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$Cr\text{-}Al_2O_3$ layered composites with a high electrical anisotropy prepared by repeated deformation processing

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Abstract

Two-phase layered composites were prepared by the repeated rolling and folding of paraffin-wax-based $Cr\text{-}Al_2O_3$ and Al_2O_3 suspensions at room temperature. The electrical resistivity of sintered samples was characterized in three mutually perpendicular directions. The ac resistivity of the material is governed by the position of the percolation threshold of this highly anisotropic system composed of an insulating Al_2O_3 matrix and $Cr\text{-}Al_2O_3$ conducting clusters. The resisitivity values differed by up to seven orders of magnitude between different directions, depending on the number of foldings and the mismatch in the plastic behavior of the starting suspensions. Above the percolation threshold the anisotropy in the resistivity strongly depends on the mismatch in the plastic behavior of the starting suspensions: it is small for a small mismatch and significantly larger for a large mismatch.
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1. Introduction

Highly dense, chromium–alumina composites can be fabricated by pressureless sintering with the addition of 1–2 wt.% aluminum.[1] The addition of Al is thought to reduce the passivating oxide layers on the chromium surfaces during sintering, and in this way improve the densification. Depending on the total metal content, the composites' electrical resistivity can vary by several orders of magnitude. Close to the percolation threshold of around 30 vol.%,[2] a small change in metal content results in a large change in resistivity. Thus, uniaxially pressed samples with a metal content close to the percolation threshold can have anisotropic electrical properties. This anisotropy is presumably due to the alignment of flake-like particles leading to a lower connectivity in the pressing direction.[2]

A higher electrical anisotropy can be achieved by using laminate composites of Al_2O_3 and a refractory metal like Cr. However, high residual stresses occur, even when using a conductive $Cr\text{-}Al_2O_3$ composite instead of pure metal layers.

Menon and Chen[3–5] proposed a colloidal rolling technique, which potentially reduces sintering mismatch and thermal stresses during cooling as a result of the decreased layer thickness and the wavy layer structure that are formed by repeated rolling and folding. A similar technique based on non-aqueous and non-polar suspensions has been successfully applied to the fabrication of ZTA composites (zirconia-toughened alumina) by some of the authors of this paper.[6] Such suspensions can be easily reshaped at room temperature over a long time period and are better suited to the dispersion of milled metal powders than aqueous suspensions.

In this study the fabrication of $Cr\text{-}Al_2O_3$ laminate composites with a high electrical anisotropy produced by repeated rolling and folding of paraffin-oil-based suspensions was investigated. The electrical resistivity parallel and perpendicular to the rolling plane was measured, and the measured values were related to the number of foldings and the resulting changes to the microstructure. As the difference in the viscosities of the starting suspensions[3–6] and the folding direction[6] were reported to have a significant influence on the evolution of the microstructure, these parameters were also varied in this study.

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2. Experimental procedure

Cr/Al_2O_3/Al powder mixtures (hereafter called Cr50) containing 50 vol.% Cr (Cr 99.8%, Alfa Aesar GmbH, Germany), 2.6 vol.% Al (AS081, Eckart GmbH, Germany) and α-Al_2O_3 (Ceralox HPA0.5, Condea Inc., USA) were attrition milled for 7 h in acetone using 3 mm-TZP balls. The milled powder had a mean particle size of about 4 μm. After drying and sieving, this Cr50 powder was wet redispersed in acetone containing 0.45 wt.% (with respect to solids) of dissolved surfactant (Solsperse 3000, Zeneca, UK). After milling in a planetary ball mill (1 h) the powder was dried for 4 h at 120 °C to chemically bond the surfactant to the particle surfaces, as reported elsewhere[7]. Pure α-Al_2O_3 powder (Ceralox HPA0.5, as received) was treated in the same way except that 1.2 wt.% of stearic acid was used as the surfactant.

