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Processing of an *in-situ* Layered and Graded Alumina/Calcium-Hexaluminate Composite: Physical Characteristics

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Abstract

A novel route to simple processing of an in-situ *layered and graded alumina/calcium-hexaluminate (CA_6) composite is described. The processing involves* partial *infiltration of a porous alumina preform with hydrolysed calcium acetate to yield a homogeneous layer of alumina and a heterogeneous graded layer of CA_6/alumina. The homogeneous layer is designed to provide strength, hardness, and wear resistance, while the graded layer is tailored to impart toughness and damage tolerance. The effect of CA_6 on the physical and graded characteristics is discussed. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

It is well recognised that the mechanical performance of ceramics is sensitive to the phase composition and morphology of their microstructures. For instance, a homogeneous and fine grained alumina offers strength, wear and fatigue resistance but it is brittle and not damage tolerant. By judiciously adjusting the composition by addition of an appropriate amount of titanium oxide, a duplex microstructure of uniformly dispersed aluminium titanate, AT (Al_2TiO_5) can be produced with improved flaw-tolerance.[1–4] Further improvement in flaw tolerance can be achieved through uniform incorporation of large alumina grains within a fine-grain alumina-AT matrix (duplex-bimodal microstructure).[5] Although these heterogeneous microstructures can impart considerable increases in damage resistance, they degrade the intrinsic strength and wear resistance.

A different but more effective approach to achieve flaw-tolerance *without* strength degradation is based on *in-situ* growth of aluminate platelets (e.g. $LaAl_{11}O_{18}$, $LaMgAl_{11}O_{19}$, $SrAl_{12}O_{19}$, $CaAl_{12}O_{19}$, and $Na_2MgAl_{12}O_{17}$) within the alumina matrix.[6–8] Strengths of over 600 MPa and fracture toughness of 6 MPa m$^{1/2}$ have been achieved in alumina composites with both elongated Al_2O_3 grains and $LaAl_{11}O_{18}$ platelets.[8]

Recent developments in layered materials have provided a new strategy for designing high performance ceramics through laminating a homogeneous layer to provide wear resistance and a heterogeneous layer to provide toughness.[9–15] Unlike more traditional layered structures which promote either toughness by interlayer crack deflection or strength by incorporating macroscopic compressive residual stresses, the new approach deliberately seeks to produce strong interlayer bonding and to eliminate residual macroscopic stresses. Accordingly, any attendant counterproductive effects of weak interlayers and residual stresses, such as enhancement of delamination failures, can be avoided.

In Part I of this series, we present results on the synthesis, phase abundance, graded character, and physical properties of an infiltration-processed layered and graded material (LGM) based on the $Al_2O_3/CaAl_{12}O_{19}$ (CA_6) system. This method is relatively simple and offers excellent control over the depth of infiltration which dictates the depth of graded layer. The presence of the *in-situ* CA_6 phase in the alumina matrix has a profound influence on the graded and physical properties of the composite. The characteristics and properties of LGM have been studied using X-ray diffraction,

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differential thermal and gravimetric analysis, and Vickers indentation.

2 Experimental Procedure

2.1 Sample preparation

Alumina powder for fabrication of preforms was obtained by wet ball milling α-Al_2O_3 (A1000SG grade Alcoa, USA, of median particle size 0·39 μm) with 3 wt% propylene glycol as antiflocculant for 2 h. The slurry was then dried and sieved until free-flowing (45 μm grid-size). The processed powder was uniaxially pressed at a pressure of 75 MPa to yield a bar sample of dimensions $5 \times 12 \times 60\,mm^3$. A partial sintering at 1100°C for 2 h was done to increase the strength and retain the porosity (approximately 46%) of the preform prior to infiltration.

