Microstructures and mechanical properties of ZrO$_2$/NiAl matrix composites elaborated from mechanofusion-processed powders

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ZrO$_2$-coated NiAl powders have been elaborated using an innovative mill process, the so-called mechanofusion process. Following processing conditions, different types of particles (size, morphology, degree of coating) can be obtained. These powders were consolidated to full density by HIPping and mechanical tests were carried out on the various elaborated products at temperatures ranging between 20–800°C. Results are compared to those previously obtained for ZrO$_2$/NiAl composites elaborated by conventional methods. It is shown that mechanical strength of ZrO$_2$/NiAl composites can be considerably improved by using the mechanofusion process. © *2003 Kluwer Academic Publishers*

1. Introduction

The ordered intermetallic NiAl is a potential candidate for high-temperature structural applications in consideration of its low density, high melting point (1638°C), good thermal stability, excellent oxidation resistance and high thermal conductivity [1, 2]. Unfortunately, the development of this material is still severely restricted due to its inherent brittleness at room temperature and its lack of mechanical strength at high temperature. It has been shown that the mechanical properties of hot pressed nickel aluminide can be improved through a grain refinement approach using a powder ball-milling process since ultra-fine structures can both prevent the nucleation of cracks and increase the strain necessary for their propagation [3]. But, due to the thermal instability of these structures, it is not actually an efficient method for high-temperature applications. Alternatively, several authors have proposed an oxide dispersion strengthening route [4, 5]. It was first shown that Al$_2$O$_3$, Y$_2$O$_3$ or ThO$_2$ particles improve yield strength and creep properties of the NiAl matrix [6] while TiB$_2$ dispersoids increase compressive strength and toughness [7]. Then, Barinov and Evdokimov [8] reported that toughness could be significantly improved by the addition of stabilized zirconia particles. For example, with a zirconia content in the range of 20–25 vol% in NiAl, the fracture toughness and the bending strength of 22 MPa m$^{1/2}$ and 1000 MPa,

are respectively obtained, whereas the corresponding values for NiAl (without particle reinforcement) are 15 MPa m$^{1/2}$ and 300 MPa respectively [8]. It was suggested that toughening mechanisms result from the volume expansion and shear stress associated with the tetragonal to monoclinic phase change of zirconia under the stress field at crack tip. Recently, Plazanet *et al.* [9] have also investigated the effect of SiC particles on the mechanical properties. It was shown that rupture strength for materials containing coarse particles ($>15 \mu$m) is considerably degraded and, consequently, SiC could not be considered as an suitable ceramic for enhancing mechanical properties of NiAl. Powder metallurgy is the usual means of producing NiAl/ZrO$_2$ composites. The components are carefully mixed, ball-milled, and then hot-pressed. As an example [9], pressing was achieved in a graphite die for 15 min at 1400°C under a pressure of 30 MPa. Post-HIPping effect was also investigated by Barinov *et al.* [10], but the conditions used were apparently insufficient to bond zirconia particles strongly and consequently to achieve a high strength.

The purpose of the present work is to investigate the effects of a new mode of ceramic distribution in the NiAl matrix using a mechanofusion coating process of NiAl particles by zirconia. These new composite powders are then HIPped in order to obtain high densities and to maintain a good cohesion between NiAl and

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zirconia. Therefore, additional improvements of mechanical properties are expected.

