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Studies of the Mechanical Properties of TiB_2–6%TaB_2–1%CoB–x%$mZrO_2$

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Abstract

Mechanical properties of TiB_2–6%TaB_2–1%CoB–x%$mZrO_2$ (x = 0, 20, 30, 40%) have been studied. The toughening mechanism, which is due to ZrO_2 dispersion, includes energy-absorbing stress-induced transformation and micro-cracking about the crack tip. A metal boride such as TaB_2 with the same crystal system is added in order to limit the TiB_2 grain growth by forming a solid solution. The fracture toughness has been determined with the SENB (Single Edge Notched Beam) and IF (Indentation Fracture) methods so that we could choose the more convenient one for our samples. Anisotropy was observed in the case of samples containing a low percentage of monoclinic zirconia because of the influence of the residual stress induced by hot-pressing. © 1997 Elsevier Science Limited.

1 Introduction

The fracture toughness is an important parameter required for the prediction of the mechanical performance of structural materials.

The metastable tetragonal zirconia is a toughening agent. In the stress field of the crack, the metastable tetragonal ZrO_2 (t-ZrO_2) precipitates are transformed to the stable monoclinic structure (mZrO_2), creating a zone of compression in and near the precipitates. The retention of the t-ZrO_2 structure depends on the magnitude of the strain energy arising from the elastic constraints. The constraints are imposed by the surrounding material depending on the shape and the volume changes associated with the transformation.[1] TiB_2 has been chosen as the constraining matrix because of its elastic Young's modulus of 530 GPa, much higher than for ZrO_2 (E = 207 GPa).[2,3] Also, due to the volume change that occurs during phase transformation, stress-induced transformation can be accompanied by the formation of small cracks within or near the transformed particles.[2,4,5] The formation of many small cracks in front of a larger crack would greatly increase the amount of surface area formed per unit extension of the larger crack. The energy absorbed during crack extension will increase and the crack will be stabilized. As a result, these ceramics containing the metastable tetragonal phase (t-ZrO_2) in their structure will exhibit high fracture toughness.

Another mechanism used to stabilize the tetragonal phase is to restrain TiB_2 grain growth and lattice strain by adding a boride such as TaB_2 which will form a solid solution with TiB_2.[6] In this paper we present our experimental results to illustrate this mechanism. In Section 2, the experimental procedure is presented. Section 3 is devoted to the influence of the mZrO_2 amount on the phase composition, the microstructure and the fracture toughness.

2 Experimental Procedure

The required amounts of the powders (TiB_2, TaB_2, CoB and mZrO_2) were automatically mixed in an agate mill for 20 min. Samples of 1·5 g weight were made by packing the mixed powder into a 12-mm internal diameter graphite die and hot-pressing using resistance heating in vacuum under an uniaxial pressure of 20 MPa. The sample was heated at 1500°C for 1 h to achieve a smaller grain size that would allow the retention of the tetragonal phase of ZrO_2. After sintering, samples were cooled under the same pressure in the same atmosphere.

The fracture toughness has been measured by an Indentation Fracture (IF) method with indenting load of 196 N on the face of the sample submitted

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to the uniaxial pressure. This method is simple, rapid and allows characterization of samples with small sizes if the two following conditions are verified:

(1) $2a << 2c$ for brittle materials with $2a$ = indent diagonal, $2c$ = total length of the cracks (see Fig. 1).
(2) Propagation of only one crack from the indentation's extremities.

For samples containing a high percentage of the monoclinic ZrO_2, the length of the cracks is short and so the first condition does not always hold. Many fissures can appear on the lateral faces of the indent and so the energy propagation in the crack is limited. To avoid the propagation of the crack and obtain a correct value of K_{1c}, the measurements have been done just after the indentation or if not, the sample has been immersed in oil in order to reduce the slow crack growth from moisture in the atmosphere.[7] To be able to use the Indentation Fracture (IF) method, the samples have been polished ultimately with 1 μm diamond paste to mechanically remove the damage caused by the grinding. As the materials are very hard, the polishing process is very delicate and takes a long time.

Fracture toughness was also measured following the Single Edge Notched Beam (SENB) technique. Notches were made with a 100-μm cutting wheel and specimens were broken using the strength evaluation procedure.

