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STRUCTURE AND PROPERTIES OF COMPOSITES
SYNTHESIZED IN SITU USING SOLID STATE
DISPLACEMENT REACTIONS

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STRUCTURE AND PROPERTIES OF COMPOSITES SYNTHESIZED *IN SITU*

USING SOLID STATE DISPLACEMENT REACTIONS

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Abstract

Solid state displacement reactions can produce *in situ* intermetallic and ceramic matrix composites in a process where an intermetallic or ceramic phase(s) and a potential reinforcing phase(s) are grown together during a solid state reaction. Interpenetrating and dispersed microstructures, important for desirable composite properties, have been produced by means of displacement reaction processing techniques. Two such composites have been synthesized which exhibit two distinct microstructures: MoSi₂ reinforced with SiC particles, which exhibits a dispersed-phase structure, and NiAl/Ni₃Al reinforced with Al₂O₃, which exhibits an interpenetrating-phase structure. Strength in bending and chevron-notch fracture toughness have been determined as a function of temperature, and measured properties compare favorably with composites produced by other means. The measured properties are discussed with regard to the observed microstructures. The potential for displacement reaction processing is assessed, and it appears to be a cost-effective synthesis method compared to others.

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Introduction

Solid state displacement reactions are reactive phase transformations whereby two or more elements or compounds react to form new product compounds that are more thermodynamically stable than the starting reactants. In certain material systems the formation of the stable product phases is accompanied by a morphological instability that causes the products to interpenetrate during growth. Displacement reactions, therefore, can be used to grow reinforcement phases *in situ*, which is becoming an increasingly important concept in composite synthesis. The rationale for *in situ* synthesis of composites is reduced cost (no expensive or hazardous reinforcements to handle), improved control of composite microstructure, and, therefore, improved properties. Microstructures that are important for composite strength and toughness, and are unattainable by other means, can be achieved using displacement reactions. Proper optimization of this processing technology can produce microstructures that are effective at dislocation pinning, retarding recovery at elevated temperatures, and increasing low-temperature toughness, such as is observed for whisker-reinforced composites. Controlling the morphology of the product phases is a critical aspect of this method.

Mechanical property improvements can be realized by producing certain composite microstructures, although the degree of improvement depends quite sensitively on the nature and distribution of the component phases. Desirable composite microstructures include 1) whisker-like reinforcing phases, 2) dispersed-particulate phases, and 3) three-dimensional interpenetrating phases. Creep strength, fracture toughness, and crack growth resistance are among those mechanical properties that are improved by composite microstructures, but these properties depend on such variables as interface fracture energy, reinforcement aspect ratio and distribution, and reinforcement volume fraction.

Whisker-like reinforcing phases can be produced by displacement reaction processing by control of the dimensionality of interdiffusion during the reaction, such as with a diffusion couple [1-5]. In contrast, displacement reactions with mixed powders, where the interdiffusion occurs randomly in three dimensions, generally lead to dispersed-phase microstructures [1-5]. Mechanical properties measured for composites synthesized with displacement reactions are essentially equal to properties of more expensive whisker or particulate composites.

Synthesis of interpenetrating-phase composites (IPCs) can be readily accomplished with certain displacement reactions [6], which seem to afford the controllability required for fabricating IPCs. IPCs have certain advantages compared to discontinuous-phase composites [7]. Among these are stability against microstructural coarsening and enhanced fracture resistance. However, it is difficult to fabricate IPCs in a controllable manner. Infiltration of porous preforms, chemical vapor infiltration, directed metal oxidation, colloidal methods, and analogs to spinodal decomposition are all methods that have been used [7]. Of particular interest are methods, such as the one presented here, that produce IPCs *in situ* without expensive lay-up processing.

This work grew out of studies on displacement reactions involving Fe + NiO and Cu + NiO, among other reactions [6, 8-10]. Other researchers [11-16] have used a similar approach, termed reaction sintering, as a method of synthesizing ceramic composites, but with limited success in producing high-quality structural materials. An example of a ceramic composite produced from reaction sintering is t-ZrO₂ + mullite from ZrSiO₄ + alumina [12]. The understanding of reaction mechanisms and reaction morphologies obtained from displacement reactions is limited, but some theoretical analyses have been published that lay the groundwork for this area [9, 17, 18]. Unfortunately, the use of these analyses for quantitative predictions is restricted to special cases where diffusion coefficients are known for all diffusing species.