2. Experimental procedures

In the mechanofusion process, mixed powders are dynamically pressed between the wall of a rotating chamber and fixed semi-cylindrical hammers, as shown schematically in Fig. 1. Scrappers are disposed in the chamber in order to break off the consolidated powders on the wall under the centrifugal force. The reactor device used in this work was previously described by Ouchetto and Chouiyakh [11] and it is quite similar to the Hasokawa AM-15F device [12]. As in a rolling mill, powders are submitted to compression and shear stresses with an important heat production due to the friction between the powder grains causing interdiffusion between the components in contact. In some processing conditions, strong bonding could be obtained leading to a real coating of the main component particles by the additional component [11]. Experimental work was performed on composites fabricated using commercial equi-atomic NiAl and partially stabilized ZrO_2 (8 wt% Y_2O_3) powders. The particle size of NiAl powder ranges between 15 and 45 μm while it is centred on 0.6 μm for the ZrO_2 powder. In their previous study, Ouchetto [11] has established that the distance between wall and hammers do not exceed one third of thickness of the powder layer formed during the rotation of the reactor chamber. For larger distances, compression and shearing forces become too weak to assure a good contact between the two materials and then only poor bonding is obtained. NiAl powder is first introduced in the reactor chamber which is rotated at a rate of 1480 rpm for 2 h in order to produce fresh surfaces on NiAl particles facilitating later ZrO_2 adhesion. Then, the ceramic powder is gradually added to avoid the formation of ZrO_2 agglomerates within the NiAl powder. For carefully controlled conditions, NiAl particles are uniformly coated by a thin layer of zirconia after a running time ranging between 8 and 55 hours. Specimen powders with 11, 21 and 30 wt% ZrO_2 were prepared following this method. Cold uniaxial compression under pressures near 450 MPa was applied to each batch of composite powders, leading to relative green densities of about 70%. Green compacts were then sealed in evacuated stainless steel cans and then HIPped at 1300°C under an argon pressure of 200 MPa for 60 minutes in an ACB-HIP6 apparatus.
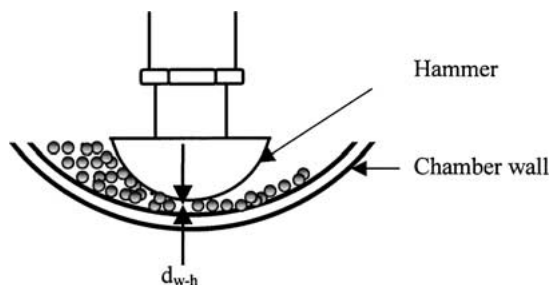
The microstructure and the chemical composition of both composite powders and resulting HIPped specimens were determined by scanning electron microscopy. X-Ray diffraction analysis were also carried out to characterise the existing phases before and after HIPping.

The Vickers hardness was measured at room temperature under a load of 300 N applied for a period of 10 s. At least five measures per specimen were taken for reliable results. The yield stress and ultimate strength were determined from compressive tests carried out on $3 \times 2.5 \times 8$ mm bars but only for specimens containing 11 and 21 wt% ZrO_2 because the NiAl-30 wt% ZrO_2 composite was too brittle to be machined. These tests were conducted in a wide temperature range with a constant cross-head speed of 0.25 mm · mn^{-1} using a MTS-810 hydraulic machine. The crack propagation behaviour were also observed by SEM.

3. Results and discussion

3.1. Microstructures

After 8 h of processing in standard conditions ($d_{w-h} = 2$ mm), SEM observations have shown that a partial coating of the NiAl particles by ZrO_2 particles is obtained for a zirconia content of 11%, but, when this content reached or exceed 21%, a continuous coating can be produced. By reducing to 1 mm the distance between the hammers and the chamber wall, we strongly increase the compression forces exerted on the NiAl powders and fragmentation mechanisms generate a significant proportion of particles with a size smaller than 10 μm. In this case, all the NiAl fragments are entirely coated (Fig. 2), whatever the zirconia content was,

Figure 1 Schematic drawing of the mechanofusion process. The distance d_{w-h} between hammer and chamber wall is adjusted to produce compression and shear stresses under the powders.
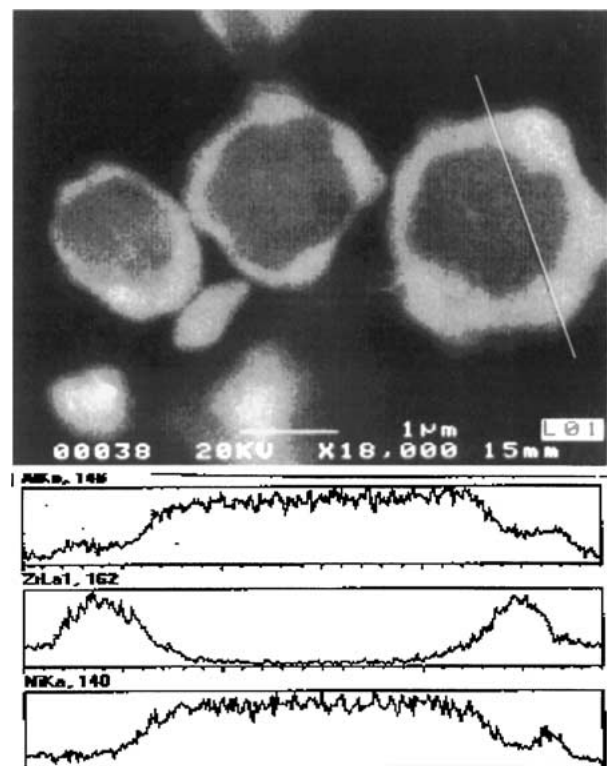