Suspensions with different solid contents of pure Al_2O_3 and Cr50 were premixed in a beaker, which was heated to 75 °C, and then subsequently homogenized on a three-roller mill (Al_2O_3-roller mill; Exact GmbH, Germany) heated to 80 °C. The main organic constituent in all the suspensions was paraffin oil (paraffin oil, Kemika, Croatia). Solsperse 3000, ODA (octadecylamine, Sigma–Aldrich, USA) and paraffin wax (INA 58/62, INA, Croatia) were added to adjust the viscosity and adhesion behavior at room temperature. Two Cr50 suspensions were prepared with different solids contents, thus different viscosities. The viscosity was not explicitly measured, but the plastic behavior when rolling the 56 vol.% Cr50 and 58 vol.% Al_2O_3 suspensions appeared comparable, whereas the rolling of the 58 vol.% Cr50 suspension required noticeably higher shear stresses. The final suspension compositions are given in Table 1.

Table 1
Compositions of the prepared 58 vol.% Al_2O_3, 56 vol.% Cr50, and 58 vol.% Cr50 suspensions

Suspension component	58 vol.% Al_2O_3 contents		56 vol.% Cr50 contents		58 vol.% Cr50 contents	
	wt.%	vol.%	wt.%	vol.%	wt.%	vol.%
Al_2O_3	86.04	58.2	–	–	–	–
Cr50	–	–	88.75	56.0	89.48	57.8
Stearic acid	1.03	2.9	–	–	–	–
Solsperse 3000	–	–	0.78	3.0	0.45	1.8
ODA	–		0.96	3.7	1.03	4.1
Paraffin oil	10.20	30.8	8.39	32.9	7.34	29.5
Paraffin wax	2.73	8.1	1.12	4.4	1.71	6.8

The Al_2O_3 and Cr50 suspensions were separately rolled on a twin-roller mill at room temperature to form sheets of 1-mm thickness. These were stacked to form two-layer composites and then repeatedly rolled to a 1-mm thickness and folded (see Fig. 1). To prevent sticking during rolling, aluminum foils were used as spacers, which were replaced after each rolling step.

The following laminates were prepared

- series A→58 vol.% Al_2O_3/56 vol.% Cr50;
- series B→58 vol.% Al_2O_3/58 vol.% Cr50.

Samples were taken for microstructural investigations and measurements of the electrical properties after each rolling step. These were debinded in an alumina powder bed (0.5 °C/min up to 200 °C, 1 h hold) and pressure-less sintered in an argon atmosphere (1500 °C for 2 h) in a graphite furnace.

After sintering, specimens of approximately 6 mm × 6 mm × 0.8 mm were cut out with a high-precision saw (Exakt MCP, Fa. Exakt GmbH, Germany). A low contact resistance for the electrical measurements was achieved with a sputtered gold layer (30–40 nm thickness) followed by coating with silver paste. The conductive layer was only applied to the whole of two opposite sample surfaces, thus ensuring that all the conducting paths were parallel. In this way it was possible to avoid measuring a mixture of longitudinal and transversal conductivities. The measurement in one direction was followed by the removal of the conductive layer by grinding. The same procedure was then

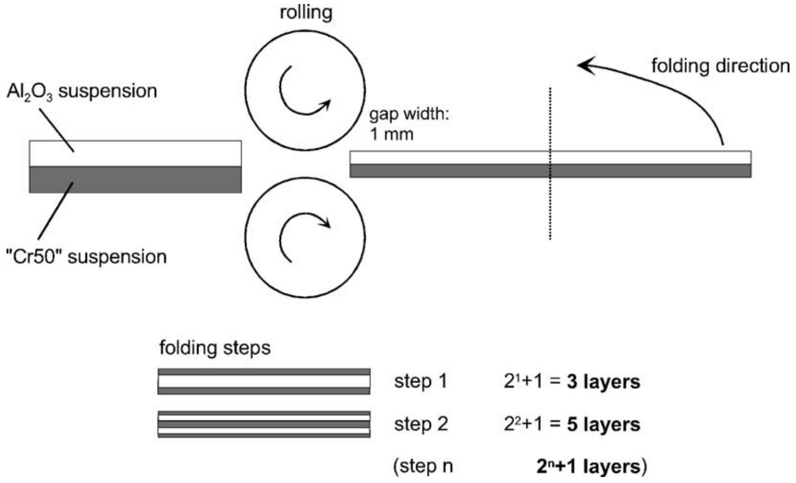

Fig. 1. Rolling-and-folding procedure used for the different experimental series.