Infiltration of the porous preform was conducted at room temperature by immersing the bottom half of the sample in a solution of calcium acetate (Unilab Chemicals) for 8 h. The partially-infiltrated preform was hydrolysed in-situ and dried at room temperature for 24 h before it was heat-treated in a high temperature furnace (Ceramic Engineering, Model HT 04/17) at 450°C for 30 min, 1200°C for 12 h, and 1600°C for 2 h, and then furnace-cooled. This complex heat-treatment was necessary to enable the growth of CA_6 grains at 1200°C and subsequent sintering at 1600°C. After sintering, the infiltrated part of the sample reacted to form the graded CA_6/alumina region while the non-infiltrated part formed the homogeneous alumina layer. A schematic diagram illustrating the process and concept of infiltration-processed LGM is shown in Fig. 1.

2.2 Sample Characterisation

Analysis of phases formed and their abundance was performed with a Siemens D500 X–ray diffractometer. The operating conditions used were: CuK_α radiation ($\lambda = 0{\cdot}15418$ nm) produced at 40 kV and 0·15° receiving slit, goniometer range = 20–60°, step size = 0·04, counting time 1 s step, and post-diffraction graphite monochromator with NaI detector and PHA. An incident beam divergence of 0·3° was used. The phase abundances of CA_6 and α-Al_2O_3 in the sintered LGM were extrapolated from a calibration curve of separately processed alumina samples containing known amounts of CA_6. This calibration curve shown in Fig. 2. was used to compute the phase abundance of CA_6 present in the graded region of sintered LGM. Depth profiling of graded phase compositions was measured by gradually polishing away the surface material with emery paper.

Simultaneous DTA and TGA measurements on the powder mixture were carried out on a Netzsch STA-409C instrument in nitrogen atmosphere at a heating rate of 20°C min^{-1} with an empty reference. The apparent porosity and bulk density of the LGM were measured following the Australian Standard AS 1774.5.[16] The standard ceramographic procedure (i.e. 1 μm surface finish) was used to prepare the cross-section of LGM for Vickers indentation. A Zwick tester was used to measure the Vickers hardness variations of the LGM from the graded region to the alumina layer at 100 N load. At least three measurements were made for each loading position. The microstructure was observed using a SEM equipped with an energy-dispersive spectrometer (EDS). X-ray mapping of Al and Ca was also performed to verify the presence of platelike CA_6 grains.

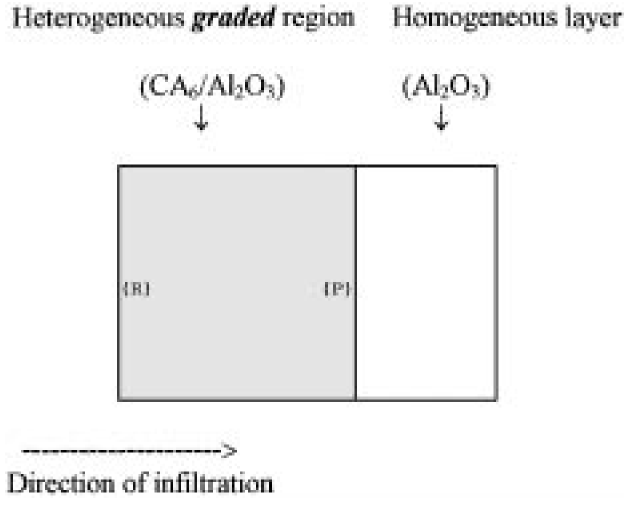

Fig. 1. Schematic diagram showing the processing concept of a layered and graded CA_6/alumina composite. The corresponding scanning electron micrographs at regions (P) and (R) are shown in Figs 7 and 8 respectively.

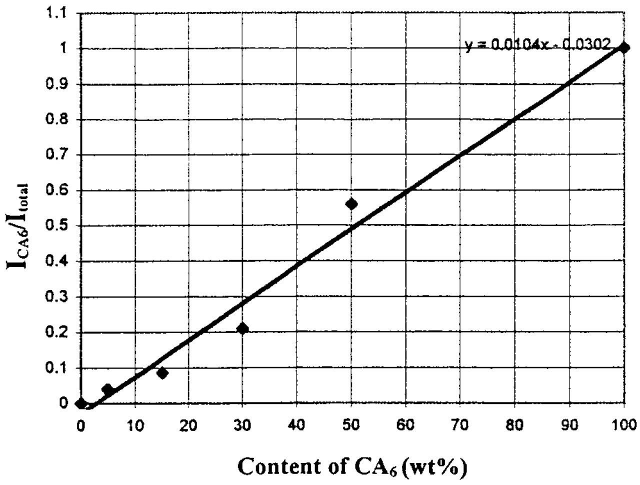

Fig. 2. Calibration curve of alumina samples containing known amounts of CA_6.