Figure 2 SEM micrograph and EDS analysis of small NiAl particles entirely coated by zirconia after 8 h of processing time.
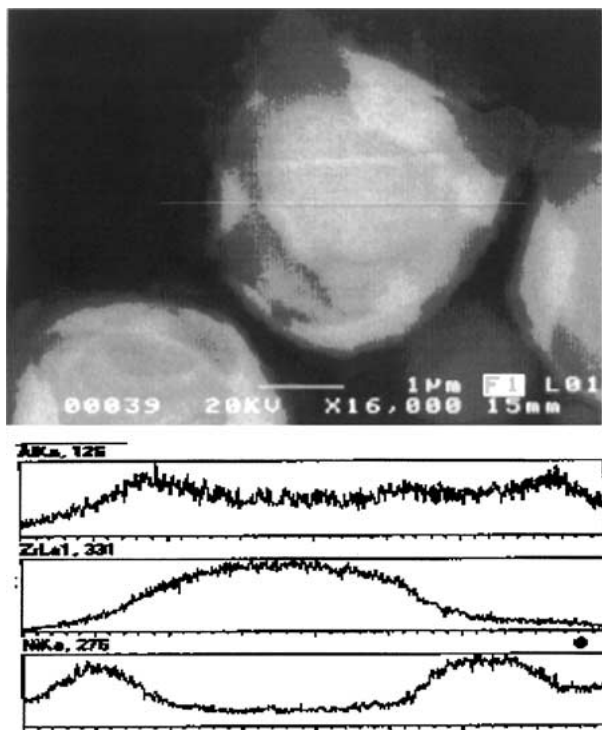
Figure 3 SEM micrograph and EDS analysis of micro-particles obtained after 55 h of processing time. Components are finely imbricated but zirconia is mainly found in the core and NiAl in the periphery.

while the remaining coarser NiAl particles are still partially or completely coated depending on the proportion of ZrO_2 put in the reactor. When particle fragmentation is induced, fresh surfaces are created; we can expect a very strong bonding between materials in contact and, therefore, very adhesive coatings. Only NiAl and ZrO_2 peaks are detected in XRD patterns of the composite powders suggesting that neither interface reactions nor component dissociation have been initiated during the mechanical-fusion processing. However, when processing time is prolonged beyond 15 hours, Ni XRD-peaks appear indicating some NiAl dissociation, but Al peaks were never detected. In this case, SEM observations and EDS analysis show that composite powders now contain numerous new ultrafine particles (<3 μm) with a core rich in Zr and Al and a surface rich in Al (Fig. 3). In these particles, NiAl and ZrO_2 components appear very finely imbricated, like in mechanical-alloying but zirconia is mainly found in the core and NiAl in the periphery. Among these micro-particles, we still find large particles of NiAl but entirely free of zirconia and surrounded by a thin pure Ni layer, which agrees with XRD analysis. It is assumed that, in the absence of cooling, the energy dissipated by friction in the powder raised the temperature which could attain locally a sufficient level to initiate NiAl dissociation at the surface of large uncoated NiAl particles. This process leaves, after long processing times, the nickel skin we have observed. As assumed by Nathan and Ahearn [13] to interpret reactions produced at NiAl/ZrO_2 interfaces in thin films, a possible evaporation of free residual Al could be put forward to explain the absence of an aluminium peak in DRX patterns.

For densification tests, three characteristic powders were used. The processing parameters of these powders are listed in Table I.

With HIP conditions used in this work, full density ($>99\%$) was achieved since SEM observations show that residual pores are practically absent in all the HIPped samples, even for the highest zirconia content. Thus, direct HIPping is a well suitable method to obtained highly consolidated intermetallic/ceramic composites. The microstructural aspects of consolidated specimens are illustrated in Fig. 4. Specimen A, elaborated from 55 h processed powders, is constituted by coarse isolated grains of pure NiAl, like the grain noted 1 in Fig. 4a, inside large regions where zirconia and NiAl phases are closely mixed at a sub-micronic scale (zone 2 in Fig. 4a). In specimen B, zirconia appears to form an interconnected network, noted at zone 1 in Fig. 4b, constituted by the coating of the large NiAl particles and by clusters of entirely coated NiAl fragments, which can easily be distinguished in the enlarged view (Zone 2 in the figure).

