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New Preparation of Powders with Fine Particles and Their High-Pressure Sintering Using SHS, SPS, and HIP

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SYNOPSIS

Various kinds of powder production methods (solution techniques) have been developed and utilized to prepare single-phase (monolithic or solid solution) and composite powders consisting of fine particles with a sharp size-distribution; sol-gel techniques using metal alkoxides and acetylacetonates, and a newly developed hydrazine method. The latter solution technique has some merits i.e. easy and simple process to produce fine sinterable powders at relatively low cost due to use of aqueous metal salts as starting materials. By adopting these powder preparation techniques, dense structural materials and functional perovskite oxides (rare-earth chromites), nanocomposite materials with high densities have been fabricated.

On the other hand, high-pressure techniques such as self-propagating high-temperature synthesis (SHS), spark plasma sintering (SPS), hot isostatic pressing (HIP), and their combined use have also been used for the fabrication of dense structural materials, i.e., silicides, nitrides, aluminides, borides, such as MoSi_2 , $\alpha\text{-Ti(N)}$, $\text{NiAl/ZrO}_2(3\text{Y})$, CrB , etc. The present paper describes briefly some characteristics of powders thus prepared, and mechanical properties of condensed materials fabricated using SHS, SPS, and HIP in relation to their microstructures.

KEY WORDS

solution technique, self-propagating high-temperature synthesis (SHS), spark plasma sintering (SPS), hot isostatic pressing (HIP)

1 Introduction

Main factors which decide mechanical, electrical, magnetic, and optical properties of ceramics and inorganic polycrystalline materials are, in the broader sense, their compositions (stoichiometric or nonstoichiometric compositions, solid solutions, and even oxygen deficiencies for the oxide ceramics) and their microstructures (nanostructures, functionally graded structures (FGM), and nanocomposites etc.). These two factors are chiefly controlled by both the raw materials (starting powders) and production process consisting of powder-compaction and heat treatment.

In the present study, a novel solution technique to produce fine oxide powders as for the starting materials, namely the hydrazine methods^{1,2)}, and various heat treatment techniques under high pressures from ~ 1 to ~ 200 MPa, i.e., self-propagating high-temperature synthesis (SHS)³⁾, hot isostatic pressing (HIP)^{4,5)}, and spark plasma sintering (SPS)^{6,7)} have been developed and utilized to fabricate dense functional and structural materials. And their mechanical and electrical properties have been investigated in relation

to their microstructure and compositions. This paper describes our studies as-mentioned above briefly, for example, dense $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ perovskite ceramics obtained from air-sinterable solid solution powders prepared by the hydrazine method²⁾, hot-isostatically pressed (HIP) $\text{Cr}_2\text{O}_3/5\text{vol}\%$ Mo nanocomposites using the sol-gel-derived (hydrazine method) fine powder⁴⁾, and $\text{NiAl/ZrO}_2(3\text{Y})$ composites fabricated by the combined use of SHS and SPS⁶⁾.

2 Formation, Sinterability and Characteristics of $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ Prepared by a Sol-Gel Technique Using Hydrazine²⁾

Lanthanum chromite LaCrO_3 and doped LaCrO_3 have been widely studied as a refractory conducting ceramics due to their electrical conductivity, high melting point ($> 2400^\circ\text{C}$), and oxidation or corrosion resistivity. In particular, doped LaCrO_3 ceramics with high electrical conductivity have been applied as electrodes for magnetohydrodynamic (MHD) power generators, interconnectors of solid oxide fuel cells (SOFCs), and conducting leads for ZrO_2 -based

heating elements. Unfortunately, LaCrO_3 shows poor sinterability and is very difficult to densify under ambient atmospheric conditions. The effect of additives and sintering atmosphere on the densification of LaCrO_3 have been widely investigated. Although the extensive literature is presented, the study of Mg^{2+} -substituted materials is still lacking with a few exceptions. In this study, we applied a new powder preparation method using hydrazine monohydrate to obtain reactive Mg^{2+} -substituted LaCrO_3 powder.

