JOURNAL OF MATERIALS SCIENCE 21 (1986) 3479–3482

Subsolidus, high temperature phase relations in the systems Al_2O_3–Cr_2O_3–ZrO_2, MgO–Cr_2O_3–ZrO_2 and MgO–Al_2O_3–ZrO_2

P. TASSOT*, G. KÖNIG‡, F. SEIFERT§, F. LIEBAU
Mineralogisches Institut, Universität Kiel, D-2300 Kiel, West Germany
‡*Martin and Pagenstecher Co., D-4150 Krefeld, West Germany*

In the temperature range 1600 to 1900° C, the system Al_2O_3–Cr_2O_3–ZrO_2 is characterized by the coexistence of ZrO_2 (unstablilized) and an (Al, Cr)$_2$O$_3$ solid solution series. In the systems MgO–Cr_2O_3–ZrO_2 and MgO–Al_2O_3–ZrO_2 a nearly stoichiometric spinel coexists with both stabilized and unstabilized ZrO_2. At temperatures above 1600° C a new ternary Mg–Al–Zr oxide becomes stable in the MgO-rich part of the MgO–Al_2O_3–ZrO_2 system.

1. Introduction

ZrO_2 in its various polymorphic forms, stabilized ZrO_2, and oxide spinels ($R^{2+}R^{3+}{}_2O_4$, R^{2+} = Mg, Fe^{2+}, R^{3+} = Al, Cr, Fe^{3+}) are important constituents of many refractory materials, due to their specific properties such as high melting points and chemical inertness. The system MgO–Al_2O_3–Cr_2O_3–ZrO_2, therefore, represents a convenient starting point for the study of spinel–zirconia ceramics and their properties. To achieve this goal, knowledge of the subsolidus phase relations, including the miscibility of the phases, is essential. The present paper deals with the phase relationships on three of the four limiting ternary systems of the above quaternary, in the relevant temperature range 1600 to 1900° C. For details of the experiments and a complete listing of results see [1].

2. Previous work

According to [2] the system Al_2O_3–Cr_2O_3–ZrO_2 is characterized, at temperatures close to the solidus, by the coexistence of unstabilized ZrO_2 (u-ZrO_2) with members of the solid solution series Al_2O_3–Cr_2O_3 in all ternary compositions. The join $MgCr_2O_4$–ZrO_2 of the MgO–Cr_2O_3–ZrO_2 system has been described as a simple eutectic subsystem ($T_E = 2005 \pm 15°$C, 43 mol % ZrO_2) by [3], with mutual solid solubilities of approximately 4 and 3 mol % of the ZrO_2 and spinel phase, respectively. In the $MgAl_2O_4$–ZrO_2 system no ternary compound has been encountered either [4–6] and solid solubility is very restricted [4]. A new high temperature phase in the MgO-rich part of the MgO–Al_2O_3–ZrO_2 system has been reported by [7] and independently by [8].

3. Experimental procedure

Starting materials were prepared from appropriate amounts of fine-grained (less than 50 μm) pure oxides, MgO, (Merck lot no. 5865), Al_2O_3 (Alcoa A17), Cr_2O_3 (Bayer) and monoclinic ZrO_2 (Dynamit-Nobel, MS 0 to 10 μm), taking the absorbed water content into account. These materials were thoroughly mixed in a corundum ball mill for 2 h with ethanol, cold pressed in an impact press into cylinders (50 mm diameter, 50 mm high) and dried at 100° C for 24 h. The cylinders were heated isothermally at 1600, 1700, 1800 and 1900 ± 15° C under oxidizing conditions in a gas–air heated combustion furnace for 6 to 24 h, and then cooled to room temperature. All bulk specimens containing Cr_2O_3 have been analysed by X-ray fluorescence to check for loss of Cr_2O_3 through volatilization during heating. Phases present in the products were identified from powder X-ray diffractograms and their composition was derived from the lattice parameters (for Mg–Al–spinels [9, 10], for Mg–Cr–spinels [11, 12] and for (Al, Cr)$_2$O$_3$ [13]), and, in some cases, by microprobe analysis.

