Mechanical behaviour of nickel aluminide–zirconia transformation-toughened particulate composite

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The fracture toughness and strength behaviour of nickel aluminide toughened by partially stabilized as well as by non-stabilized zirconia dispersoids were investigated in the range of zirconia content up to 40 vol%. The temperature dependence of the mechanical properties of the composite with an optimal zirconia content was examined. A considerable increase both in fracture toughness and in bending strength was achieved compared to the base nickel aluminide. To reveal the nature of the toughening and strengthening effects, X-ray diffraction measurements were performed before and after fracture. Residual stresses imposed on zirconia particles were evaluated. Trends in mechanical behaviour have been discussed in terms of microstructure development.

1. Introduction

Heat-resistant intermetallic alloy NiAl is a good candidate for elevated temperature structural applications, except for its inherent brittleness and low fracture toughness, usually less than $10\ \mathrm{MPa\,m^{1/2}}$. Details of the mechanical properties of NiAl have been recently reviewed [1]. The brittleness of NiAl is due to the relatively high non-metallic component of interatomic bond [2], and to anisotropy of the active slip systems [3, 4]. At room temperature, the predominant $\langle 1\,0\,0\rangle\{0\,1\,1\}$ slip family yields only three independent slip systems and cannot provide plasticity on the macrolevel of the polycrystalline NiAl, according to Von Mises criteria. It was recently shown that climb, and not activation, of secondary slip systems, is responsible for the brittle-to-ductile transition in NiAl [5]. This transition occurs at a relatively low temperature, about $300\,^\circ\mathrm{C}$. At lower temperatures, the fracture toughness of NiAl is about 4–$6\ \mathrm{MPa\,m^{1/2}}$ [1], i.e. is in the same range as for many ceramics. Therefore, toughening of NiAl seems to be an important problem.

To improve the mechanical properties of NiAl, microstructural modification methods can be utilized. Powder metallurgy technology allows the microstructure to be controlled over a wide range. Transformation toughening involving the tetragonal to monoclinic phase change of zirconia, has proved to be a most effective means of toughening many brittle oxides and other high-melting brittle materials [6–8]. For example, a fracture toughness of $21\ \mathrm{MPa\,m^{1/2}}$ and a bending strength of $900\ \mathrm{MPa}$ have been obtained for zirconia-toughened molybdenum, compared with $12\ \mathrm{MPa\,m^{1/2}}$ and $< 700\ \mathrm{MPa}$, respectively, for molybdenum without dispersoids [8]. To satisfy the requirements for transformation toughening, severe microstructural control is needed, namely the tetragonal zirconia particles should be stable in the matrix, but transform to monoclinic modification in the stress field at the crack tip. The volume expansion and shear strain associated with the tetragonal–monoclinic transformation results in various toughening mechanisms, including microcracking, reduction of the tension at the crack tip due to the volume effect of transformation, crack branching, etc. The relative contributions of the toughening depend on the properties of the constituents and vary with microstructure. Therefore, the aim of this work was to investigate the dependence of zirconia-toughening effects in NiAl on constituents and processing prehistory.

2. Experimental procedure

Experimental work was performed on composites fabricated using a commercial nickel aluminide powder (31.5 wt% Al) having an oxygen content up to 0.4 wt%. The mean particle size was about $17\ \mu\mathrm{m}$. Three kinds of zirconia powders were used: (A) partially stabilized zirconia powder containing 2 mol% Y_2O_3 prepared by co-precipitation from an aqueous solution of zirconium oxychloride and yttrium chloride with ammonia; (B) zirconia powders without stabilizers, or (C) with 3 mol% Y_2O_3, both obtained by plasma-assisted vapour-phase synthesis. The mean particle size of type A powders was about $3.15\ \mu\mathrm{m}$, with a specific area of $4.5\ \mathrm{m^2\,g^{-1}}$. For series B and C, respective values were $1.22\ \mu\mathrm{m}$ and $5.8\ \mathrm{m^2\,g^{-1}}$. SEM measurements revealed that type A powder was strongly agglomerated, consisting of nanometre-sized grains. X-ray diffraction revealed that the tetragonal zirconia content was equal to $> 90\%$, 60–70% and about 100% in the series A, B and C, respectively.

To prepare the composite materials, mixing of the NiAl and ZrO_2 powders was performed by high-intensity attrition milling in acetone using zirconia milling media. This procedure allows the maximal zirconia particle size to be equalized at about 3–4 μm, independently of the initial particle size distribution. The NiAl average particle size was decreased to 0.9 μm.