For the work presented here, *in situ* synthesis of two composites, MoSi₂/SiC [1-5] and Ni-Al/Al₂O₃ [5], by means of displacement reactions has been demonstrated with diffusion couples and blended-powder compacts. Composite morphologies that have been observed include an interconnected cellular-phase structure, forming an IPC structure, and a dispersed particulate-phase structure. Reactions that form dispersed particulate-phase composites yield randomly oriented particulate-like composites when initiated from blended powders. When begun from two-dimensional structures, such as a diffusion couple, the resulting microstructure can consist of aligned platelets of a minor phase (whisker-like reinforcement) within a matrix because of

directional interdiffusion during the reaction. An example of a dispersed particulate-phase composite, MoSi₂/SiC, with relevance to current and future high-temperature structural materials is discussed. An example of an intermetallic IPC having an interconnected cellular morphology is Ni-Al/Al₂O₃.

Experimental Approach

MoSi₂/SiC Composites

A solid state displacement reaction between Mo₂C and Si was used to synthesize a MoSi₂/SiC composite [1-5]. Diffusion couples and vacuum hot-pressed (VHP) powder compacts were produced and studied. Slices of VHP Mo₂C (99.5% purity) and (111) Si single crystal (99.99% purity) were used for diffusion couples, which were prepared from cut and polished pieces 0.5 cm x 0.5 cm and 0.3-cm thick. These were placed in a Mo holder with pieces of Al₂O₃ and Mo foil to hold the Mo₂C and Si pieces in contact at elevated temperatures. The couples were heated in a vacuum furnace operated at pressures less than 10⁻⁴ Pa. Powders of Mo₂C (d <45 μm, 99+% purity) and Si (d <45 μm, 99.99% purity) were blended for the VHP powder compacts. The powders were blended in a 5:1 Si:Mo₂C mol ratio in a vibratory ball mixer and hot-pressed at 27.5 MPa in graphite dies under a vacuum of about 10⁻² Pa. A hot-press die diameter of 7.62 cm was used with ~ 130 g of blended powders. Carbon powders, in the form of carbon black, were added to some of the VHP materials. Final hot-pressing temperatures ranged from 1700°C to 1800°C.

NiAl/Al₂O₃ Composites

Composites were synthesized by displacement reactions between NiAl and NiO powders to produce a composite material consisting of NiAl or NiAl+Ni₃Al+γ-Ni and Al₂O₃. Powders of NiAl (d <45 μm, 99.5% purity) and NiO (d <45 μm, 99% purity) were blended for the VHP powder compacts. The powders were blended in 4:1 and 3:2 NiAl:NiO mol ratios in a vibratory ball mixer and hot-pressed at 27.5 MPa in graphite dies under a vacuum of about 10⁻² Pa. A hot-press die diameter of 7.62 cm was used with ~ 185 g of blended powders. A hot-pressing temperature of 1300°C for 3 h was used for the NiAl-based VHP compacts.

Mechanical Property Tests

Bend strength and chevron-notched-bar fracture toughness were determined for all materials as a function of temperature in a four-point bend fixture having a 40-mm lower span and a 20-mm upper span. The specimen sizes were all 4 mm x 4 mm x 50 mm (nominal). The chevron notches were cut with a 60° included angle such that the tip of the chevron was approximately flush with the specimen surface. All chevron notches were measured after fracture testing and a geometry factor was calculated for each specimen. Chevron-notched specimens of AD995 alumina and Pyrex glass were tested at room temperature to calibrate the calculated geometry factor. Seven Pyrex specimens and 6 alumina specimens were tested, and the average fracture toughness values obtained were 0.81 ± 0.13 MPa√m and 4.30 ± 0.16 MPa√m, respectively. These values compare favorably with those reported in the literature [19]. All bend tests were conducted in air at a crosshead speed of 8.5 x 10⁻⁴ mm/s in a MoSi₂-element vertical tube furnace. All bend data were corrected for the fixture compliance.