3 Results and Discussion

3.1 Phase Relations

X-ray diffraction of the LGM showed the presence of single α-Al_2O_3 phase in the homogeneous non-infiltrated layer and a mixture of CA_6 and α-Al_2O_3 phases in the graded layer. Depth profiling of the graded layer by XRD (Fig. 3) showed that the phase abundance of CA_6 was approximately 56 wt% on the surface and decreased gradually with polished depth (Fig. 4). The graded nature of this material is clearly revealed. This concentration profile of CA_6 is in good agreement with the fully graded AT/Al_2O_3[17] AT/ZTA[18] and CA_6/Al_2O_3[19] systems.

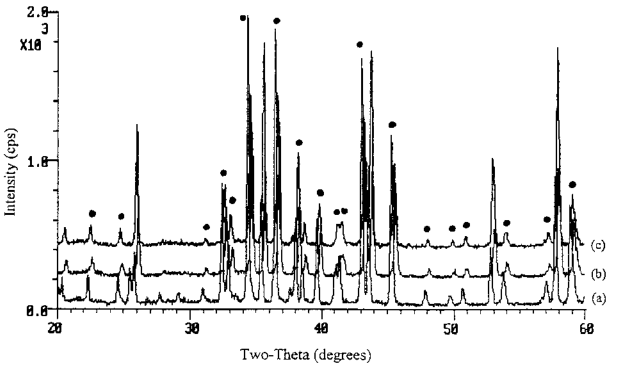

Fig. 3. XRD plots of the graded region polished to various depths: (a) 0 mm, (b) 0·1 mm, and (c) 0·2 mm. Note that the peak intensities of CA_6 (●) decrease with polished depth.

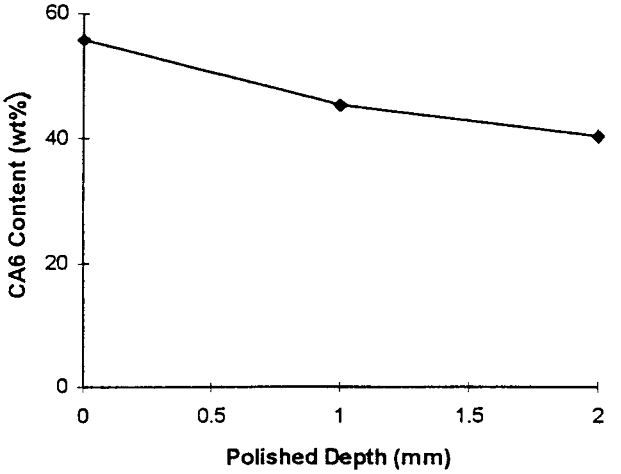

Fig. 4. Phase abundance of CA_6 as a function of polished depth.

The formation of *in-situ* CA_6 is believed to occur via an endothermic reaction between Al_2O_3 and $CaCO_3$ at approximately 1000°C the following reaction:

$$6Al_2O_3 + CaCO_3 \rightarrow CaAl_{12}O_{19} + CO_2 \quad (1)$$

The amount of CA_6 formed *in-situ* would depend on the rate and duration of infiltration. Less than 30 wt% CA_6 formed in LGM samples which were infiltrated for less than 8 h.[19]

The processes of hydrolysis of calcium acetate to form calcium hydroxide and its subsequent reaction with ambient CO_2 to form calcium carbonate are as follows:

$$Ca(CH_3COO)_2.H_2O + H_2O \rightarrow Ca(OH)_2 + 2CH_3COOH \quad (2)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3)$$

Table 1. Average values of shrinkage, apparent porosity and bulk density of a sintered LGM sample