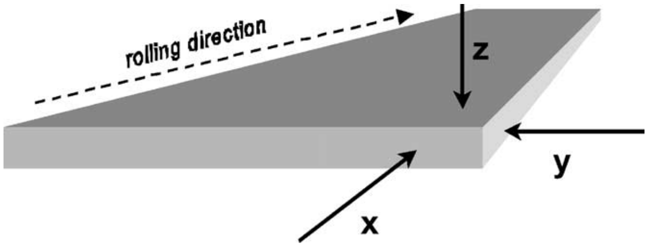

Fig. 2. Schematic presentation of directions in which the characterization was performed, relative to the rolling direction.

repeated for the measurements in the other two directions. The ohmic resistance R was measured at room temperature by making ac measurements (LCR meter Hewlett Packard 4284A, $f = 100\,\text{kHz}$, four-point contact) along both plane directions (x and y) and a direction normal to the plane (z) (Fig. 2). The specific electrical resistivity was calculated from the relation $\rho = R \times A/L$, where A is the sample cross-sectional area and L is the sample length.

Ground-and-polished cross-sections were also investigated using light microscopy (Olympus BX60, Japan) and scanning electron microscopy (JEOL 5800, Japan).

3. Results and discussion

The measured ac resistivity is shown as a function of the number of foldings for the sample series A (Fig. 3). The measurements in the x and y directions are in good agreement, whereas the measurements in the z direction exhibit different trends. The samples have a low electrical resisitivity of 0.1 Ωm (Fig. 3) in the x and y directions up to seven folding steps; this is followed by a sharp increase to around 1×10^5 Ωm after an additional folding step. With further foldings the resisitivity in both directions remains constant. The resistivity in the z direction is initially high (1×10^6 Ωm), but starts to decrease after five folding steps. It reaches a minimum of 1×10^2 Ωm after the sixth folding step. Further folding results in an increase of the resistivity to 1×10^7 Ωm.

The electrical behavior of the investigated ceramic–metal composites is governed by the position of the percolation threshold (p_c). As a consequence of the anisotropic microstructure, the p_c is anisotropic and so are the electrical properties.

The decrease in resistivity in the x and y directions results from conduction through the continuous Cr50 layer. The model of De Bondt et al.[8] accurately describes a composite system like the Cr50 layer. They modeled the percolation behavior of a system composed of an insulating matrix and anisotropic, partially oriented conducting particles. They showed that for such a system the p_c decreases with an increase in the aspect ratio of the conducting particles, but tends to remain between 30 and 40 vol.% of the conductor phase. The Cr50 layer contains 52.6 vol.% of metal phase and, is therefore, well above the p_c.

