O U R N A L O F

Ceramic Processing Research

Simultaneous synthesis and consolidation of a nanocrystalline 8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}-Al₂O₃ composite by high-frequency induction heating

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Nanopowders of Fe_2O_3 , Cr, Si, and Al powders were fabricated by high-energy ball milling. A high-density nanocrystalline $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ composite was simultaneously synthesized and consolidated by a high-frequency, induction-heated sintering (HFIHS) method within two minutes from mechanically activated powders of Fe_2O_3 , Cr, Si, and Al. The advantage of this process is that it allows very quick densification to near theoretical density and prohibits grain growth in nano-structured materials. The hardness of the composite was about 1060 kg/mm².

Keywords: Nanostructured materials, Sintering, Synthesis, Hardness, Composite materials.

Introduction

Many industrial applications, such as in heating elements, high-tensile components in heat exchangers, or substrates for catalysts applied in catalytic converters and filter systems in automobiles require long-term resistance to oxidation. Iron-aluminium-chromium alloys are applicable as structural materials and coatings for high-temperature applications [1]. Their excellent corrosion resistance is due to the formation of a dense, protective alumina scale. Alumina $(\alpha$ -Al₂O₃ in particular) demonstrates a low oxidation rate constant, even at temperatures above 1,000 °C [2]. The effects of adding silicon to the high-temperature oxidation resistance and microwave properties of steels have been presented by several authors [3, 4]. They suggest that silicon has a beneficial effect on the oxidation resistance and microwave properties of steel. However, the alloy exhibits a low frictional resistance due to its low hardness. One method to improve hardness is adding Al₂O₃ to form composite nanostructured materials [5]. Traditionally, discontinuously reinforced metal matrix composites have been produced by several processes, including powder metallurgy, spray deposition, mechanical alloying, casting, and self-propagating high-temperature synthesis (SHS). A technique that uses SHS developed by Borovinskaya and coworkers [6] in the 1970s, refers to a process in which materials with a sufficiently high heat of formation are synthesized in a combustion wave, which after ignition, spontaneously propagates throughout the reactants and converts them into the product. SHS is extremely attractive, producing a high- purity product due to the volatilization of low boiling point impurities at elevated temperature, and high productivity due to very high reaction rates.

Nanocrystalline materials have received much attention as advanced engineering materials, due to their improved physical and mechanical properties [7, 8]. Nanomaterials typically possess high strength, high hardness, excellent ductility, and toughness. Therefore, increasing attention has been paid to developing potential nanomaterial applications [9]. The grain sizes are much larger in sintered materials than in pre-sintered powders, due to the rapid grain growth that occurs during the conventional sintering processes. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 2 µm or larger during conventional sintering [10]. So, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. Highfrequency, induction-activated sintering methods, which can be used to quickly manufacture dense materials within 2 minutes, can control grain growth effectively [11, 12].

The goals of this study were to fabricate a newly-dense nanocrystalline Al_2O_3 -reinforced Fe-Cr-Al-Si composite within two minutes from mechanically-activated powders via a high-frequency, induction-activated sintering method and to evaluate its hardness and grain size.

Experimental Procedures

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Powders of 99 % pure Fe_2O_3 (< 5 µm, Alfa Co.), 99.5%

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pure Al (< 45 μ m, Alfa Co.), 99.5% pure Si (< 45 μ m, Alfa Co.), and 99.8% pure Cr (< 10 μ m, Alfa Co.) were used as the starting materials. Fe₂O₃, 3.58Cr, 0.67 Si, and 4.1 Al powder mixtures were milled in a high-energy ball mill (Pulverisette 5 planetary mill) at 250 rpm for 4 h to produce activated nanopowders. Tungsten carbide balls (8.5 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of the balls to the powder was 30 : 1. Milling resulted in a significant reduction of the grain size.

After milling, the mixed powders were placed in a graphite die (outside diameter of 45 mm, inside diameter of 20 mm, height of 40 mm) and then introduced into an induced current activated sintering system (Eltek, South Korea), which is shown schematically in [11]. The four major stages in the synthesis are: Stage 1) evacuation of the system, Stage 2) application of a uniaxial pressure, Stage 3) heating of the sample by an induced current, and Stage 4) cooling of the sample. The process was conducted under a vacuum of 40 mtor(5.33 Pa).

Microstructural information was obtained from product samples that were polished at room temperature. Compositional and microstructural analyses of the products were conducted using X-ray diffraction (XRD) and a scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDAX). The Vickers hardness was measured by performing indentations on the sintered samples at a load of 5 kg and a dwell time of 15 s.