For the above methods, different formulas are used to determine the K_{1c} values from the experimental results.

For the SENB method, the formula is:

$$K_{1c}(\text{SENB}) = \frac{Y 3 P L \sqrt{a}}{2 b W^2}$$

$$Y = 1{\cdot}93 - 3{\cdot}07 \left(\frac{a}{W}\right) + 14{\cdot}53 \left(\frac{a}{W}\right)^2 - 25{\cdot}11 \left(\frac{a}{W}\right)^3 + 25{\cdot}80 \left(\frac{a}{W}\right)^4$$

a = length of the notch
W = thickness of the sample ($\approx$ 2·5 mm)
L = outer span (10 mm) used in the three-point flexure tests
P = load (20 kgf)
b = width of the sample ($\approx$ 4 mm)

For the IF method, the formula is:

$$K_{1c}(\text{IF}) = \frac{0{\cdot}0231 P}{(2c_x + 2c_y)^{3/2}}$$

$2c_x$ = length of the crack in the x axis (see Fig. 1)
$2c_y$ = length of the crack in the y axis

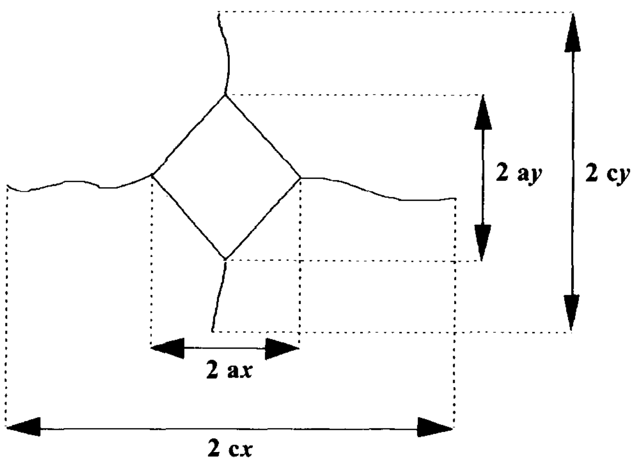


Fig. 1. Schematic view of the cracks initiated at the extremities of the diamond indent by the Indentation Fracture (IF) method.

Investigations by X-ray diffraction were also carried out to determine the crystalline phase of the ZrO_2. Line traces were obtained over a wide range of 2θ values but the emphasis was placed for 2θ values included between 26° and 37° as this profile contains the two strongest lines of the monoclinic phase (m) at 28·3° (111) and at 31·7° $(11\bar{1})$ and the strongest line of the metastable tetragonal phase (t) at 30·5° (111). The percentage of phases was calculated from the relative intensities of the two monoclinic peaks and the tetragonal peak $(\frac{t}{t+m})$ after the correction of the background counts. X-ray diffraction traces were obtained on ground, fractured and polished samples.

3 Influence of $mZrO_2$ Amount on the System TiB_2–6%TaB_2–1%CoB–x%$mZrO_2$

3.1 Influence on the phase composition and the microstructure

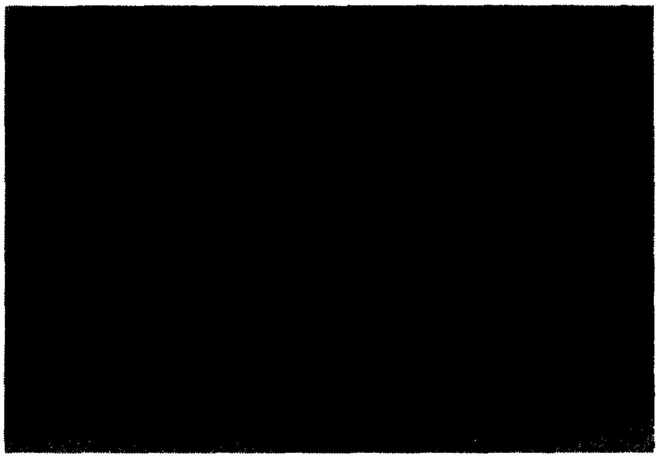
Using X-ray diffraction, the proportion of the tetragonal phase (t) comparing to the monoclinic one (m) has been determined. Studies have been achieved as a function of the amount of $mZrO_2$ and for ground, fractured and polished samples. Experimental results are gathered in Table 1. This table shows that the state of the sample (ground,