Sample	*Shrinkage (%)*	*Apparent porosity (%)*	*Bulk density ($g\,cm^{-3}$)*
LGM	14	0·5	3·8

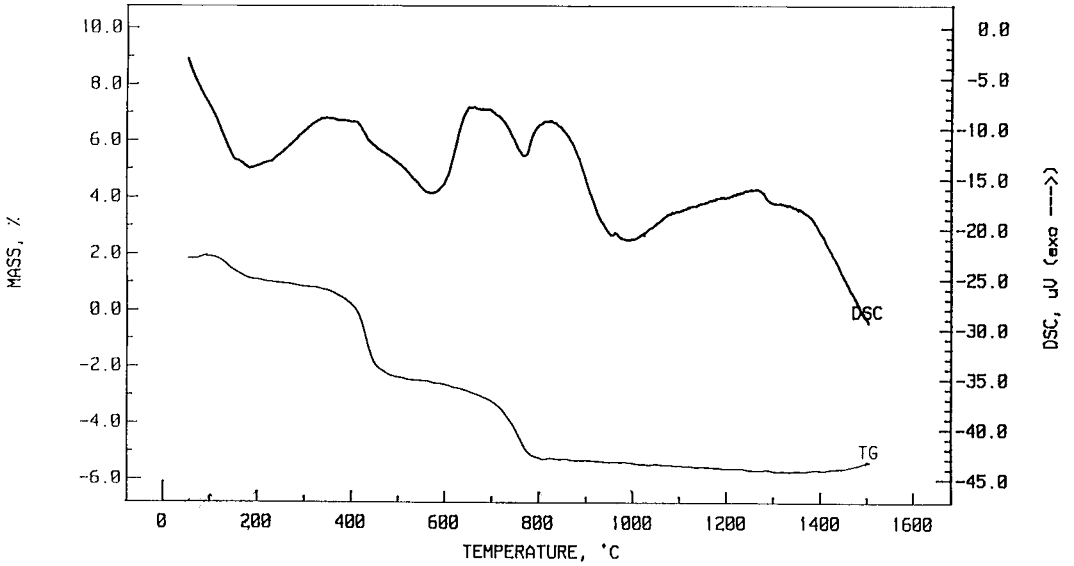

Fig. 5. DTA and TGA plots of LGM sample from 20 to 1500°C.

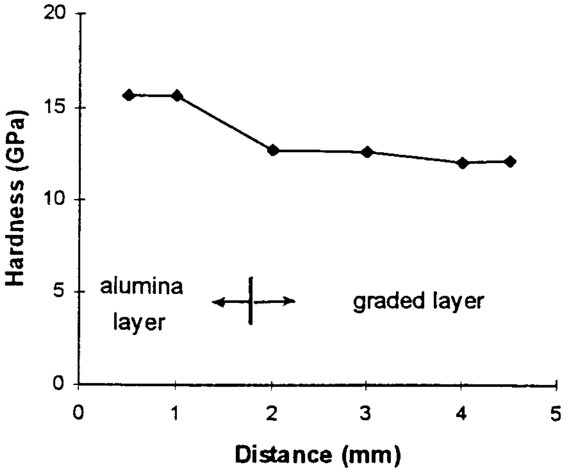

Fig. 6. Microhardness profile across the LGM from the alumina layer to the graded layer.

To the best of our knowledge, there is no literature information on the study of CA_6 formation by differential thermal and gravimetric analysis. The thermogram of sample recorded in the temperature range 20–1500°C is shown in Fig. 5. The endotherms at approximately 200, 500, 750 and 1000°C can be ascribed to the removal of hydroxyl ions, decomposition of propylene glycol, decomposition of calcium carbonate, and formation of CA_6 respectively. The formation temperature of CA_6 reported here agrees favourably with that of monocalcium aluminate which formed at between 900–1000°C.[20] The decomposition of propylene glycol and calcium carbonate gave rise to a precipitous drop in mass at approximately 450 and 750°C respectively.