To choose a compaction method, experiments were made with (i) hydrostatic cold pressing followed by sintering at a temperature of 1440 °C of the initial NiAl powders, (ii) explosive-wave compacting followed by heat treatment at 1400 °C in a vacuum of the initial NiAl powders, and (iii) attrition milling followed by hot uniaxial pressing at a temperature 1400 °C and a pressure of 20 MPa for 15 min in carbon/carbon moulds of the initial NiAl powders and composite mixtures. The details of explosive compacting were described elsewhere [9]. The relative density of the intermetallic matrix was found to be about 83%, 100% and > 97% theoretical, respectively, in these processing methods. For some sets of specimens of the hot-pressed composites, post-hot isostatic pressing (post-HIP) at a temperature of 1400 °C and a pressure of 200 MPa was employed using an ABRA HIPing apparatus filled with argon gas. Post-HIPing was performed without encapsulation of the specimens.

No heat effects of the interaction between NiAl and zirconia were revealed by the DTA method in the temperature range up to 1500 °C. This result was confirmed by the X-ray diffractometry of the specimens before and after the exposure of the composites at 1100 °C for 100 h.

Specimens of NiAl and composite materials were tested in a wide temperature range to determine the ultimate bending strength and fracture toughness. A standard side-edge notched beam (SENB configuration) specimens were utilized in the fracture mechanics experiments. The specimens were notched with a thin diamond saw-wheel. The depth of the notch tip 0.5 of the specimen width, the measured notch tip curvature radius was ∼ 50 μm. The specimens of $3 \times 6 \times 40$ mm^3 size were tested in a three-point bending mode, with a span of 24 mm in fracture toughness experiments, and 28 mm for ultimate bending strength determination. The crosshead speed was 8×10^{-6} m s^{-1}. To estimate the bending strength at high temperature, corrections for non-linearity of the load–displacement behaviour were made according to Barinov's method [10].

The Vickers hardness was measured at room temperature at an indentor load of 10 N applied for a period of 10 s. At least five specimens per experimental point were tested in all mechanical properties measurements to obtain reliable values.

X-ray diffractometry was performed to evaluate the content of tetragonal zirconia on the initial (polished) surface of the specimens, as well as on the fracture surface after testing. A DRON-4 diffractometer and CoK_α radiation were utilized.

Some tribological characteristics were also measured using a rod-on-disc technique at a normal load

of 28.5 N and rotation speed of 350 min^{-1} for a period of 6 h. A high-strength steel U-8 was applied as a friction counter-pair material.

3. Results and discussion
3.1. Effect of processing method
Fig. 1 shows the temperature dependence of the fracture toughness of the NiAl specimens which have been fabricated by various methods. The fracture toughness of the specimens prepared by the attrition milling of initial powders followed by hot pressing is much higher than that for other materials. It can be supposed that the large-angle grain boundaries which were formed during hot pressing of the attrition-milled powder are significantly more effective obstacles for crack propagation than low-angle boundaries between the substructure units in explosive-wave compacted specimens. The lowest level of fracture toughness in the specimens which have been prepared by hydrostatic room-temperature compaction followed by sintering is due to the high pore content. The fracture mode of the latter was intergranular, contrary to transgranular fracture revealed for both the explosive-compacted and hot-pressed specimens, by scanning electron microscopy. It should be noted, that the explosive-compacted materials have the highest level of bending strength, being lower in fracture toughness compared with the attrition-milled and hot-pressed materials. Therefore, there is no simple correlation between strength and fracture toughness behaviour. Obviously, attrition milling results in a lowering of the brittle-to-ductile transition temperature. These experiments result in choice of the attrition-milling technology followed by uniaxial hot pressing at a temperature of 1400 °C and a pressure of 20 MPa for 15 min to prepare the high-toughness composite materials [11].
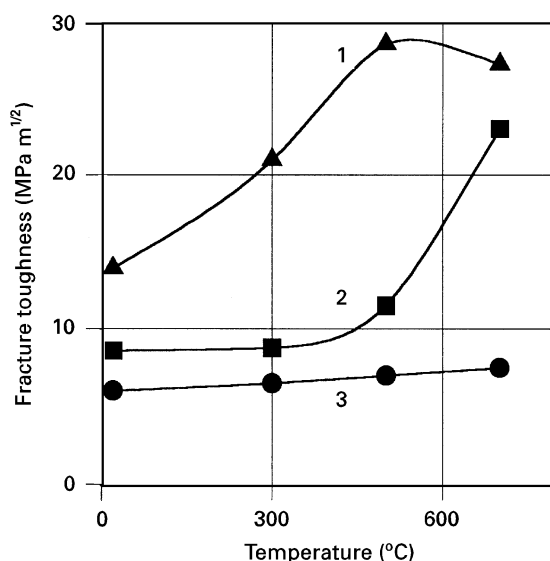