Table 1. Proportion of the tetragonal (t) ZrO_2 phase compared with the monoclinic (m) phase $(\frac{t}{t+m})$ for ground, fractured and polished samples

Sample No.	*1*	*2*	*3*
Ground	12·9	10	6·9
Fractured	12	8	6
Polished	12	8·5	5

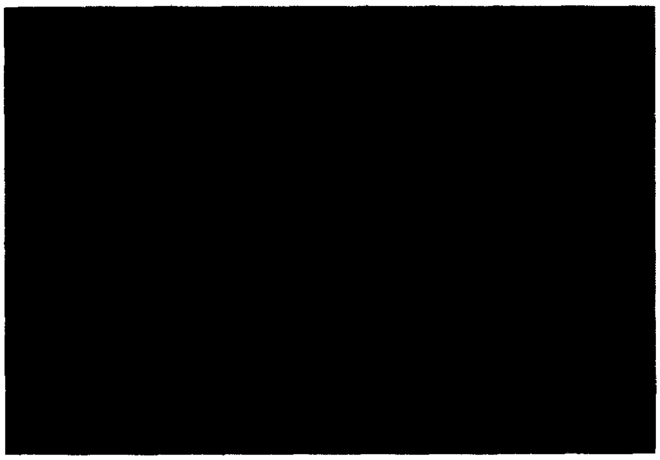
Sample 1: (x = 20 wt%) 73%TiB_2–6%TaB_2–1%CoB–20%$mZrO_2$
Sample 2: (x = 30 wt%) 63%TiB_2–6%TaB_2–1%CoB–30%$mZrO_2$
Sample 3: (x = 40 wt%) 53%TiB_2–6%TaB_2–1%CoB–40%$mZrO_2$

fractured or polished) influences very slightly the proportion of the tetragonal phase comparing to the monoclinic one. So we can consider that the samples are quite homogenous. Besides, with decreasing mZrO_2 content, the stabilized tetragonal fraction increases due to the constraint effect by the surrounding matrix.



(A)

(B)



(C)

Fig. 2. Energy dispersive X-ray analysis showing Ti amount (gray areas) for TiB_2–6%TaB_2–1%CoB–x% mZrO_2; A: x = 20%; B: x = 30%; C: x = 40%.

According to the composition of the samples, when the percentage of mZrO_2 increases, the relative percentage of TiB_2 decreases (the amount of the TiB_2 phase is a function of the initial weight percentage of monoclinic ZrO_2: $1{-}0{\cdot}06{-}0{\cdot}01-\frac{x}{100}$). This is confirmed on the EDX pictures (Fig. 2) where we can see that the Ti amount decreases (grey areas) when x increases. EDX analysis has also shown that Ta distribution in the sample is uniform. On the X-ray diffraction patterns (Fig. 3), the TiB_2 and TaB_2 peaks are overlapped and slightly translated:

TiB_2: $2\theta = 27{\cdot}6°$ (001) and $2\theta = 34{\cdot}2°$ (100)
TaB_2: $2\theta = 27{\cdot}3°$ (001) and $2\theta = 33{\cdot}9°$ (100).

Previous studies done by T. Watanabe *et al.*[6] have shown that the appropriate addition of boride improves the mechanical properties of TiB_2–CoB alloys. TaB_2 forms with TiB_2 a solid solution