Preparation; Eight compositions, denoted A through H, were chosen for this study (Table 1). A mixed aqueous solution of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, was introduced in a five-necked flask and stirred for 10 min at room temperature, and then hydrazine monohydrate ($(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$) was added dropwise to the mixed solution at 80°C , with continuous stirring, until the resulting suspension reached pH 11.5. Then, the resulting suspension was heated for 2 h at the same temperature. The product was separated from the suspension by centrifugation, washed in hot water and then dried at 120°C under reduced pressure.

Formation of LaCrO_3 ; Fig. 1 (a) shows a DTA curve of the amorphous starting powder A, which consisting of aggregates ($< 20\text{ nm}$) of small transparent particles (Fig. 2(a)). After two successive endothermic peaks, a sharp exothermic peak was observed; this was found to result from the crystallization of monoclinic LaCrO_4 . In addition, an endothermic peak resulting from decomposition of LaCrO_4 at 725° to 805°C was also confirmed. In this temperature range TG data showed a weight decrease of 6.27% (Fig. 1(b)), corresponding to the decrease of $1/2 \cdot \text{O}_2$ per LaCrO_4 . The specimens above 810°C gave the characteristic XRD pattern of orthorhombic LaCrO_3 . The results indicate that LaCrO_4 decomposed into

LaCrO_3 and $1/2 \cdot \text{O}_2$ at 725° to 805°C . Fig. 2(b) shows a TEM photograph of LaCrO_3 powder prepared by heating for 1 h at 1000°C . Definite signs of particle growth were seen and many individual particles ($\sim 0.2\text{ }\mu\text{m}$) gave a roundish morphology.

Formation of $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$; Powders B through H were also amorphous. All of them, except for powder H, revealed exothermic and endothermic peaks corresponding to the crystallization of $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_4$ and decomposition of this into $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$, respectively. For powder H, the specimens heated at temperatures above the endothermic peak were mixtures of $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ and La_2MgO_x ; other powders above the endothermic peak showed a single-phase XRD pattern. Fig. 3 shows the

Fig.1 (a) DTA and (b) TG curves for starting powder A.

Table 1 Chemical compositions of starting powders and characteristics of $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ ceramics sintered for 2 h at 1600°C in air.

Sample	x in $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$	Bulk and relative density ($\text{Mg} \cdot \text{m}^{-3}$, %)	Grain size G_s (μm)	Activation energy E_a (eV)	Electrical conductivity σ at 1000°C ($\text{S} \cdot \text{m}^{-1}$)
A	0	6.36 (93.9)	2.1	0.15	1.1×10^2
B	0.05	6.37 (94.6)	2.5	0.14	4.1×10^2
C	0.10	6.36 (95.1)	3.0	0.13	7.1×10^2
D	0.15	6.39 (96.1)	3.7	0.12	8.8×10^2
E	0.20	6.46 (97.9)	3.9	0.12	1.9×10^3
F	0.25	6.46 (98.5)	4.3	0.11	3.2×10^3
G	0.30	—	—	—	—
H	0.35	—	—	—	—

Fig.2 TEM photographs of (a) as-prepared powder and (b) LaCrO_3 powder obtained by heating for 1 h at 1000°C .

variation of lattice parameters for $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ obtained by heating for 1 h at 900°C ; the lattice parameters a , b , and c increased linearly up to $x \sim 0.28$ with increased Mg^{2+} -content. Thus, single-phase $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ solid solution where $x = 0$ to 0.28 , was found to be formed at low temperatures by a sol-gel technique using hydrazine.

Characteristics of $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ ceramics; Calcined powders A to F ($1000^\circ\text{C}/1\text{ h}$) isostatically cold-pressed at 392 MPa were sintered for 2 h at 1600°C in air. All the sintered compacts exhibited only perovskite phase. Table 1 shows the bulk and relative densities of $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ ceramics; the relative densities increased with increased Mg^{2+} -content. Finally, $\text{La}(\text{Cr}_{0.75}\text{Mg}_{0.25})\text{O}_3$ ceramics had a density of 98.5% of theoretical. SEM photographs for fracture surfaces of LaCrO_3 and $\text{La}(\text{Cr}_{0.75}\text{Mg}_{0.25})\text{O}_3$ ceramics reveal a homogeneous structure consisting of fine grains from 2.1 to $4.3\text{ }\mu\text{m}$ (Fig. 4, Table 1). It should be noted that the dense ceramics could be fabricated by sintering for 2 h at 1600°C in air, suggesting that $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ powders prepared by the present method were highly sinterable.