Results and Discussion

MoSi₂/SiC System

Composites made by VHP of blended Si and Mo₂C powders at 1350°C for 2 h followed by densification at temperatures in the range of 1600 to 1800°C undergo the following displacement reaction (Table I) as determined by X-ray diffraction (XRD) and quantitative metallography:

Based on the presence of only a trace amount of the ternary $\text{Mo}_5\text{Si}_3\text{C}$ phase, the reaction proceeds nearly to completion at 1600°C [1-5]. The $\Delta G_{\text{Total}}^{298}$ for reaction (1) is -310 kJ/mol and approximately 25% volume shrinkage occurs. Consideration of the ternary Mo-Si-C phase diagram [20] (Figure 1) and analysis of diffusion couples between Mo_2C and Si indicate the following reaction sequence and characteristics: 1) Si is the fastest diffusing species and the ternary $\text{Mo}_5\text{Si}_3\text{C}$ phase forms initially in the Mo_2C phase, followed by the MoSi_2 phase, 2) the SiC is observed to grow at the interface between the ternary $\text{Mo}_5\text{Si}_3\text{C}$ phase and MoSi_2 , but within the ternary phase, 3) the SiC growth direction is into the ternary phase, 4) the initial SiC morphology is plate-like with an aspect ratio of ~ 20 , 5) the SiC plates undergo a Rayleigh instability and pinch-off into discrete particles approximately $1 \mu\text{m}$ in diameter at longer times, 6) the grain size of the MoSi_2 phase is less than $1 \mu\text{m}$, and 7) the composites, after final consolidation, occupy compositions within a three-phase triangle given by MoSi_2 -SiC- $\text{Mo}_5\text{Si}_3\text{C}$. Two additional reactions were investigated by adding C powders to explore other compositions within the three-phase field (Table I and Figure 1):

Figure 1. The 1600°C cross section through the Mo-Si-C phase diagram (from ref. 20).

Adding C reduces the MoSi_2 grain size, increases the porosity for equal VHP times, and moves the final composition into the interior of the three-phase triangle (Figure 1) towards C as expected. It is clear that other compositions within the triangle can be achieved by control of the relative amounts of Mo, Si, and C.

Processing by means of VHP of blended Mo_2C and Si powders results in a dispersed-particulate phase composite because of the pinch-off instability of the SiC plates at 1600 to 1800°C . Mechanical properties (strength and toughness) of the composite materials as a function of

Table I. Physical Properties of MoSi₂/SiC *In Situ* Composites

Material	VHP Temp (°C)	C addition (mol%)	Vol. Frac. SiC	Vol. Frac. Mo ₅ Si ₃ C	MoSi ₂ grain size (μm)	density (g/cm ³)
VHP-1	1700	0.0	0.30	trace	1.0	5.366
VHP-2	1800	0.0	0.30	trace	1.6	5.499
VHP-3	1800	0.3	0.33	0.05	1.2	5.317
VHP-4	1800	0.6	0.38	0.1	0.9	5.175

temperature and composition suggest several trends (Figures 2 and 3). Both strength and toughness are highest for the material made by reaction (1) consolidated at 1800°C. This material has the largest grain size, smallest volume fraction of SiC and Mo₅Si₃C, and least porosity. Adding C reduces both fracture strength and toughness, and does not increase elevated temperature strengths. An apparent ductile-brittle transition (DBT) occurs at ~ 1000°C for all these materials. Above this DBT, with the exception of the material with the highest C content and smallest grain size, the materials behave identically with respect to strength decrease as a function of test temperature, suggesting that strength above the DBT is controlled by deformation within the MoSi₂, which is the continuous phase. The fact that the DBT is ~ 1000°C rather than 1300°C [21] is likely due to the fine grain size and increased contribution of grain boundary sliding to the deformation of the material.

Figure 2. Four-point bend fracture strength as a function of temperature for VHP-1, -2, -3, -4 materials. Reported strengths are 0.2% offset yield strengths above the DBT of 1100°C for all materials.

The elevated temperature strength of the material with the highest C content suggests that deformation for this material above the DBT is controlled by a different process because the rate of strength decrease with temperature is lower compared to the other materials. It may be that the MoSi₂ is no longer continuous given the higher volume fractions of SiC and Mo₅Si₃C. This should result in a material more resistant to deformation at elevated temperatures because SiC

Figure 3. Four-point bend chevron-notched fracture toughness K_C as a function of temperature for VHP-1, -2, -3, -4 materials.

does not deform at 1000°C. However, little is known of the mechanical properties of the $\text{Mo}_5\text{Si}_3\text{C}$ phase, an appreciable component of VHP-4.