Figure 1 Temperature dependence of fracture toughness of NiAl: (1) attrition milling and hot uniaxial pressing, (2) explosive compaction followed by heat treatment, (3) cold hydrostatic pressing and sintering.

3.2. Effect of zirconia content

The dependence of the ultimate bending strength of the composites on the zirconia dispersoids content is shown in Fig. 2. The composites with type A zirconia powders were studied in these experiments. Figs 3 and 4 demonstrate the effect of zirconia on the fracture toughness and Vickers hardness, respectively.

There is a peak in mechanical properties at a zirconia particulate content of about 20 vol%. The increase in mechanical properties is supposed to result from the increasing contribution of the phase transformation of metastable tetragonal zirconia to stable monoclinic phase under the action of external mechanical loading. A decrease in these properties when the zirconia content is more than 20 vol% is probably due to the continuous zirconia network formation and to superposition of the residual tangential tensile stresses in the intermetallic matrix. According to Trefilov and Moiseev [12], the latter effect becomes significant when the distance between dispersed particles is
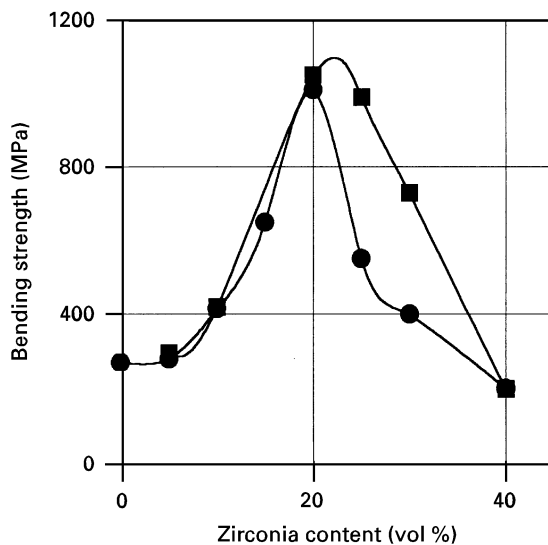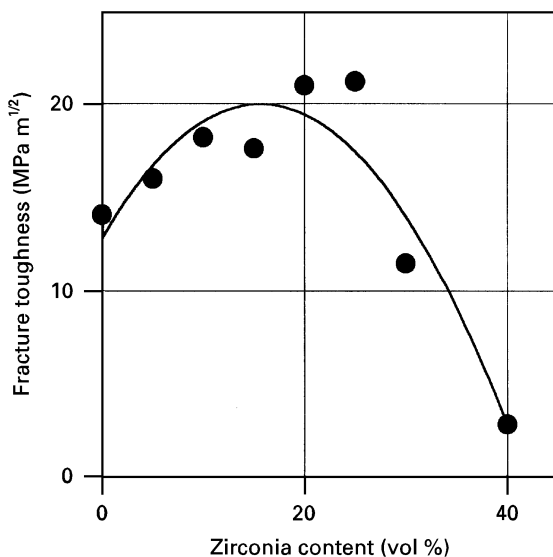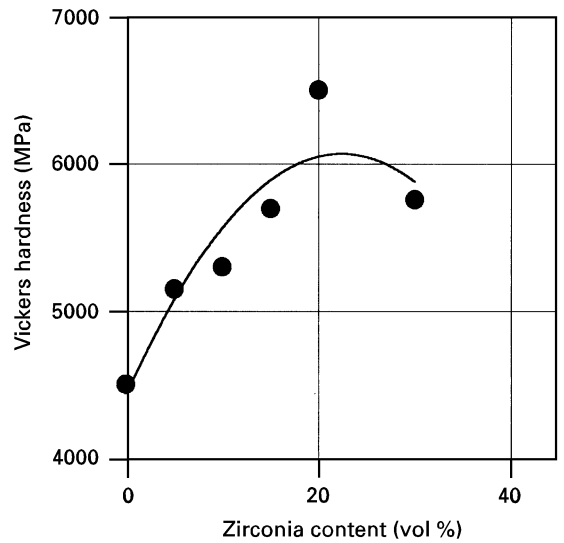

Figure 4 Dependence of Vickers hardness on zirconia content.

greater than four diameters of the particle. This condition is evaluated to correspond to the ZrO_2 volume content of $\sim 20\%$. A hot-pressing temperature of $1400\,^{\circ}C$ seems to be insufficient to sinter dispersed zirconia particles.