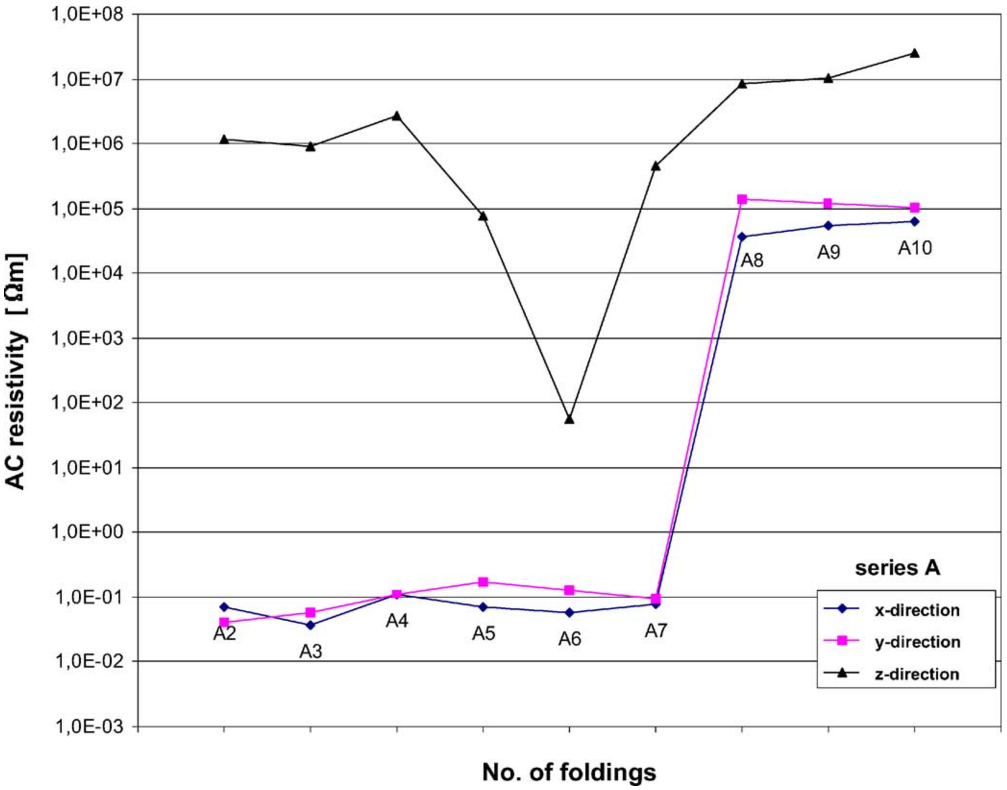

Fig. 3. The ac resistivity vs. number of foldings for sample series A (58 vol.% Al_2O_3/56 vol.% Cr50) relative to the rolling plane.

The microstructure development as a function of the number of folding steps is shown in Figs. 4 and 5. In the *z* direction the electrical paths existing in the Cr50 layers are broken by the insulating Al_2O_3 layers, which results in a high resistivity along this direction. Because an inherent feature of the repeated-rolling-and-folding processing technique is thinning and creasing of the layers[9] it is unavoidable that after several folding steps the Cr50 layers come into contact and thereby form conducting paths in the *z* direction. For sample A this happened after six folding steps. As can also be seen from the microstructures, the layered structure begins to break up with additional foldings. This results in the