Representative polished cross-sections (Figure 4) imaged by scanning electron microscopy (SEM) reveal the differences between the compositions and show the uniform dispersion of the three phases in the composites (see Table I). Photomicrographs of fracture surfaces (Figure 5) reveal the MoSi_2 grain size and show that the SiC particles lie mainly on the grain boundaries and at triple points. This suggests that the MoSi_2 grain size is controlled by the SiC volume fraction and spacing (Table I). The pinning of the MoSi_2 grain boundaries is likely a consequence of the nearly simultaneous growth of the dispersed SiC phase and the growth of the MoSi_2 matrix phase. Observations of reinforcement phases located at grain boundaries following high-temperature processing are common and suggest grain boundary pinning of the continuous phase. Compared to other MoSi_2 composites [22-24], the materials produced *in situ* have a grain size and reinforcement size about one order of magnitude smaller. To the best of our knowledge, the *in situ* MoSi_2 material has the finest grain size of any MoSi_2 product.

The composite material's increased toughness, in comparison to that of pure MoSi_2 , which has a toughness of about 3 to 5 $\text{MPa}\sqrt{\text{m}}$ [22-24] (Figure 6), appears to originate with SiC-particle bridging in the crack wake and crack deflection at the SiC/ MoSi_2 interfaces. The failure mode of the MoSi_2 phase appears to be transgranular cleavage at room temperature, and many examples of SiC particle pullout can be seen in the fractographs (Figure 5). The highest toughness would, therefore, be expected for the material with the largest volume fraction of SiC within the MoSi_2 grains, which would be the material with the largest grain size. The fracture toughness is nominally equivalent to whisker- and particle-reinforced MoSi_2 materials [22-24] (Figure 6), which suggests that *in situ* techniques can be used in place of expensive and hazardous whiskers to obtain significant property improvements.

Figure 4. SEM photomicrographs of polished cross-sections of (a) VHP-2, (b) VHP-3, and (c) VHP-4. Dark regions are SiC particles, lightest regions are Mo₅Si₃C regions, gray matrix is MoSi₂.

Figure 5. SEM photomicrographs of room-temperature fracture surfaces of (a) VHP-2, (b) VHP-3, and (c) VHP-4. Dark regions are SiC particles, lightest regions are Mo₅Si₃C regions, gray matrix is MoSi₂. Evidence for SiC bridging and pullout can be seen from impressions left on fracture surface.

Figure 6. Comparison of room temperature fracture toughness values for various MoSi₂/SiC composites as a function of SiC volume percent. Other fracture toughness data are from references 22-24.

Ni-Al/Al₂O₃ System

The phase compositions of the Ni-Al/Al₂O₃ materials are determined by the amount of NiO blended with the NiAl. These expected compositions are shown in the following reactions:

To determine phase morphologies and compositions of these two materials, SEM and XRD were used (Table II). Adding 20 mol% NiO to NiAl resulted in single-phase NiAl regions surrounded by Al₂O₃ regions, with only a trace amount of Ni₃Al. Since the NiAl phase field extends from 42 atom% Ni to 65 atom% at 1200°C, the amount of Ni₃Al observed in VHP-5 (Table II) is consistent with the formation of Ni-rich NiAl (namely Ni_{1.5}Al) as the major phase. Adding 40 mol% NiO to NiAl resulted in production of NiAl + Ni₃Al + γ-Ni three-phase regions surrounded by the Al₂O₃. It is apparent that the material produced by reaction (5), VHP-6, is not fully reacted. Given sufficient time, the γ-Ni should combine with the NiAl to produce Ni₃Al. In neither VHP-5 nor VHP-6 was the NiAl₂O₄ spinel phase identified.

The Ni-Al-O ternary phase diagram [25] (Figure 7) shows the location of the two compositions (idealized) for reactions (4) and (5). Some spinel must be formed initially, but the predicted stable phases are NiAl, Ni₃Al, and Al₂O₃. A probable reaction sequence is that γ-Ni and spinel form, followed by Al₂O₃, then excess Ni is incorporated into NiAl or Ni₃Al.