Fig. 5 shows the temperature dependence of electrical

Fig.3 Lattice parameters of $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$ obtained by heating for 1 h at 900°C .

conductivity (σ) of several ceramics in a plot of $\log(\sigma T)$ against $1/T$; σ is well represented by the function $(1/T)\exp(-E_a/kT)$, where E_a is the activation energy. The linear dependence in this plot is characteristic of the small-polaron hopping transport. The data of E_a and σ at 1000°C are given in Table 1. Among these ceramics, $\text{La}(\text{Cr}_{0.75}\text{Mg}_{0.25})\text{O}_3$ showed the value of $3.2 \times 10^3\text{ S}\cdot\text{m}^{-1}$, in which the magnitudes of σ are comparable to those of Sr^{2+} - and Ca^{2+} -substituted LaCrO_3 . Increases in the conductivity up to the Mg^{2+} -substituting level of $x \leq 0.25$ must be attributed to the formation of Cr^{4+} ions as a result of charge compensation caused by the hopping polarons between Cr^{3+} and Cr^{4+} ions.

LaCrO_3 exists in two polymorphic modifications: orthorhombic (low-temperature form) and rhombohedral (high-temperature form). Reversible transformation between them occurs at $\sim 290^\circ\text{C}$. Fig. 6 shows an average value of thermal expansion coefficient α from room

Fig.4 SEM photographs for fracture surfaces of (a) LaCrO₃ and (b) La(Cr_{0.75}Mg_{0.25})O₃ ceramics.

Fig.5 Log(σT) for (a) LaCrO₃, (b) La(Cr_{0.85}Mg_{0.15})O₃, and (c) La(Cr_{0.75}Mg_{0.25})O₃ ceramics s as a function of 1/T.

Fig.6 Thermal expansion coefficients (room temperature to 1000°C) of La(Cr_{1-x}Mg_x)O₃ ceramics as a function of Mg²⁺-content.

temperature to 1000 °C, at which temperature SOFCs are operated. In the application of Mg-doped LaCrO₃ ceramics to interconnectors, the agreement of α between the ceramics and cubic ZrO₂ as an electrolyte is required. The average α value of 10.1 × 10⁻⁶ /K for La(Cr_{0.75}Mg_{0.25})O₃, which exhibited the highest α, was obtained; this coefficient was in good agreement with that (10.0 × 10⁻⁶ /K) of cubic ZrO₂(10Y).

3 Microstructure and Mechanical Properties of Hot-Isostatically-Pressed Cr₂O₃/5vol% Mo Nanocomposites⁴⁾

Cr₂O₃ is an important refractory material because of its high melting temperature (~2300 °C) and high-temperature oxidation resistance. The oxide shows poor sinterability in air and requires high temperatures > 1600 °C in reducing atmosphere to achieve high density. Previously we reported that dense Cr₂O₃ ceramics (98.8% of theoretical) were obtained by hot isostatic pressing (HIP) (1100 °C/2 h/196 MPa) using sol-gel-derived powder. Although among ceramics, Cr₂O₃ has a higher fracture toughness of ~ 4 MPa · m^{1/2}, the bending strength (260 MPa) is low. The purpose of the present study was to improve the strength of Cr₂O₃ ceramics by dispersion of metal-particulate. Dense Cr₂O₃/5vol% Mo nanocomposites (99.3% of theoretical) with improved strength could be successfully fabricated by HIPing (1200 °C/196 MPa/2 h).

Fabrication; Sol-gel-derived (hydrazine method) Cr₂O₃

Fig.7 TEM photograph of Mo powder.

Table 2 Characteristics of monolithic Cr_2O_3 and $\text{Cr}_2\text{O}_3/5\text{vol}\%$ Mo composite.