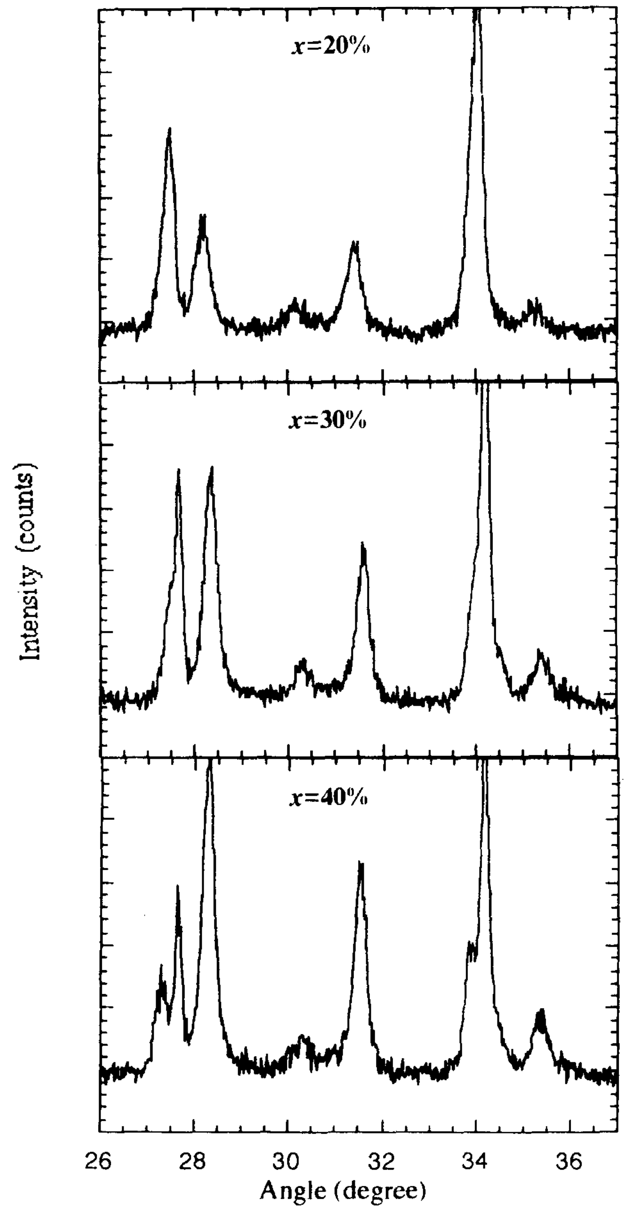


Fig. 3. X-ray diffraction patterns of ground samples made with TiB_2–6%TaB_2–1%CoB–x% mZrO_2 (x = 20, 30, 40%).

(Ti, Ta)B_2 which allows restraint of TiB_2 grain growth and lattice strain. SEM pictures (Figs 4 and 5) show that Ta is located around Ti grains and the matrix is probably formed by the (Ti, Ta)B_2 solid solution.

The samples which do not contain mZrO_2 or which contain a low weight percentage (20%) are porous (small dark zones in Figs 4.A and 5.A). CoB allows a better densification of the material at as low a temperature as 1500°C and is found to be present according to the EDX analysis. The location of CoB cannot be determined exactly since the grain size in the microstructure is very small and the amount of this material is quite low.