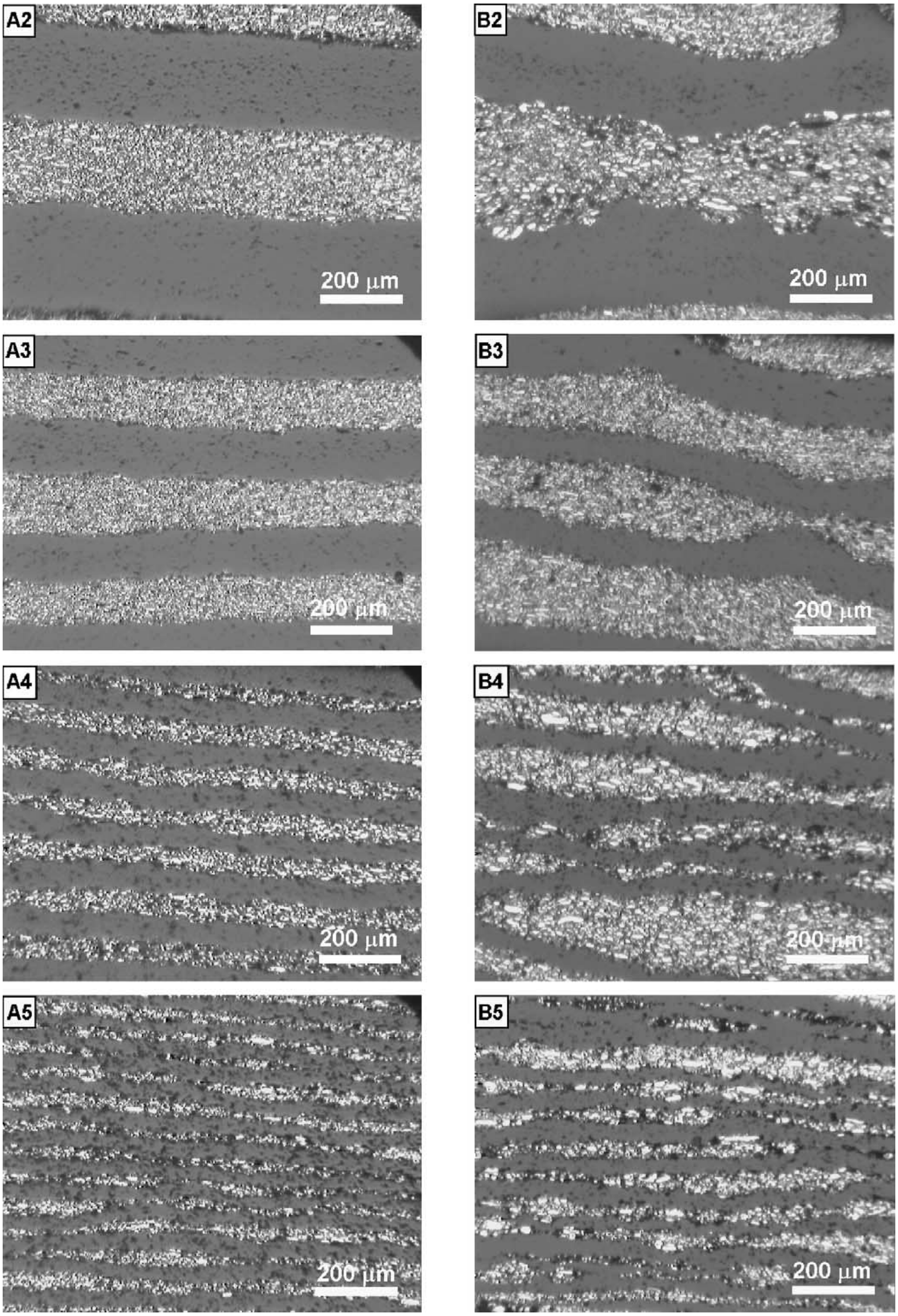

Fig. 4. Optical micrographs of polished cross-section of the *x*–*z* plane of sample series A and series B up to five foldings (number given corresponds to the number of folding steps).