3.2. Mechanical properties

The Vickers hardness values obtained for the different consolidated composites are listed in Table II. As expected, adding zirconia into the nickel aluminide matrix leads to a significant increase in hardness (ranging between 50 and 75%) since the hardness of pure NiAl is about 3260 MPa [9]. These hardness values are notably higher than those reported in the literature for similar compositions [8, 9]. However, for a ZrO_2 content of 20%, Barinov and Evdokimov [8] have found a surprisingly high hardness (6500 MPa) that largely exceed our results.

The yield stress and the ultimate strength of NiAl-11wt%ZrO_2 and NiAl-21wt%ZrO_2 were derived from compressive tests performed at various temperatures with constant strain-rate of 5.2×10^{-4} s^1. The results are shown in Fig. 5. For comparison, the temperature dependence curves of the compressive yield strength of a NiAl compound and a NiAl-10vol%ZrO_2 composite studied by Ryu *et al.* [14] are also displayed in the figure. This comparison is reasonable since volumetric and weight compositions are quite similar by reason of the small difference between NiAl and ZrO_2 densities. At room temperature, the compressive yield stress of the composites is much higher than that of the NiAl intermetallic compound which is about 700 MPa. It must be pointed out that yield stress of composites produced by mechanofusion is considerably higher than that obtained for composites elaborated by simple ball-milling of Ni, Al and ZrO_2 powders, as in the work of Ryu *et al.* [14].

TABLE I Mechanofusion processing parameters used to produce ZrO_2 coated NiAl powders

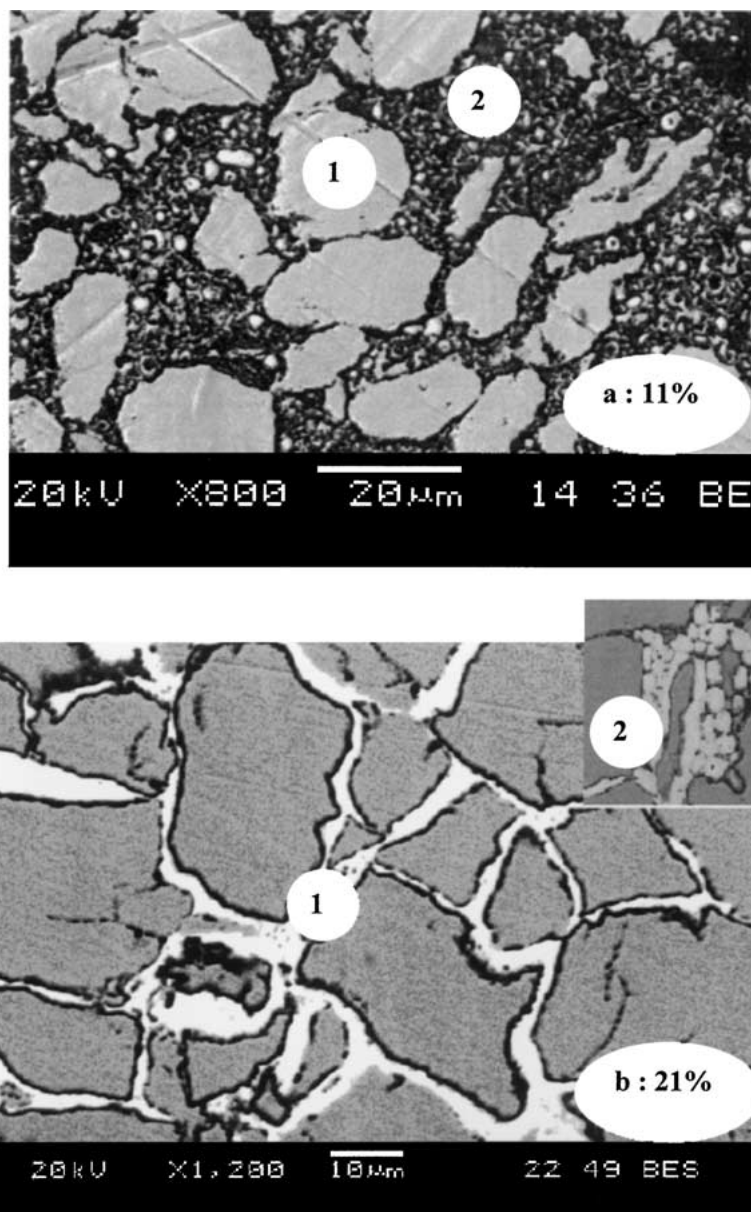| Powder reference	ZrO_2 content (wt%)	Processing time (h)	d_{w-h} (mm)
A	11	55	0.9
B	21	8	2
C	30	8	2