It is commonly accepted that both stress field-induced phase transformation and transformation-induced microcracking may be principal reasons for the fracture-toughness enhancement in zirconia-toughened composites. The higher thermal expansion coefficient of NiAl ($15.1 \times 10^{-6}\,K^{-1}$), compared with that of zirconia ($11.6 \times 10^{-6}\,K^{-1}$), leads to compressive stress being imposed on the zirconia dispersoids during cooling from the temperature of the brittle-to-ductile transition in the nickel aluminide matrix (about $500\,^{\circ}C$ [13]) to room temperature. These compressive stresses inhibit phase transformation in zirconia, but the appropriate tangential tensile stresses in the intermetallic matrix can initiate the microcracking process. The value of tangential stress due to the thermal expansion mismatch, can be estimated using equations given elsewhere [14]. It is supposed in the calculations that above $500\,^{\circ}C$ the internal stresses are relieved by plastic deformation in the NiAl matrix. Using the properties of NiAl and ZrO_2 [1, 15], the residual stress, due to the cooling from the brittle-to-ductile temperature to room temperature, at the matrix/particle interface are $\sigma_r = -2\sigma_t = -257$ MPa. This value is considerably smaller than that for transgranular crack initiation in the nickel aluminide matrix. Consequently, the transformation toughening rather than microcracking appears to be the major contribution to the fracture toughness and strength increments.

Fig. 5 shows micrographs of the fracture surface of NiAl (Fig. 5a) and NiAl–20 vol% ZrO_2 composite (Fig. 5b) after testing at $500\,^{\circ}C$. Zirconia dispersoids result in the complicated crack trajectory, with its transition between different cleavage planes. This is believed to result in additional fracture resistance increment.

X-ray diffraction studies which have been performed on the polished surface of the composites

Figure 2 Dependence of ultimate bending strength on zirconia content: (●) non-HIPed, (■) post-HIPed.

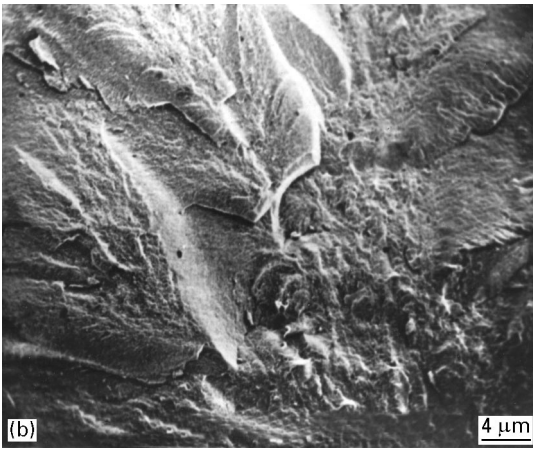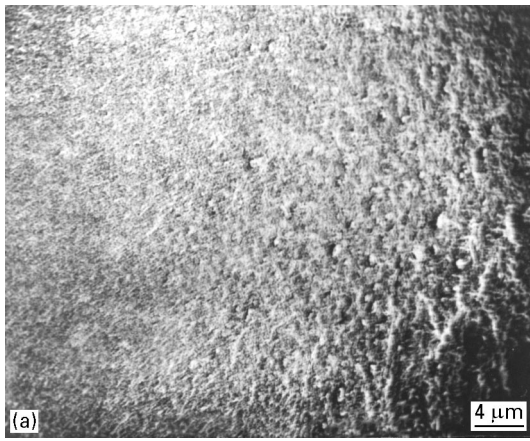*Figure 3* Dependence of fracture toughness on zirconia content.

Figure 5 Fracture surface micrographs of (a) NiAl and (b) NiAl–20 vol% ZrO_2.

Figure 6 X-ray diffraction patterns for NiAl–20 vol% ZrO_2 (a) before and (b) after fracture mechanics testing of specimens: t-Z, tetragonal ZrO_2, m-Z, monoclinic ZrO_2.