Results and Discussion

The X-ray diffraction results for the high-energy, ballmilled powders are shown in Fig. 1. The Fe₂O₃, Cr, Si, and Al reactant powders were detected, while the Fe-Cr-Al-Si alloy and Al_2O_3 were not detected. Based on the above



Fig. 1. XRD pattern of the mechanically activated Fe_2O_3 , Cr, Si, and Al powders.



Fig. 2. FE-SEM image and EDS of the mechanically activated Fe₂O₃, Cr, Si, and Al powders.

results, a mechanical alloy was not formed during the milling. Fig. 2 shows an FE-SEM image and EDS of high-energy, ball-milled powders. The powders are very fine and agglomerated. In EDS, O, Al, Si, Fe, and Cr are detected in the same position, and Fe, Cr, Al, and Si are also detected in the same position.

Fig. 3 shows the variations in the shrinkage displacement and surface temperature of the graphite die with heating time during the processing of the Fe-Cr-Al-Si and Al_2O_3 system. When an induced current was applied, the shrinkage displacement slowly increased with temperature up to (a) point, then increased abruptly at the lower temperature of 550 °C. The X-ray diffraction pattern of a sample heated to (a) point in Fig. 3 and 980 °C is shown in Fig. 4. In Fig. 4(A), The Fe₂O₃, Cr, Si, and Al reactant powders were detected, while in Fig. 4(B), the Fe-Cr-Al-Si alloy and Al_2O_3 were detected. Based on the above results, the synthesis was formed during the heating. The net reaction can be considered as a combination of the following two reactions:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 \tag{1}$$

$$2Fe + 3.58Cr + 2.1Al + 0.67Si \rightarrow 8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$$
(2)

Reaction (2) is the well known exothermic reaction for which the standard enthalpy of reaction ranges from -847 kJ to -811 kJ over the temperature range of 700 °C (just



Fig. 3. Variations of the temperature and shrinkage displacement with heating time during high-frequency, induction-heated sintering of the $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ composite.



Fig. 4. XRD patterns of the $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ system heated to (a) point (A) and heated to 980 °C (B).



Fig. 5. FE-SEM image of the $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al_2O_3 composite heated to 980 °C.

above the melting temperature of Al, 660 °C) to 1,500 °C (just below the melting point of Fe, 1,536 °C). The abrupt increase in the shrinkage displacement at the ignition temperature in Fig. 3 is due to the increase in density resulting from the change in the molar volume associated with the formation of $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ from the reactants (Fe₂O₃, Cr, Si, and Al) and the consolidation of the product.

An FE-SEM image of the 8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}-Al₂O₃ composite is shown in Fig. 5. The figure shows that the structure consisted of nanophases, and pores were not detected. Thus, nearly a full density of nanocomposite was obtained. The average grain sizes of the sintered Fe-Cr-Al-Si alloy and Al₂O₃ were not significantly larger than the initial powders, indicating the absence of significant grain growth during sintering. This retention of the grain size is attributed to the high heating rate and the relatively short exposure of the powders to the high temperature. The role of the current in sintering has been the focus of several attempts to explain the observed enhancement of sintering and the improved characteristics of the products. The role played by the current has been interpreted in terms of the rapid heating rate due to Joule heating, the presence of a plasma in pores separating powder particles, and the intrinsic contribution of the current to mass transport [13-16].

Vickers hardness measurements were made on polished sections of the $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ composite using a 5 kg_f load and a 15 s dwell time. The calculated hardness value of the $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ composite was 1060 kg/mm². This value represents an average of five measurements. This is considered to be the fracture toughness of $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ composite, because cracks were not produced around the indent. The absence of reported hardness and toughness values for the $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ composite precludes making direct comparisons to the results obtained in this study. However, the hardness and fracture toughness of Al₂O₃ with a grain size of 4.5 µm were previously

reported as 1,800 kg/mm² and 4 MPa·m^{1/2}, respectively [17]. The hardness of the $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ composite is less than that of monolithic Al₂O₃, but the fracture toughness is greater than that of Al₂O₃ due to the addition of the ductile Fe-Cr-Al-Si alloy.

Conclusions

Nanopowders of Fe_2O_3 , Cr, Si, and Al powders were fabricated by high-energy ball milling. Using the highfrequency, induction-activated sintering method, we accomplished simultaneous synthesis and densification of a nanostructured $8.33Fe_{0.24}Cr_{0.43}Al_{0.25}Si_{0.08}$ -Al₂O₃ composite from mechanically activated powders. Complete densification could be achieved within a processing time of two minutes under an applied pressure of 80 MPa and an induced current. The average grain sizes of the Fe-Cr-Al-Si alloy and Al₂O₃ prepared by HFIHS were lower than 100 nm, respectively. The average obtained hardness value was 1060 kg/mm².

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