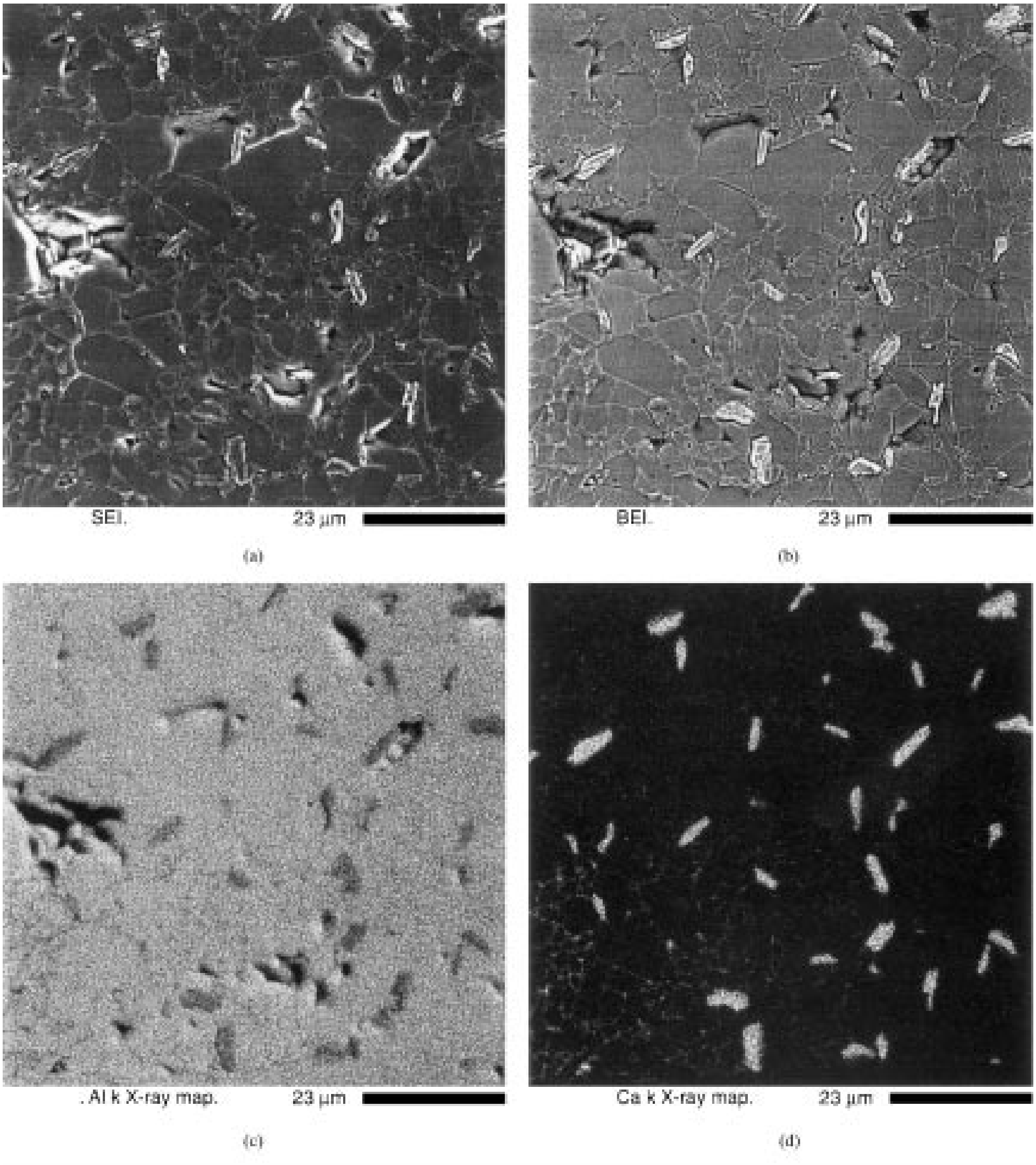

Fig. 7. Scanning electron micrographs of the graded layer showing a typical CA_6-poor area (corresponds to region P in Fig. 1). (a) Secondary electrons imaging; (b) back-scattered electrons imaging; (c) Al X-ray map; (d) Ca X-ray map.