Figure 7 Temperature dependence of bending strength of (●) NiAl, and NiAl–20 vol% ZrO_2 composites: (■) type A, (▲) type B, (▼) type C zirconia powders.

before mechanical testing and on the fracture surface reveal that the relative tetragonal zirconia content decreases from 60 vol% to 10 vol% after fracture of the specimen containing 20 vol% type A ZrO_2 particles (Fig. 6). This result confirms the non-contradiction of the assumption that polymorphous transformation in zirconia makes a major contribution to strengthening and toughening of the composites.

3.3. Effect of post-hot isostatic pressing

Post-hot isostatic pressing results in about a two-fold strength increase of the specimens with a zirconia dispersoid content of 25–30 vol% compared to non-HIPed specimens (Fig. 2), probably due to the re-arrangement of particles and the healing of some pores and cavities along interparticle boundaries [16]. The post-HIPing procedure was not effective in improving the mechanical properties at lower zirconia contents, as well as for the materials with 40 vol%. Obviously, a post-HIPing temperature of 1400 °C is insufficient to sinter the zirconia particles in a continuous network.

3.4. Temperature dependence of mechanical properties

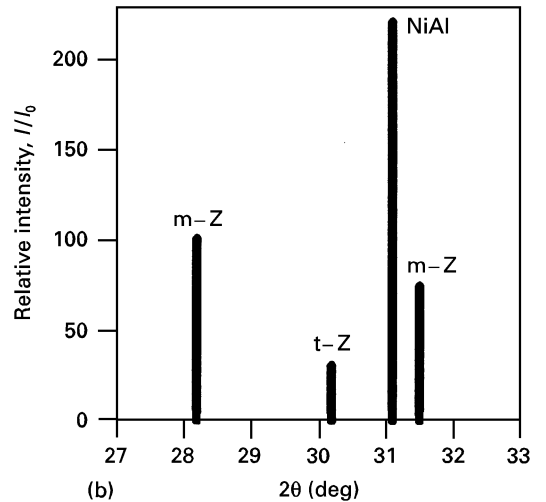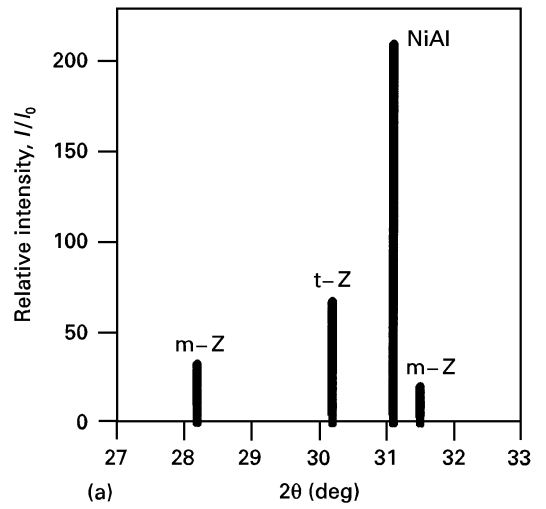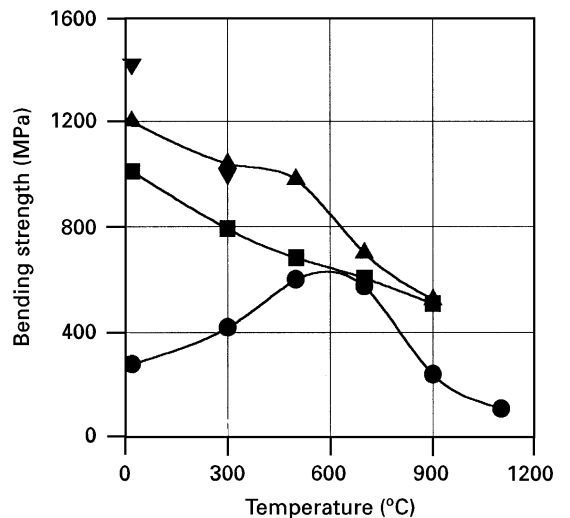Fig. 7 shows the temperature dependence of bending strength of the materials containing 20 vol% zirconia dispersoids. A more than four-fold enhancement in bending strength is achieved at room temperature. The strengthening effect decreases with an increase in temperature, solely because of the lowering of the

chemical driving force for the tetragonal–monoclinic transformation. In addition, the residual compressive stress imposed on the zirconia grains decreases with temperature, due to the recovery resulting in a change of the value of the Gibbs' free energy of transformation causing the monoclinic phase to be more stable.