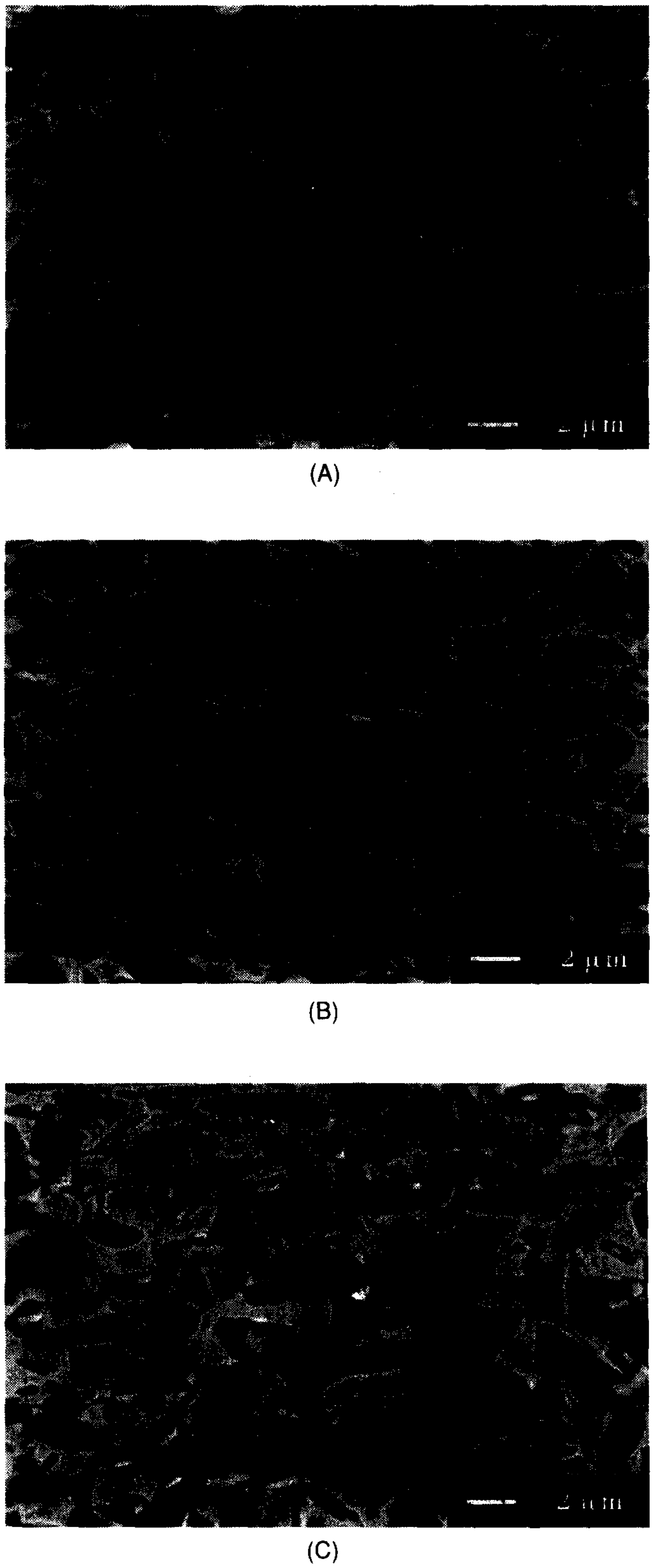


Fig. 4. Scanning electron microscope pictures of TiB_2–6%TaB_2–1%CoB–x% mZrO_2; black grains: TiB_2, grey matrix: ZrO_2, white grains: TaB_2. For x = 20%, small dark zones are the pores (scale 2 μm). A: x = 20%; B: x = 30%; C: x = 40%.