3.2 Physical characteristics

Results of shrinkage, apparent porosity and density for the sintered LGM sample are shown in Table 1. The results show that dense LGM samples with low open porosity (0·5%) could be achieved through pressureless sintering at 1600°C. Similar encouraging results were obtained for the fully graded AT/Al_2O_3[17], AT/ZTA[18] and CA_6/Al_2O_3[19] systems.

Figure 6 shows the hardness profile of LGM from the homogeneous alumina layer to the heterogeneous graded CA_6/alumina layer. The gradual drop in hardness from the alumina interface verifies the presence of a continuous CA_6 concentration gradient in the graded layer. The decrease in hardness commensurates with an increase in abundance of softer CA_6 phase away from the interface. This graded hardness behaviour has also been observed for the graded AT/ZTA system.[18]

The plate-like morphology of CA_6 grains in the CA_6-poor and CA_6-rich areas of the graded layer are clearly shown in Figs 7 and 8 respectively, and is verified by Ca X-ray mapping. The alumina grains in CA_6-poor area are significantly larger than in the CA_6-rich area. It appears that the presence of more CA_6 has a grain-size refinement effect. The *in-situ* formed CA_6 grains appear to be very strongly bonded with the matrix. Further work on the graded microstructures and their effects on the flaw-tolerance and contact damage of the LGM are in progress and will be reported in due course.

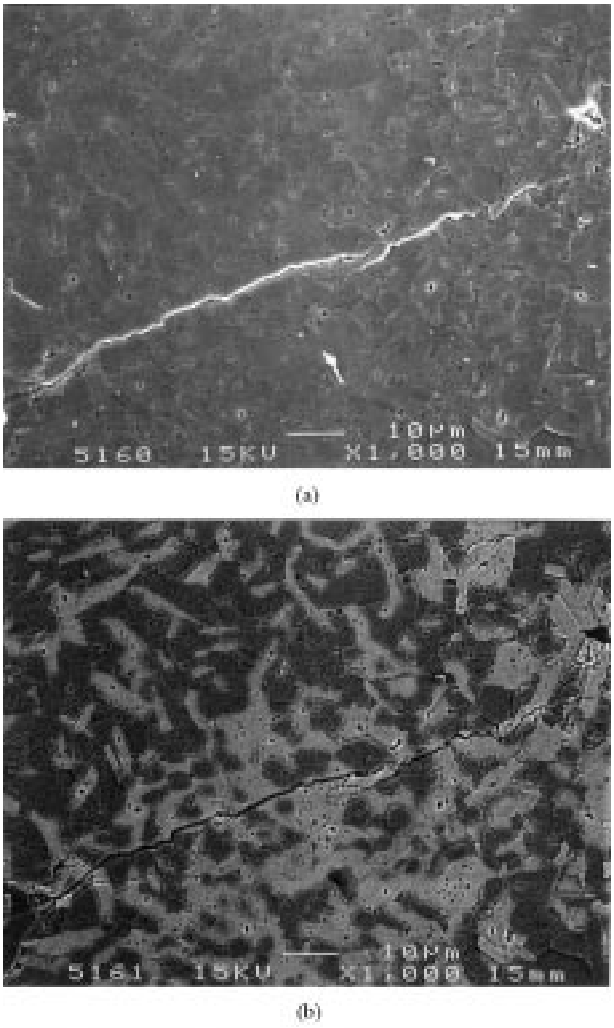

Fig. 8. Scanning electron micrographs of the graded layer showing a typical CA_6-rich area (corresponds to region R in Fig. 1). (a) Secondary electrons imaging; (b) back-scattered-electrons imaging.

4 Conclusions

A composite of layered and graded alumina/CA_6 with unique properties has been synthesised using an infiltration process. The presence of *in-situ* CA_6 phase in the graded layer has a profound influence on the physical characteristics of the composite. The infiltration approach offers an elegant means for tailoring the composition and microstructure of layered and graded materials to achieve specific desirable properties.

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