Composition $\text{Cr}_2\text{O}_3/\text{Mo}$ (vol%)	Bulk and relative density ($\text{Mg}\cdot\text{m}^{-3}$, %)	Grain size of Cr_2O_3 G_s (μm)	Bending strength σ_b (MPa)	Fracture toughness K_{IC} ($\text{MPa}\cdot\text{m}^{1/2}$)
100/0	5.16 (99.0)	3.7	280	3.9
95/5	5.42 (99.3)	0.35	620	4.6

powder (particle size $\sim 0.08\mu\text{m}$ after $900^\circ\text{C}/2\text{h}$ calcination) and commercially available Mo (99.9% pure), containing nanoscale and submicrometer-sized particles powders, as shown in Fig. 7 (a) and (b), were used as starting materials. Appropriate amounts of both powders with the composition of $\text{Cr}_2\text{O}_3/\text{Mo}=95/5\text{vol}\%$ ^{*1)} were mixed for 1 h by planetary ball-milling with zirconia balls and ethanol in a zirconia pot and then dried at 80°C . The mixed powders were pressed uniaxially into pellets at 98 MPa and then isostatically cold-pressed at 343 MPa. The green compacts, covered with BN powder, were sealed in a Pyrex glass tube under a reduced pressure. HIPing conditions for densification of powder compact were as follows: (i) a heating rate of $600^\circ\text{C}/\text{h}$, (ii) an increasing pressure rate of $\sim 180\text{MPa}/\text{h}$ above 800°C , and (iii) sintering for 2 h at 1200°C and 196 MPa. Monolithic Cr_2O_3 was also fabricated under the same conditions.

Microstructure and mechanical properties; The sintered compacts consisted only of Cr_2O_3 and Mo; no reaction products were detected. Table 2 shows the bulk and relative densities of the composite materials. The relative densities were calculated using the theoretical densities of Cr_2O_3 ($5.21\text{Mg}\cdot\text{m}^{-3}$) and Mo ($10.20\text{Mg}\cdot\text{m}^{-3}$). The addition of Mo promoted the densification of Cr_2O_3 ; Mo-dispersed

Fig.8 SEM (secondary electron image) photograph for fracture surface of $\text{Cr}_2\text{O}_3/5\text{vol}\%$ Mo composite.

Cr_2O_3 composites gave a higher density (99.3%) than that (99%) of monolithic Cr_2O_3 . Fig. 8 shows a SEM (secondary electron image) photograph for the fracture surface of monolithic Cr_2O_3 , indicating the grain size of $\sim 3.7\mu\text{m}$. The Mo particles in the composite could not be clearly resolved by the observation; however, the presence of homogeneous-dispersed Mo particles was proved by the backscattered electron image on the polished surface (Fig. 9). Fig. 10 show the TEM photograph of the composite. The grain size of the Cr_2O_3 matrix was $\sim 0.35\mu\text{m}$, which was smaller than that ($\sim 3.7\mu\text{m}$) of monolithic Cr_2O_3 described above;

^{*1)} Three kinds of specimens were prepared: $\text{Cr}_2\text{O}_3/\text{Mo}=95/5$, $90/10$, and $85/15\text{vol}\%$ Mo. Among these, the composites fabricated from $\text{Cr}_2\text{O}_3/\text{Mo}=95/5\text{vol}\%$ gave the best data in mechanical properties.

Fig.9 SEM (backscattered electron image) photograph for polished surface of $\text{Cr}_2\text{O}_3/5\text{vol}\%$ Mo composite.

Fig.10 TEM photograph of $\text{Cr}_2\text{O}_3/5\text{vol}\%$ Mo composite; arrows indicate Mo particles within the Cr_2O_3 grains.

Fig.11 SEM photograph for crack propagation around the Vickers indentation of $\text{Cr}_2\text{O}_3/5\text{vol}\%$ Mo composite.

As for the fracture toughness (K_{IC}) measured by the microindentation technique, as shown in Table 2, the K_{IC} value of monolithic Cr_2O_3 was $3.9 \text{ MPa} \cdot \text{m}^{1/2}$, which agreed with data reported previously. On the other hand, the composite material showed the value of $4.6 \text{ MPa} \cdot \text{m}^{1/2}$. It is clear that homogeneous-dispersed Mo particles acted as a toughening agent. The crack propagation around the Vickers indentation was examined by SEM. As can be seen in Fig. 11, intergranular Mo particles prevent the propagation of cracks; the cracks propagated with deflections. Accordingly, the crack-deflection must be responsible for the toughening effect. Thus, the fracture toughness, as well as strength, was found to be improved by the addition of 5 vol% Mo.