Figure 4 Microstructural aspects of hipped composite powders. (a) 11% ZrO$_2$: we can observed large non-coated grains of NiAl (noted 1) and regions containing numerous micronic grains where zirconia and NiAl are intimately imbricated. (b) 21% ZrO$_2$: presence of an interconnected network af zirconia (noted 1) partially constituted by very small NiAl particles entirely coated by zirconia, like in the enlarged area noted 2 in the figure.

The strengthening effect is commonly attributed to the residual stress distribution in the matrix caused by the presence of the tetragonal zirconia phase. It was demonstrated that under the action of a stress field this phase is able to transform to the monoclinic form [15]. Because of the volume expansion and shear strain developed in the transformed zirconia particles, a compressive stress is generated in the matrix which can account for increases in toughness and strength since crack propagation is effectively impeded. In the present work, both hardness and compressive tests show that strengthening appears greater for specimen A than for specimen B though zirconia content is two times highr in the last case. Globally, reinforcement depends on the volumetric fraction of ceramic dispersed into the matrix, but another important parameter we must consider is the fineness of the dispersion and, as suggested by microstructural observations, the behaviour of the two composites may be very different. Apparently, a finely dispersed zirconia, as in specimen A, creates a more favourable strain-stress state than a regular but coarser dispersion, like in specimen B. Moreover, the NiAl grain growth could be more strongly inhibited than in other modes of ceramic dispersion like powder mixing. The greater values of the yield stress of materials produced by mechanofusion could be explained on this basis.

The decrease in yield strength with increasing temperature for composites A and B is similar to previous observations of Ryu *et al.* [14]. However, at all temperatures, the compressive yield strength of our specimens remains much higher than that reported by these authors. The yield stress decrease could be associated with

TABLE II Hardness of NiAl and NiAl-matrix composites

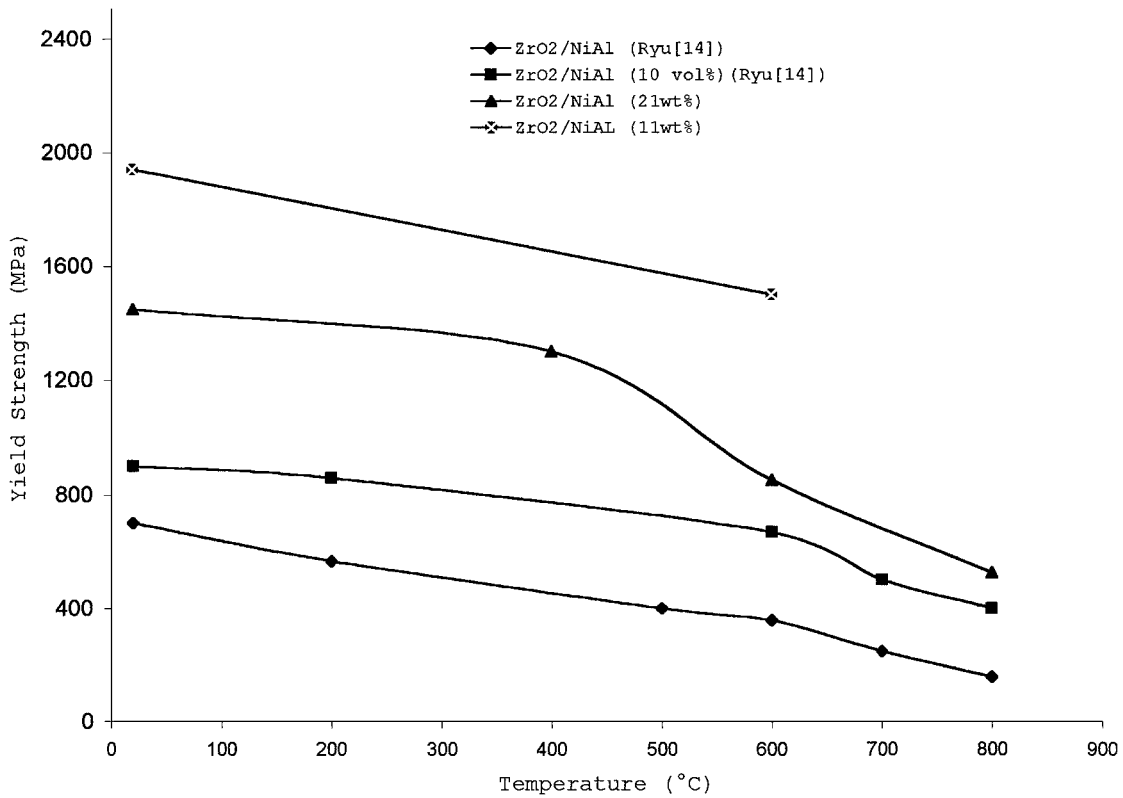| ZrO$_2$ (%wt)	0	11%	21%	30%
H_v (MPa)	3260 (Plazanet [9])	5730	4930	5040