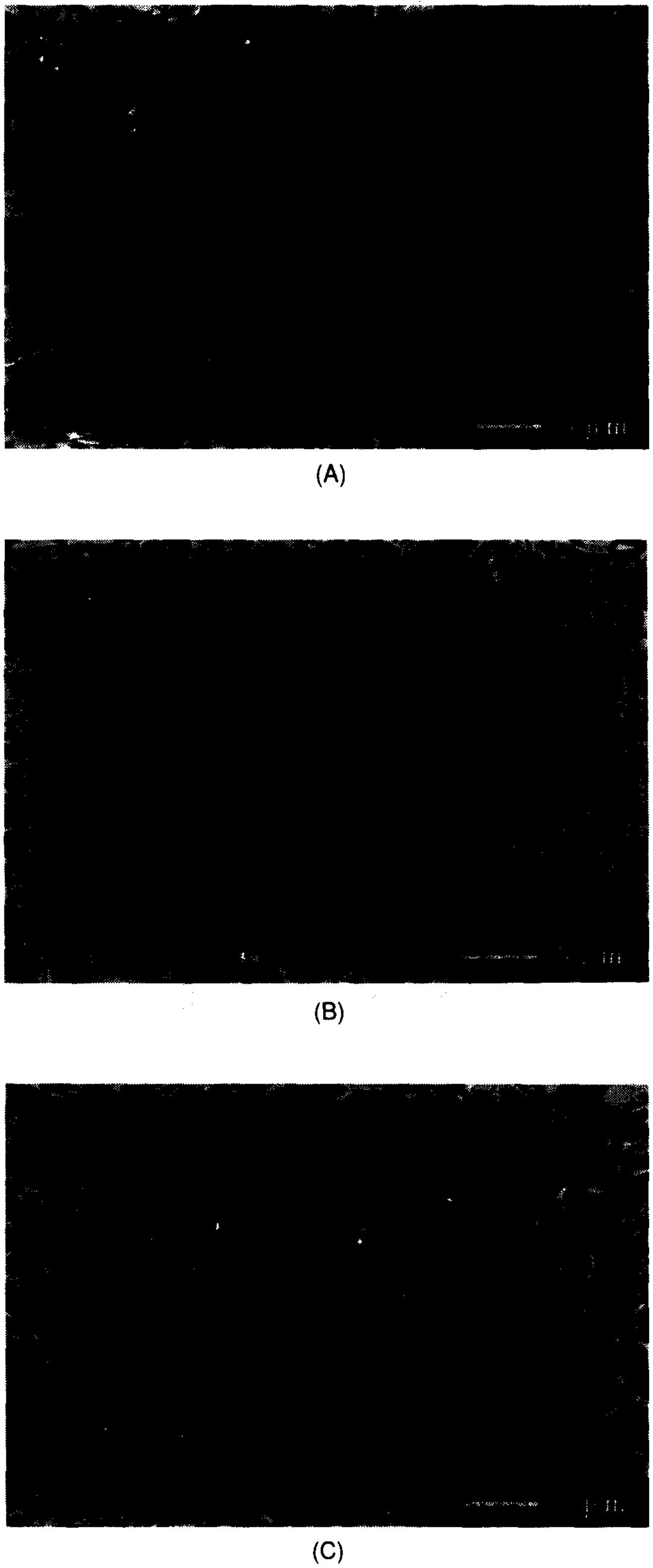


Fig. 5. Scanning electron microscope pictures of TiB_2–6%TaB_2–1%CoB–x% mZrO_2; black grains: TiB_2, grey matrix: ZrO_2, white grains: TaB_2 (scale 5 μm). A: x = 20%; B: x = 30%; C: x = 40%.

3.2 Influence on the fracture toughness

We examined the influence of the residual stress induced by the hot-pressing on the fracture toughness and determined the K_{Ic} values.

Measurements by the IF method have been achieved on the sample face submitted to the uniaxial hot pressing. Because of this pressure the grains are crushed in the plane perpendicular to the hot pressing direction. Therefore propagation of the crack is more difficult in the hot-pressing direction. Another reason for this phenomenon is that CoB, which is liquefied during the sample fabrication, segregates preferentially along the grain boundaries in the hot-pressing direction. Table 2 and Fig. 6 give the average values of the cracks length (c_x and c_y) according to Fig. 1. The lengths of the cracks are different in the direction c_x and in the perpendicular direction c_y especially for the low amounts of mZrO_2. For the higher percentages of mZrO_2 these two parameters become almost equal (see Fig. 6).

For the SENB method, the notch was made on a barrette face perpendicular to the face submitted to the hot pressing (Fig. 7). The crack propagation was then observed and measured in the perpendicular direction. For samples with a low percentage of mZrO_2, the K_{Ic} value is a little high because in this method the crack propagation is considered only in one direction. However, in the IF method the length of the cracks in the two directions c_x and c_y (in a plane perpendicular to the HP direction) are taken into consideration so this method gives more accurate K_{Ic} values for low percentages of mZrO_2.

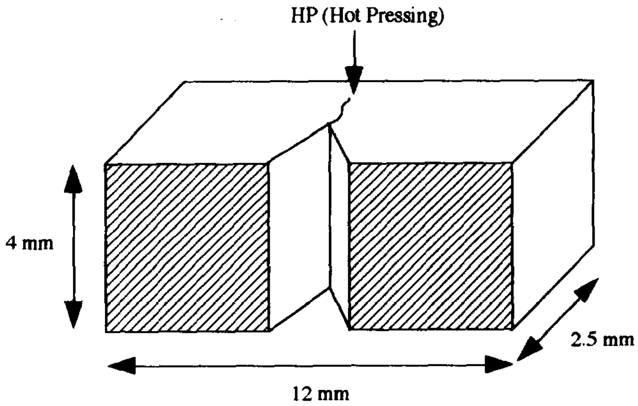


Fig. 7. Schematic view of the position of the notch on a barrette for the SENB method (HP: hot pressing direction).