Table II. Physical Properties of Ni-Al/Al₂O₃ Composites

Material	VHP Temp (°C)	NiO addition (mol%)	Vol. Frac. NiAl	Vol. Frac. Ni ₃ Al	Vol. Frac. γ -Ni	Vol. Frac. Al ₂ O ₃	Average cell size (μ m)	density (g/cm ³)
VHP-5	1300	20	0.79	trace	0	0.21	5 $\pm$ 4	6.031
VHP-6	1300	40	0.11	0.43	0.18	0.28	5 $\pm$ 4	6.209

Figure 7. An isothermal cross-section of the Al-Ni-O system at 800°C [25]. Predicted compositions of VHP-5 and VHP-6 are indicated on the diagram.

In contrast to the MoSi₂/SiC/Mo₅Si₃C system, the Ni-Al/Al₂O₃ system does not form a dispersed-phase composite; rather, it forms an IPC consisting of interconnected cellular composite morphology (Figures 8 to 10). For both VHP-5 and VHP-6 materials, the structure can be described as unconnected regions or cells of intermetallic material surrounded by a thin shell ($\sim 1\text{-}\mu\text{m}$ thick) of Al₂O₃. Alternatively, because the interconnected Al₂O₃ cells constitute a closed-shell Al₂O₃ foam structure, the material can also be considered as an intermetallic-filled foam structure (Figure 8). Backscatter SEM of VHP-6, the NiAl/Ni₃Al/Al₂O₃ composite, reveals that both NiAl and Ni₃Al are within the Al₂O₃ cells (Figure 9). The average cell sizes, computed using linear intercepts, were 5 $\pm$ 4 μ m for both VHP-5 and VHP-6. Although some of the Al₂O₃ is incorporated within the intermetallic regions, the majority of it is within these thin shells surrounding the intermetallic regions. Interestingly, the Al₂O₃ appears as a fine-grained layer (Figure 10) having an average grain size of less than 1 μ m, and the Al₂O₃ layer is only one grain in thickness.

The strength and toughness of these two IPCs were determined as a function of temperature (Figure 11). Both materials failed in a brittle manner at room temperature; however, fracture toughness values of 10 to 15 MPa $\sqrt{\text{m}}$ were measured. The VHP-5 material (NiAl only) was ductile at 700°C with an ultimate strength of 412 MPa and an ultimate strain of 9.1 $\times 10^{-3}$.

Figure 8. Backscatter SEM photomicrographs of polished cross sections of a) VHP-5 and b) VHP-6 materials showing interconnected network or foam structure of Al₂O₃ cells containing Ni-Al intermetallic regions.

Figure 9. High-magnification backscatter SEM photomicrograph showing regions of NiAl , Ni_3Al , and $\gamma\text{-Ni}$ in the Ni-Al intermetallic regions. Backscatter contrast scales with increasing atomic number such that Ni -rich regions are brightest.

Figure 10. High-magnification SEM photomicrograph showing structure of Al_2O_3 shell.

Figure 11. Four-point bend strength and chevron-notched fracture toughness K_Q for the Ni-Al/ Al_2O_3 system, VHP-5 and VHP-6 materials. Strengths are reported as 0.2% offset yield strengths above the DBT, and toughness values are reported as peak-load toughness.

Strengths for this material at 700°C and above are reported as 0.2% offset yield strengths. The VHP-6 material (NiAl + Ni_3Al) was ductile at 900°C with an ultimate strength of 186 MPa and an ultimate strain of 5×10^{-3} . Strengths at 900°C and above for VHP-6 are reported as yield strengths, also.

The load-displacement curves for the chevron-notched specimens for both materials at elevated temperatures indicated significant R-curve behavior (Figures 12 and 13, VHP-6 only), indicative of some measure of crack-wake bridging. The initiation fracture toughness was calculated at 9.9 $\text{MPa}\sqrt{\text{m}}$, rising to 14.5 $\text{MPa}\sqrt{\text{m}}$ at an a/W of 0.8 (Figure 13). This R-curve was computed based on a small-scale bridging assumption. The reported K_Q or peak-load toughness values (Table III) are consistent with these R-curve calculations. It can be shown that K_Q values should fall between initiation and final toughness values for rising R-curve materials [26], as observed here. The K_Q of VHP-5 (NiAl only) was 10.1 $\text{MPa}\sqrt{\text{m}}$ at room temperature and 12.1 $\text{MPa}\sqrt{\text{m}}$ at 600°C, at the peak bend strength. Toughness for VHP-6 was 15.5 $\text{MPa}\sqrt{\text{m}}$ at room temperature and 12.0 $\text{MPa}\sqrt{\text{m}}$ at 600°C. These toughness values compare favorably to those measured by others for monolithic NiAl and NiAl-based composites [27, 28] (Table III and Figure 13).