Figure 5 Temperature dependence of the compressive yield stress of NiAl and ZrO$_2$/NiAl matrix composites.

a matrix softening due to the diminishing of the residual stresses [15].

The compressive ultimate strength at room temperature reaches up to 2500 MPa and 1800 MPa for composites A and B respectively but weak ductility is still observed as failure begins at strains lower than 1%. The ultimate strength evolution with increasing temperature is quite similar to that of the yield stress and ductility slightly increases up to 2%. It can be noticed that at 800°C, the ultimate strength for the less resistant composite B is better then 500 MPa.

The crack propagation behaviour, observed on fractured specimens, is illustrated in Figs 6 and 7 for composites A and B respectively. Fig. 6, relative to
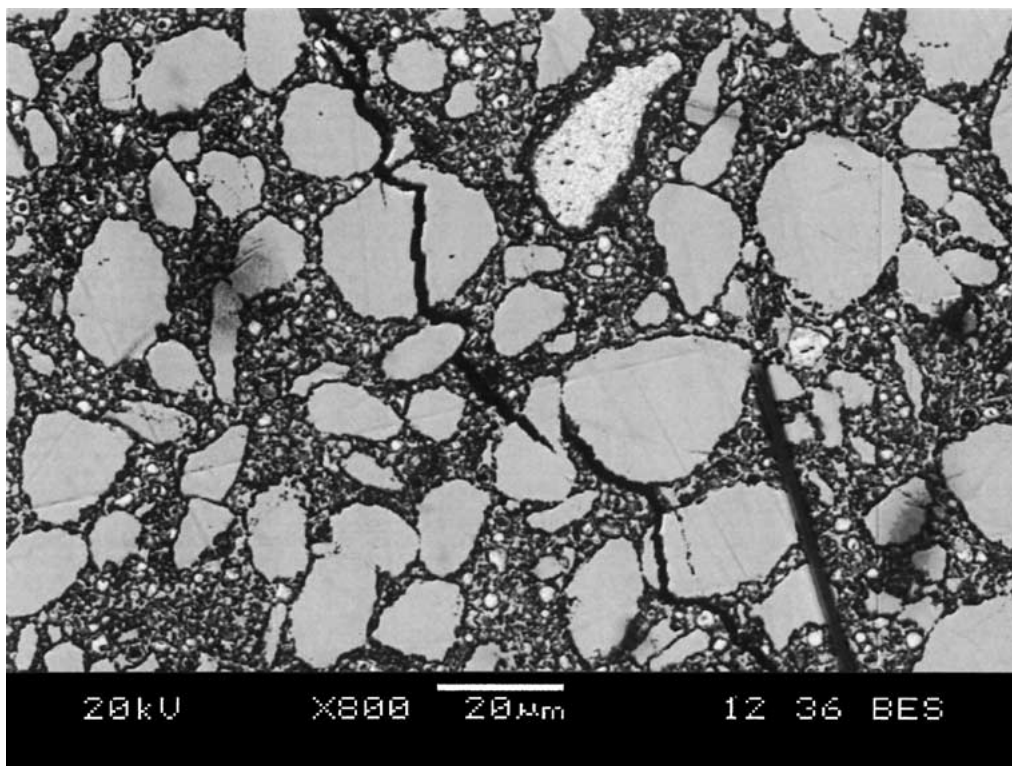