4 Toughening and Strengthening of NiAl with Al_2O_3 by the Addition of $\text{ZrO}_2(3\text{Y})$ ⁶⁾

Intermetallic compound NiAl is much of interest as a potential material in the aerospace industry because of its high melting temperature ($T_m = 1638^\circ\text{C}$), low density ($d = 5.913 \text{ Mg} \cdot \text{m}^{-3}$), and high thermal conductivity ($75 \text{ W} \cdot \text{m}^{-1} \text{ K}^{-1}$). Two principal problems present in the material, which need to be improved in practical use, (1) poor fracture toughness and (2) lack of high-temperature strength. Various approaches, such as dispersion of ceramic particles, incorporation of metal precipitates and introduction of continuous fibers, have been performed to improve the mechanical properties. However, their simultaneous improvements were unsuccessful. In the present study well-densified NiAl^{*)}/10 mol% $\text{ZrO}_2(3\text{Y})$ composites with improved mechanical properties were obtained by the

^{*)} $\text{Cr}_2\text{O}_3/5\text{vol}\%$ Mo composites with a higher density (99.4% of theoretical) were fabricated by HIPing for 2 h at 1300°C under the same pressure. Their strength (520 MPa) was low. This must be due to large Cr_2O_3 matrix grains ($\sim 2.8 \mu\text{m}$).

^{*)} As will be described, NiAl contains a trace amount of $\alpha\text{-Al}_2\text{O}_3$.

combined use of SHS and SPS. In addition, high strength >800 MPa could be retained up to $\sim 800^\circ\text{C}$. The mechanical properties are discussed in relation to microstructures.

Fabrication; NiAl was prepared by self-propagating high-temperature synthesis (SHS) using Ni (99.9% pure, particle size $\sim 2.5\ \mu\text{m}$) and Al (99.6% pure, $\sim 27.6\ \mu\text{m}$) powders. Thoroughly mixed powders in a Ni:Al molar ratio of 1:1, without compacting, were put in a carbon crucible; then, the crucible was placed in a stainless-steel high-pressure chamber. After evacuation, Ar gas (99.99% pure) was introduced into the chamber up to 0.1 MPa and the powders were ignited by a red-hot carbon ribbon. The combustion temperature was 1640°C , agreeing with the melting temperature of NiAl. The resulting porous product was ground for 5 min; the particle size of pulverized NiAl was $\sim 46\ \mu\text{m}$. The powder obtained thus was NiAl with a trace amount of $\alpha\text{-Al}_2\text{O}_3$ (Fig. 12). As-received $\text{ZrO}_2(3\text{Y})$ (99.9% pure, $\sim 0.023\ \mu\text{m}$) was calcined for 1 h at 1000°C to improve its dispersibility in the following mixing process; the particle size of the resulting powder was $\sim 0.1\ \mu\text{m}$.

Weighed quantities in the composition of NiAl/ $\text{ZrO}_2(3\text{Y}) = 90:10$ mol%^{*4)} were mixed in ethanol for 1 h. The mixed powders were isostatically cold-pressed at 343 MPa after uniaxial pressing. Densification was performed by spark plasma sintering (SPS). The green compacts (20 mm in diameter and ~ 10 mm in height) were put in a carbon mold and then sintered for 10 min at 1300°C and 30 MPa under a reduced pressure. Heating and cooling rates were 100° and $\sim 50^\circ\text{C/min}$, respectively.

Fig.12 X-ray diffraction pattern of product obtained by SHS.

Characteristics and microstructure of composites; The sintered compacts consisted of three phases: NiAl, tetragonal(*t*) ZrO_2 , and $\alpha\text{-Al}_2\text{O}_3$. Their bulk and relative densities calculated using the theoretical densities of NiAl ($5.913\ \text{Mg}\cdot\text{m}^{-3}$) and *t*- $\text{ZrO}_2(3\text{Y})$ ($6.067\ \text{Mg}\cdot\text{m}^{-3}$); no consideration was given for $\alpha\text{-Al}_2\text{O}_3$, were determined to be $5.93\ \text{Mg}\cdot\text{m}^{-3}$ and 99.9%, respectively. The composites with almost full-density could be successfully fabricated by SPS. Fig. 13 shows microphotographs for (a) polished (secondary electron image) and (b) fracture (backscattered electron image) surfaces of the composite, indicating the presence of both *t*- ZrO_2 ($\sim 0.2\ \mu\text{m}$) and Al_2O_3 ($\sim 0.5\ \mu\text{m}$) particles which are located along the grain boundaries of the NiAl ($\sim 46\ \mu\text{m}$) matrix. No grain growth of NiAl was observed.

