was conducted to mix the metal powders with ceramic particles, and mixing was maintained at 150 rpm for 10 h. An H_2O-based solution containing 2 wt% poly vinyl alcohol was added to prepare a powder paste with viscosity. AISI 304 stainless steel was used as a substrate for the cladding, and its composition was obtained through analysis of the molten metal (Table 3). The powder paste was doctor-bladed in a 10 mm × 100 mm × 1.5 mm shape onto the substrate and then dried at a temperature of 110 °C for 24 h. The cladding process was conducted using a 6-axis robot (Kuka, KR 100–3, Germany) and a gas tungsten arc welder (Lorch, V40, Germany). Specific cladding conditions are shown in Table 4. The cladding speed was set to 1.8 mm/s and 1.2 mm/s to observe the growth of particles when the heat input was modified.

Table 1
Specifications of raw powders.

Powder	Particle size (μm)	Purity (%)	Supplier
TiO_2	< 20	> 99	Sigma-Aldrich
WO_3	< 20	> 99	Sigma-Aldrich
Ni	< 45	> 99	Praxair
Al	< 45	> 99	Sam-chun
Fe	< 45	> 99	CNPC powder
C	1.7[a]	> 99	Schunk
TiC	1.5[a]	> 99.7	Korloy

[a] The value represents average particle size.

2.2. Characterization

XRD analysis was used to conduct a phase analysis by an X-ray diffractometer (MiniFlex, Rigaku, Japan) with monochromatic Cu-Kα radiation (λ = 0.154056 nm) by applying 40 kV and 40 mA. The specimen for XRD was employed with the slag removed by polishing the surface. Powder morphology was observed with a field emission-scanning electron microscope (FR-SEM) (Quanta200F, Thermo Fisher, USA) using the secondary electrons (SE) mode. In addition, the microstructures of specimens were investigated using the back-scattered electrons (BSE) mode of the FE-SEM in conjunction with an energy dispersive spectrometer (EDS). The EDS results were measured at least five sites, and data corresponding to the average were used. To measure the area of reinforced particles, FE-SEM photographs were used for image analysis, and equivalent circle diameters were calculated from cross-section images [27]. Specimens for cross-section analysis were prepared by etching with mixing sulfuric acid, nitric acid and iron chloride. The mechanical properties were measured at a weight of 1.96 N for 15 s through Vicker's microhardness equipment (Mitutoyo, HM-200, Japan).

3. Results and discussion

3.1. Thermodynamic calculation

To investigate the preference of the reduction reaction of oxides by alloying elements, changes in the Gibbs' energy of reactions (ΔG) occurring when oxides (such as TiO_2 and WO_3) were reduced by Al and C were calculated using Factsage®, a commercial thermodynamic calculation software (Fig. 1). The values for ΔG with respect to the reaction between carbon and oxides (WO_3 and TiO_2) were negative when exceeded 632 °C and 1320 °C, respectively. However, ΔG was also a negative value over the entire temperature range when the two oxides were reduced by Al, which implies that alumina (Al_2O_3) and metal Ti could be formed as aluminum reacts with the oxides. The reduction of TiO_2 by C at high temperatures over 1645 °C was found to be more feasible than when it was reduced by Al, as the value of ΔG was more negative than that in the reduction by Al. In addition, the ΔG values for the WO_3 reduction reaction by the two reducing materials intersected at 2008 °C, which shows that reduction by C prefers a high temperature. The comparison of ΔG values for the two reducing materials shows that the formation of WC is more feasible than the formation of TiC.

To form a new phase during the cladding process, a sufficient amount of time is required to enable the materials to make contact and undergo a reaction, and the reaction needs to be thermodynamically stable. In the GTAC process, the temperature of the molten pool rises to 2500 °C, but at one point the temperature profile is in the form of a peak due to continuous movement of the heat source [28]. Powder activated through HEM increases the contact with liquid metal due to particle refinement and shortens the reaction time [29]. Also, increasing the holding time, which can be controlled by travel speed, at a higher temperature than the reaction temperature can improve homogeneity and stability through particle growth, by enabling interaction with the metal matrix; this occurs during solidification.