The K_{Ic} values measured by the IF and SENB methods are collected in Table 3 and illustrated in Fig. 8. For both methods, the best value of the fracture toughness is obtained for 30% mZrO_2. For a higher percentage of mZrO_2, K_{Ic} values decrease slightly (see Fig. 8) because of microcracks linkage.[2,5]

Table 2. Length of the cracks for different percentage of monoclinic ZrO_2 according to the Indentation Fracture (IF) method

x %mZrO_2	2 C_x (μm)	2 C_y (μm)
0	341	524
20	296	425
30	256	288
40	278	283

Table 3. Average values of K_{Ic} obtained for different percentage of mZrO_2.

x% mZrO_2	K_{Ic} ($MPa\ m^{0.5}$) SENB method	K_{Ic} ($MPa\ m^{0.5}$) IF method
0	6	4·6
20	7·0	6·0
30	7·4	10·1
40	6·2	8·8

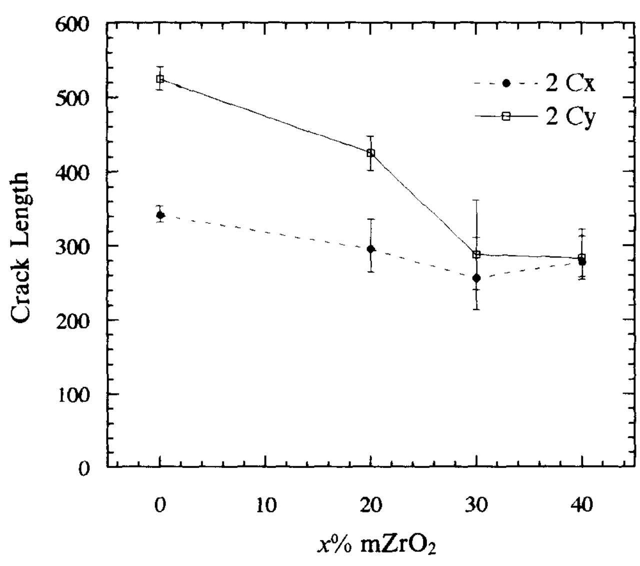


Fig. 6. Length of the cracks (average values with their error bars) for different percentage of monoclinic ZrO_2.

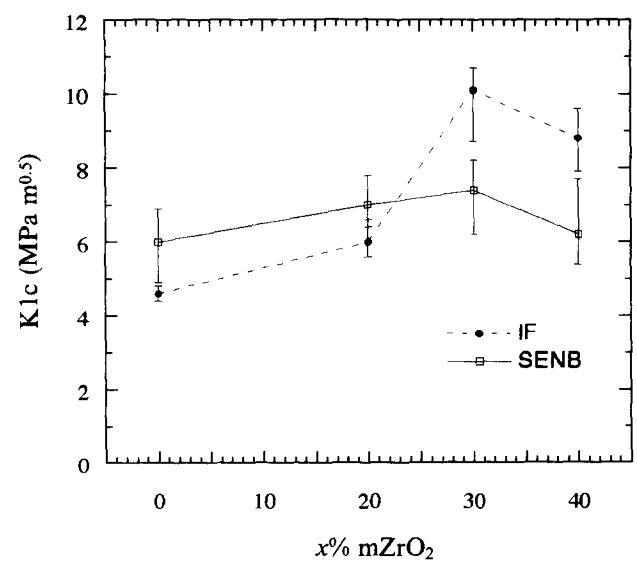


Fig. 8. Comparison of K_{Ic} values by the Indentation Fracture method and by the Single Edge Notched Beam method.

4 Conclusion

Our experimental results (shifts of X-ray peaks for TiB_2 and TaB_2 and SEM pictures showing Ta located around Ti grains) allow us to confirm that the improvement of the mechanical properties is due to the formation of a solid solution between TiB_2 and TaB_2 which limits the TiB_2 grain growth.

The conditions to use the Indentation Fracture (IF) method ($2a << 2c$ and propagation of only one crack from the indent's extremities) are not always verified for samples with a high percentage of monoclinic ZrO_2. Therefore the Single Edge Notched Beam (SENB) technique is probably the more convenient method for our samples with a high percentage of $mZrO_2$. However, in samples containing a low percentage of $mZrO_2$, the K_{1c} results obtained by SENB method do not take into consideration a possible anisotropy of the crack lengths. Therefore both methods are of interest depending on the amount of $mZrO_2$.

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