Fracture toughness and strength at room temperature; The fracture toughness (K_{IC}) evaluated by the single-edge-notched-beam (SENB) method and three-point bending strength (σ_b) showed the values of $8.8\ \text{MPa}\cdot\text{m}^{1/2}$ and 1045 MPa, respectively. These values were higher than those ($4.7\ \text{MPa}\cdot\text{m}^{1/2}$, 800 MPa) of the materials without $\text{ZrO}_2(3\text{Y})$.

Fig.13 SEM photographs for (a) polished and (b) fracture surfaces of NiAl/10 mol% $\text{ZrO}_2(3\text{Y})$ composite; white and black particles forming continuous boundary layers around NiAl grains represent *t*- ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$, respectively.

*4) Four kinds of specimens were prepared: NiAl/ $\text{ZrO}_2(3\text{Y}) = 95/5$, 90/10, 85/15, and 80/20 mol%. Among these, the composites fabricated from NiAl/ $\text{ZrO}_2(3\text{Y}) = 90/10$ mol% gave the best data in mechanical properties.

Fig.14 Bending strength of (a) NiAl/10 mol% $\text{ZrO}_2(3\text{Y})$ composite and (b) NiAl material as a function of temperature.

addition^{*5)} and the data ($4 - 6 \text{ MPa} \cdot \text{m}^{1/2}$, $\sim 750 \text{ MPa}$) of pure NiAl reported previously. Accordingly, it can be assumed that the mixture of $t\text{-ZrO}_2$ and Al_2O_3 forming continuous boundary layers around the NiAl grains plays an important role in the improvement of mechanical properties.

High-temperature strength; the bending strength as a function of temperature is shown in Fig. 14, compared with those of the materials without $\text{ZrO}_2(3\text{Y})$ addition. Data for the latter materials agreed with the results of pure NiAl. On the other hand, the brittle-to-ductile transition of the composites occurred at $\sim 800^\circ\text{C}$. It should be noted that the strength $> 800 \text{ MPa}$ could be retained up to the transition temperature of 800°C , although it decreased with increased temperature. Fig. 15 shows a SEM photograph for the polished surface of the material without $\text{ZrO}_2(3\text{Y})$ addition after high-temperature bending tests at 800°C , indicating the evidence of NiAl deformation. On the other hand, no deformation of NiAl was observed in the composite treated under the same conditions. This result suggests the pinning effect of the grain boundary layers for the crack propagation.

In conclusion, high-temperature strengthening obtained in the NiAl matrix composites must be explained in terms of the effective pinning of the grain boundary layers with a high strength at elevated temperatures.

Fig.15 SEM photograph for polished surface of NiAl material after high-temperature bending tests at 800°C .

5 Summary

A growing trends towards highly functional materials/devices from “advanced ceramics” to “electronics/photonics age” through “age of semiconductors of Si, GaAs, SiC” requires both highly purified fine oxide/nanocomposite (inorganic) powders and key-device-production process utilizing the properties of these powders. Solution (liquid) techniques including a newly-developed “Soft-chemical process” will be one of the solutions (answers) to these technological demands.

On the other hand, intermetallic compounds, vast areas of which have still not been investigated and developed until today, will be promising materials used for aerospace and automobile industries, and energy generating high-temperature applications in the next generation. However, in the practical applications of these compounds there are many hurdles to be jumped over, i.e., low energy consumption, small amount of wastes, and recyclable substance in production of the materials, etc. Combined use of the self-propagating high-temperature synthesis (SHS) and the spark plasma sintering (SPS) processes has many advantages of fabrication of intermetallics-based materials. This review introduced briefly our study corresponding to these items up to now.

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*5) Sintering conditions were the same as those of the composites with 10 mol% $\text{ZrO}_2(3\text{Y})$ addition. The relative densities were 99.2%. Microstructural observations revealed that the Al_2O_3 particles were dispersed at the grain boundaries of NiAl ($\sim 60 \mu\text{m}$) matrix.

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