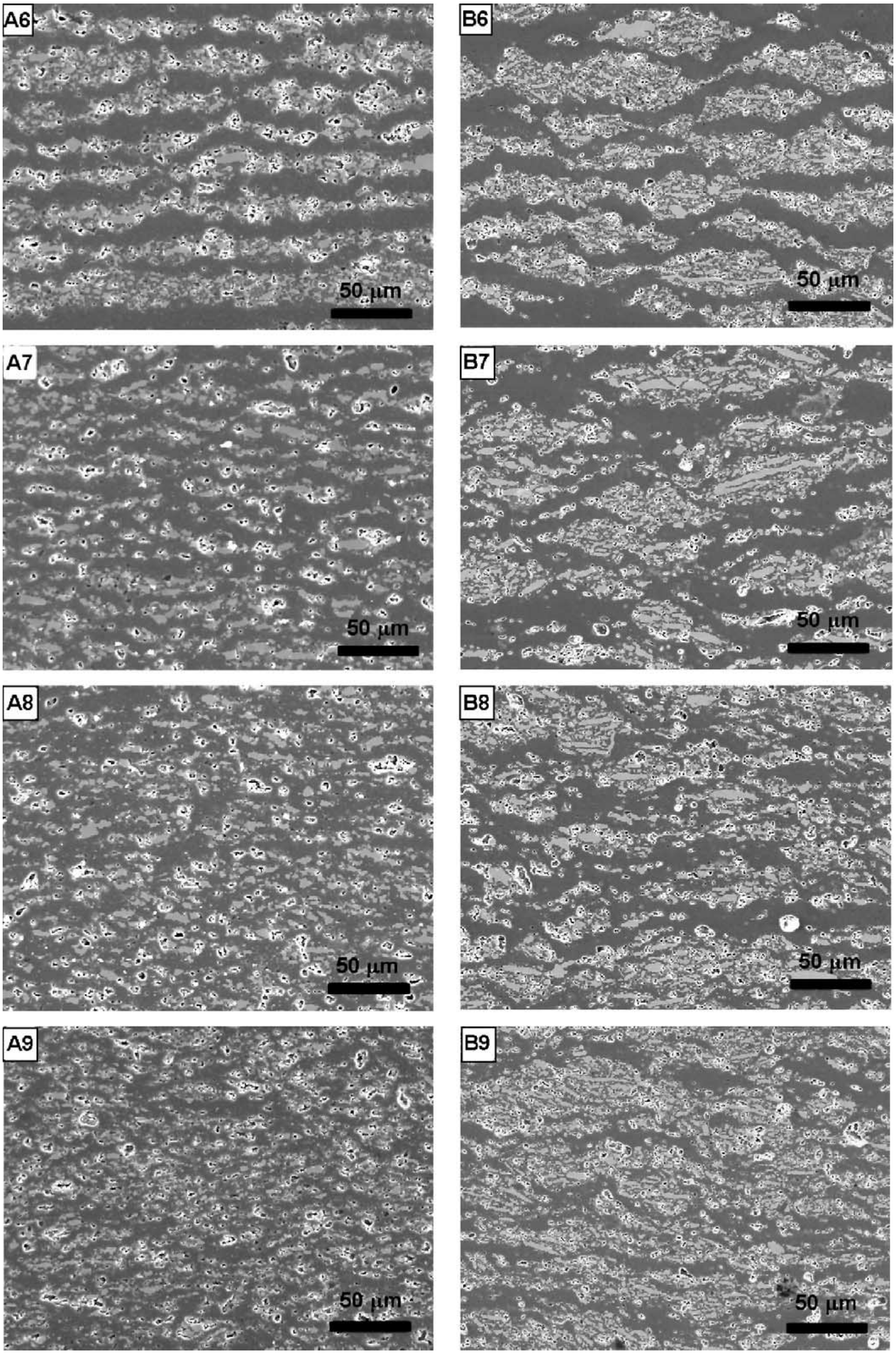

Fig. 5. SEM micrographs of polished cross-section of the *x*–*z* plane of sample series A and series B from six to nine foldings (number given corresponds to the number of folding steps).

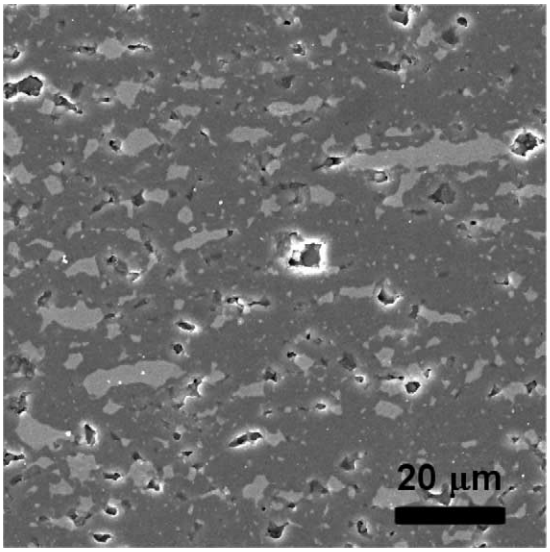

Fig. 6. SEM micrograph of polished cross-section of the *x*–*z* plane of sample series A after 10 folding steps.

loss of continuous conducting paths in the *x* and *y* directions after eight foldings and the homogenization of the sample. Since the concentration of metal particles in the homogenized sample A is 25.8 vol.%, which is below the p_c, such a sample cannot conduct in any direction. This is consistent with the high resisitivities measured along all the directions of sample A. However, some electrical anisotropy can still be detected, even for a large number of folding steps. This indicates that there is still some anisotropy in the phase morphology and phase distribution, which can be clearly seen from Fig. 6.

The rolled samples of series B show a behavior similar to series A up to seven folding steps (Fig. 7). However, the drop in the resistivity in the *z* direction occurs earlier (folding step four) and is more pronounced (down to 1 Ωm). Also remarkable is the rise of resistivity in the *z* direction after seven folding steps just like series A. In the *x* and *y* planes the resistivity remains around 0.1 Ωm, independent of the number of folding steps.

The microstructures of series A and series B are compared in Figs. 5 and 8. The resulting microstructures give support to the explanation proposed by Chen et al.[9], that the difference in the flow properties of the two constituent suspensions (phases) is the key factor in the microstructure refinement during large plastic deformation. In the case of series A, where the different suspensions have a comparable plastic behavior, the layers are equally thinned during earlier rolling steps before they finally break up at around folding step eight. For series B, where the sus-