Figure 6 SEM micrograph of a deformed specimen surface showing the crack propagation behaviour in the 11% ZrO$_2$ composite.
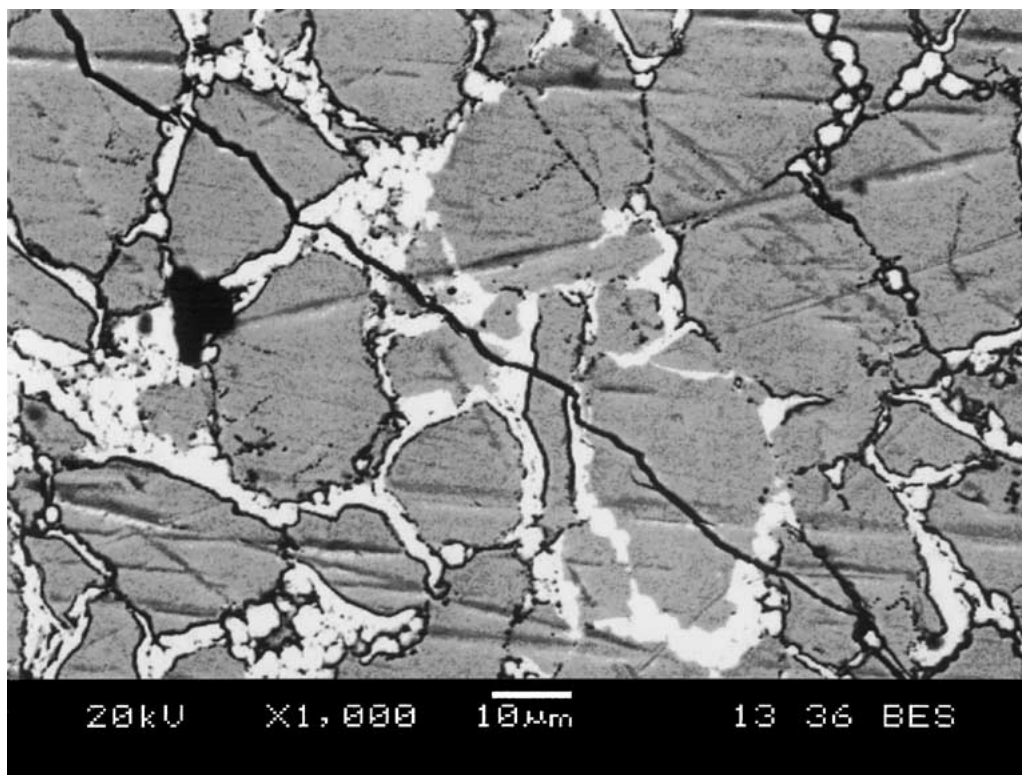
Figure 7 SEM micrograph of a deformed specimen surface showing the crack propagation behaviour in the 21% ZrO_2 composite.

composite A, shows a dual propagation mode. For some large pure NiAl particles transgranular propagation occurs while some other particles are by-passed. In regions constituted by very small ZrO_2/NiAl particles, small deflections probably occur, but the propagation mode is not clear, precisely by reason of the high microstructural fineness. In composite B, where NiAl grains are entirely coated by zirconia, the crack propagation is quasi exclusively transgranular, as it can be seen in Fig. 7. This last type of fissuring confirms the existence of strong ZrO_2/NiAl interfaces.

4. Conclusions

NiAl particles were coated by partially stabilized zirconia by using a mechanofusion process. These powders were consolidated by HIPping and the properties of the resulting materials were characterized in comparison with composites produced by more classical powder metallurgy processes. The major results of this work are summarized as follows:

1. Processing parameters can be adjusted to fabricate entirely coated NiAl powders with strong interfacial bonding between zirconia and NiAl;

2. Composites containing 10 wt%, 20 wt% and 30 wt% of zirconia were successfully consolidated to full density by hipping of mechanofusion processed powders. The HIP level parameters were 1300°C, 200 MPa and 60 minutes;

3. The ZrO_2/NiAl composites elaborated by mechanofusion exhibit a strong increase in yield strength compared to those resulting from conventional elaborating processes. This increase ranges between 200% at room temperature and 30% at 800°C. The reason for this remarkable improvement is mainly due to the high degree of zirconia dispersion we can produce with mechanofusion-processed composite powders;

4. These results indicate a new effective possibility to overcome the poor high temperature strength of NiAl intermetallic compounds.

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