Two SEM fractographs (Figure 14) of representative regions of VHP-5 (NiAl only) reveal the source of the brittle behavior and the source of the fracture toughness and R-curve behavior. The NiAl regions are debonding from the Al_2O_3 "cells" at the NiAl/ Al_2O_3 interface to promote crack-wake bridging (Figure 14a), but are themselves failing by transgranular cleavage at room temperature. The fracture surface is macroscopically very rough as determined by stereo SEM due to the crack debonding along the NiAl/ Al_2O_3 cellular interfaces. At temperatures at and above the DBT for this material (700°C), the fracture surface reveals large plastic stretching of

Figure 12. Chevron-notch load-displacement curves for VHP-6 material ($\text{NiAl} + \text{Ni}_3\text{Al} + \gamma\text{-Ni}$) showing nonlinear load-displacement regions near the peak load.

Figure 13. Computed R-curve for VHP-6, 600°C test using small-scale bridging assumption and chevron-notch geometry. Other fracture toughness data are from references 27 and 28.

the NiAl regions (Figure 14b). The fracture surface at these temperatures is very rough, and ductile rupture features can be observed in the NiAl bridging ligaments. Also evident are imprints in the NiAl ligaments of the small Al_2O_3 grains that make up the cells (Figure 14b).

Figure 14. SEM fractographs of VHP-5 material (NiAl only) showing (a) room temperature cleavage of NiAl regions within Al_2O_3 cell and (b) ductile rupture features observed in NiAl bridge at 700°C. Note debonding at Al_2O_3 /NiAl interface in (a) and impressions of fine-grained Al_2O_3 cell on NiAl bridge in (b).

Table III. Mechanical Properties of MoSi₂ and NiAl Composites

Material	Temp (°C)	Strength (MPa)	Toughness (MPa√m)	Comments	References
MoSi ₂	RT	150	3 to 5	4 pt. bend (4PB) and chevron-notch (CVN)	22, 23
MoSi ₂ /SiC _w	RT	300	8	4PB, CVN, VLS SiC _w	22
MoSi ₂ /SiC _p	RT	300	7.5	4PB, CVN, α-SiC platelets	24
MoSi ₂ /SiC	RT	380	7	4PB, CVN, <i>in situ</i> SiC, VHP-2	present
MoSi ₂	1000	150	--	4 pt. bend (4PB) and chevron-notch (CVN)	22, 23
MoSi ₂ /SiC _w	1000	275	--	4PB, VLS SiC _w	22
MoSi ₂ /SiC _p	1000	330	6 to 7.5	4PB, CVN, α-SiC platelets	24
MoSi ₂ /SiC	1000	520	10	4PB, CVN, <i>in situ</i> SiC, VHP-2	present
NiAl	RT	35	6-12	4PB, VHP NiAl	27, 28
NiAl/Al ₂ O ₃ (FP)	RT	240	3.5 to 8.5	4PB, FP Al ₂ O ₃ fibers	27
NiAl/Cr(Mo)	RT	--	17	3PB notch, DS eutectic	28
NiAl/Al ₂ O ₃	RT	320	14	4PB, CVN, <i>in situ</i> Al ₂ O ₃ , VHP-6	present
NiAl	600	85	--	4PB, VHP NiAl	27
NiAl/Al ₂ O ₃ (FP)	600	325	--	4PB, FP Al ₂ O ₃ fibers	27
NiAl/Cr(Mo)	--	--	--	3PB notch, DS eutectic	28
NiAl/Al ₂ O ₃	600	330	11	4PB, CVN, <i>in situ</i> Al ₂ O ₃ , VHP-6	present