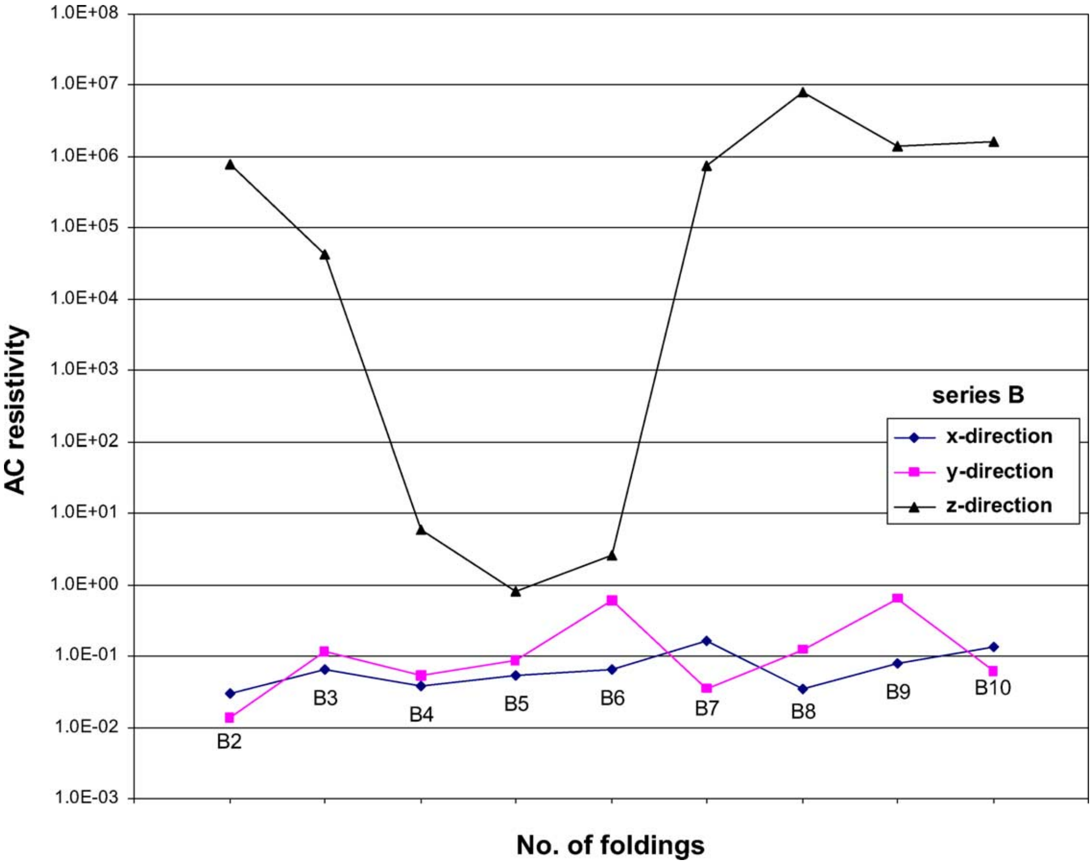

Fig. 7. The ac resistivity vs. number of foldings for sample series B (58 vol.% Al_2O_3/58 vol.% Cr50) relative to the rolling plane.