The temperature dependence of the NiAl matrix strength in the temperature range 20–500 °C has the opposite tendency, as a result of the brittle-to-ductile transition, and because of enhancement of the work-hardening processes with temperature. The effect of strengthening diminishes at temperatures above 500 °C, indicating that the phase transformation in zirconia, rather than the common disperse strengthening mechanism, makes the major contribution to strength.

The fracture toughness of both NiAl without disper-soids and NiAl–20 vol% ZrO_2 composite increases in the temperature range up to 500 °C, owing to the enhancement of plastic relaxation near the crack tip (Fig. 8). A decrease in both fracture toughness and bending strength in the temperature range above 500 °C can be attributed to softening of the NiAl matrix, due to enhanced diffusional processes, e.g. climb of dislocations.

It should be noted that the fracture toughness of the composite is lower than that of the intermetallic matrix at a temperature of 700 °C because of the embrittlement of the ductile matrix by brittle dispersoids.

3.5. Effect of zirconia prehistory
To increase the strength, the zirconia particles of the B and/or C types are the most effective, the effect being most pronounced when zirconia with 3 mol% Y_2O_3 is utilized. At least two reasons can be considered. First, types B and C particles have more favourable (spherical) morphology in respect to the residual stress-field distribution in the matrix than that for type A particles
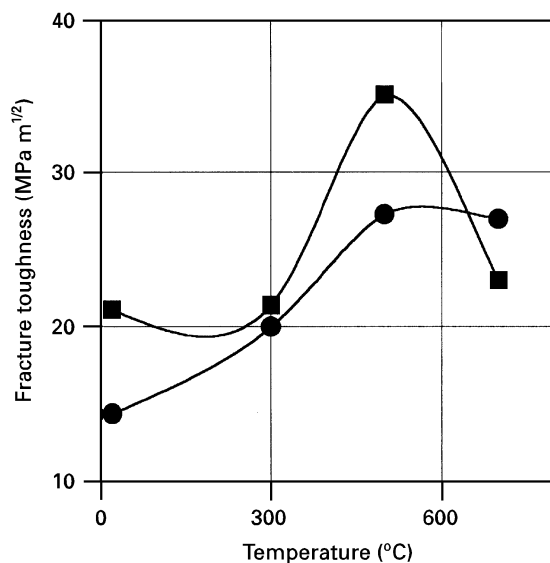
which have non-regular shape. Moreover, agglomerates of type A particles contain very fine grains of zirconia in the microstructure, being more resistant to the tetragonal–monoclinic transition in the field of applied stress.

Room-temperature strength of the NiAl–ZrO_2 (type C) composite is believed to be greater than that of NiAl–ZrO_2 (type B) composite, solely because of the higher content of the tetragonal phase in type C zirconia powder [17].

3.6. Tribological and oxidation tests
Tribological tests using a high-strength steel U-8A as a friction counter-pair, reveal that the normalized specific wear (0.15 kg km^{-1} cm^{-2}) of the composite NiAl–20 vol% ZrO_2 is lowered by 1.5 times compared with the intermetallic matrix without dispersoids.

Introduction of the zirconia dispersoids into the NiAl matrix decreases the average mass increment rate from 5×10^{-1} g m^{-2} h^{-1} for NiAl to 1.62×10^{-1} g m^{-2} h^{-1} for NiAl–20 vol% ZrO_2 composite after exposing the specimens at a temperature of 1000 °C for 25 h. This is supposed to be due to the contribution of the highly heat-resistant zirconia to the exposed surface of the specimen.

Thus, the present study suggests that the mechanical (and other) properties of the brittle low-strength, low-toughness nickel aluminide can be significantly improved by addition of zirconia dispersoids in metastable tetragonal modification.

4. Conclusion
Examination of the mechanical behaviour of the NiAl with addition of the partially stabilized, as well as non-stabilized, zirconia dispersoids indicates the enhancement of both the fracture toughness and bending strength. Apparently, transformation toughening is the major contribution to the mechanical properties increment. The effect was achieved even if non-stabilized zirconia was utilized, solely because of the stabilization action of the compressive residual stress imposed on zirconia particles during cooling from the hot-pressing temperature. Post-HIPing allows the mechanical properties of the composites with high (above 20 vol%) zirconia content to be improved. The composites are sufficiently more resistant to wear and to high-temperature oxidation than the pure intermetallic matrix.

Figure 8 Temperature dependence of fracture toughness of (●) NiAl and (■) NiAl–20 vol% ZrO_2.

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