Displacement Reaction Morphologies

Reactions 1 to 3 produce a dispersion of SiC within MoSi₂ where the SiC phase is not interconnected, while reactions 4 and 5 produce an IPC consisting of an interconnected, cellular structure. The reasons for these contrasting behaviors are not completely understood and are the topic of current research [17, 18]. However, it has been previously observed that both morphologies observed in the diffusion couples of these two systems (dispersed or aggregate versus layered) are produced during solid state displacement reactions and that a partial explanation lies in the relative ratios of diffusivities of the components [6, 8-10]. Interdiffusion of Si into Mo₂C acts to destabilize planar growth interfaces to produce a dispersed structure, while interdiffusion of O into NiAl acts to stabilize planar growth interfaces to produce layered structures (Figure 15). In one case, the reaction occurs near the AB interface (unstable aggregate or dispersed growth), and in the other, it occurs near the new αβ interface (stable layered growth). When these reactions are carried out with blended powder compacts, the aggregate morphology produces a dispersed-phase composite while the layered morphology produces an IPC consisting of interconnected cells.

In the MoSi₂/SiC system (Mo-Si-C ternary diagram, Figure 1), the true displacement reaction occurs between the ternary Mo₅Si₃C phase and the Si phase to form MoSi₂ + SiC (see Figure 15 for schematic starting phase equilibrium diagram). The reaction between Si and Mo₂C to give Mo₅Si₃C will tend to produce a stable layer of Mo₅Si₃C because of the equilibrium join between Mo₂C and Mo₅Si₃C. A layer of MoSi₂ is then observed to form between the Si and the Mo₅Si₃C phase, and the SiC then forms at the MoSi₂/Mo₅Si₃C interface within the Mo₅Si₃C phase. The SiC grows initially as platelets into the Mo₅Si₃C phase and is later entrained within the MoSi₂ phase as the Mo₅Si₃C decomposes into MoSi₂ + SiC. The reason for the SiC morphology selection, in particular, remains to be determined.

In the Ni-Al/NiO system, the planar interfaces are apparently stabilized during interdiffusion (as suggested in Figure 15), and the interconnected network of Al₂O₃ cells develop around the Ni-Al intermetallic regions. This is in accord with reaction products observed after diffusion took place at 1200°C in a couple between NiO and Ni₂Al₃. The products consisted of discrete and stable layers of Ni/NiAl₂O₄/Al₂O₃/NiAl. It would be expected that any γ-Ni that formed during the reaction would be located at the Al₂O₃/NiAl interface.

Mechanically, the dispersed-phase composite behaves much like a whisker or fine particulate composite (Figure 6), with a nominal increase in low temperature toughness due to crack-particle interactions leading to small-scale bridging. Limited R-curve behavior would be expected, analogous to that observed in whisker composites. The cellular composite structure, or IPC, appears to possess superior mechanical properties compared to the dispersed-phase composite. This supports the validity of arguments suggesting that IPCs have a more desirable microstructure for improving fracture toughness than do dispersed-phase composites [7]. This has been related to the topology of the structure and the realization that a three-dimensional, interconnected reinforcement phase can offer isotropic resistance to crack propagation [7]. The crack path may be more tortuous, cannot avoid either phase, and will inevitably result in crack bridging by the phase that has the largest strain to failure. In the case of the Ni-Al/ Al_2O_3 composites, the intermetallic phase serves as the bridging phase, and the mechanical properties are enhanced by its ductility at elevated temperatures.

Figure 15. Schematic equilibrium diagram showing AB-C starting reactants not in equilibrium reacting in diffusion couple geometry to form new phases α and β . Relative diffusivities can control resulting interface stability and, therefore, product morphology.

Conclusions

The ability to produce a variety of composite structures *in situ* is an advantage of solid state displacement reaction processing. Dispersed-phase and interpenetrating-phase composites were produced from morphologically unstable and stable interfaces during displacement reactions. Significant toughness improvements relative to unreinforced base materials were observed for both systems. Such improvements, ranging from two to three times the fracture toughness of unreinforced materials, were observed in non-optimized materials, yet these improvements rival those from more expensive composites. The ability to produce inhomogeneities on more than one scale for an IPC structure would offer greater improvements, and the ability to fix the particle aspect ratio by control of the dimensionality of interdiffusion holds promise for producing microstructures with aligned, high-aspect ratio particles. Higher toughness values and improved creep resistance are anticipated for these materials. Fracture toughness and R-curve analyses indicate that an IPC structure is superior to a dispersed-phase composite structure. A substantial advantage exists for displacement reaction processing with regard to materials cost. Expensive and potentially hazardous reinforcement materials are eliminated.

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