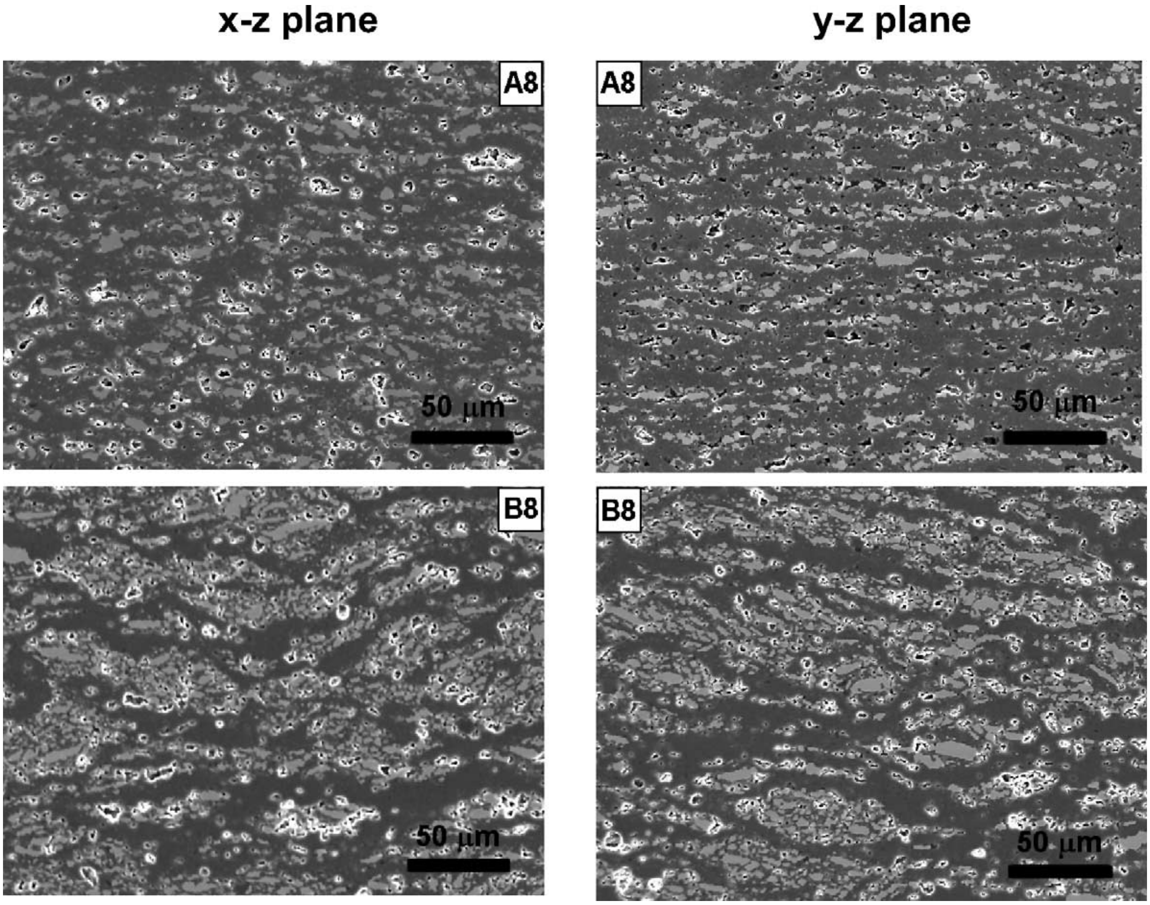

Fig. 8. Comparison of the phase distribution within the sample A and sample B after eight folding steps.

pensions have a higher viscosity mismatch, the layers are not equally thinned and are significantly more creased. The interconnection of the conducting layers occurs earlier and results in a decrease in the resistivity after just four foldings. With the application of additional folding steps the resisitivity in the *z* direction behaves in a similar way to sample A, while in the *x* and *y* directions no increase in the resistivity is detected, unlike sample A. As shown in Fig. 8, in the microstructures of sample A, the Cr50 layers are decomposed with their Al_2O_3 grains joining the Al_2O_3 layer forming a matrix with discrete particulate Cr inclusions at a fraction below p_c. In sample B, however, the Cr50 layers while disintegrating, remain as Cr50 clusters oriented along the *x*–*y* plane and with a very high aspect ratio. Such clusters, which are internally above the p_c (with a volumetric fraction approaching 0.5, which is much higher than the overall Cr fraction of 0.258), can be treated as conducting particles within the insulating Al_2O_3 matrix. The p_c for such system is necessarily anisotropic and, consequently, much lower along the *x* and *y* directions than along the *z* direction, as shown by De Bondt et al.[8] Based on the measurements performed it is evident that in the *x* and *y* directions the system is above the p_c, while for the *z* direction it is below the p_c.

4. Conclusions

The resistivity of the Cr-Al_2O_3/Al_2O_3 layered composites, produced by a repeated-rolling-and-folding processing technique, is highly anisotropic as a result of the anisotropic phase distribution and anisotropic percolation threshold for the conductive phase. The position of the percolation threshold changes during the processing (depending on the number of folding steps) and reflects the anisotropic phase distribution within the composite. The microstructure development and the electrical properties of the investigated Cr-Al_2O_3/Al_2O_3 layered composites are strongly influenced by the mismatch in plastic behavior of the suspensions. In the case of a small mismatch the layers are first equally thinned, then broken up, and finally both phases are homogeneously distributed throughout the sample. Because the overall metal content is below the percolation threshold the final material is electrically insulating in all directions (like series A after eight folding steps). In the case of a larger mismatch in the plastic behavior of the suspensions the harder, Cr50 layers are broken up into highly elongated clusters in the softer Al_2O_3 suspension. This results in a composite that is conductive in the x and y directions and insulating in the z direction.

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