4. Results

Two forms of ZrO_2-rich phases have been observed in the products: monoclinic ZrO_2 (m-ZrO_2), chemically

TABLE I Representative results on the system Al_2O_3–Cr_2O_3–ZrO_2 at 1800° C, 24 h

Bulk composition		Lattice constants (Al, Cr)$_2$O$_3$ phase	
Planned	Measured	*a* (nm)	*c* (nm)
40.0/15.0/45.0	40.2/14.7/45.1	0.4822 (1)†	1.3153 (3)
33.3/33.3/33.3	33.5/33.1/33.4	0.4868 (1)	1.3283 (6)
15.0/40.0/45.0	15.0/39.8/45.2	0.4911 (1)	1.3425 (1)
20.0/20.0/60.0	20.1/20.0/59.9	0.4868 (1)	1.3288 (5)

m-ZrO_2 lattice constants were in the ranges a = 0.5145–0.5152 nm, b = 0.5201–0.5207 nm, c = 0.5317–0.5320 nm, β = 99°5′–99°12′.
*The product phase assemblage is monoclinic ZrO_2 (m-ZrO_2) + (Al, Cr)$_2$O$_3$ throughout. Chemical compositions (in mol %) are given in the form Al_2O_3/Cr_2O_3/ZrO_2.
†Parenthesized figures represent estimated standard deviations in units of the figure quoted to their immediate left.

**Present address*: IRSID, F-57210 Maizieres-les-Metz, France.
§Present address: Bayerisches Geoinstitut, Postfach 10 12 51, D-8580 Bayreuth, West Germany.

0022–2461/86 $03.00 + .12

TABLE II Representative results on the system $MgO-Cr_2O_3-ZrO_2$ at 1800° C, 24 h

Bulk composition		Products
Planned	Measured	
33.5/33.5/33.0*	33.5/33.4/33.1	m-ZrO_2, PC (a = 0.83332 (5))
40.0/40.0/20.0	40.1/40.3/19.5	m-ZrO_2, PC (a = 0.83327 (3))
55.0/23.0/22.0	54.7/23.1/22.2	c-ZrO_2 (a = 0.5072 (1)), PC (a = 0.83365 (2)), MgO
43.5/28.5/28.0	44.0/28.5/27.5	c-ZrO_2 (a= 0.5071 (1)), PC (a = 0.83350 (11)), MgO
25.0/25.0/50.0	24.9/25.3/49.8	m-ZrO_2, PC (a = 0.83330 (3))
25.0/38.0/37.0	24.9/38.0/37.1	m-ZrO_2, (a = 0.83376 (3)), Cr_2O_3

*Chemical compositions (in mol %) are given in the form $MgO/Cr_2O_3/ZrO_2$. PC = picochromite, close to $MgCr_2O_4$. a = lattice constants (in nm).

†Parenthesized figures represent estimated standard deviations in units of the figure quoted to their immediate left.

close to pure ZrO_2, and cubic ZrO_2 (c-ZrO_2) which is the form stabilized through significant amounts of MgO. In the temperature range studied here, m-ZrO_2 is unstable, and it results in the products from inversion from a probably tetragonal high temperature phase [14]. In discussing the phase relations at high temperature, we will, therefore, use the term u-ZrO_2 for the unstabilized form of ZrO_2.

4.1. The system $Al_2O_3-Cr_2O_3-ZrO_2$

In agreement with [2], only the two-phase assemblage u-ZrO_2 + $(Al, Cr)_2O_3$ solid solution has been encountered in the entire temperature range studied. A heat treatment of 24 h duration is sufficient to produce, from the starting materials, a homogeneous $(Al, Cr)_2O_3$ phase. Chemical analyses of the bulk products (Table I) as well as the lattice constants of the $(Al, Cr)_2O_3$ phase indicate that loss of chromium during heating is negligible. From microprobe analyses it is inferred that the ZrO_2 content of the $(Al, Cr)_2O_3$ phase is less than 2 wt %, and no indications for a solubility of $(Al, Cr)_2O_3$ in ZrO_2 could be derived from the lattice constants of the latter phase.

4.2. The system $MgO-Cr_2O_3-ZrO_2$

Results are tabulated in Table II and the subsolidus phase diagram is depicted in Fig. 1. The topology of the system remains unchanged in the temperature range studied: it is subdivided by two two-phase fields, u-ZrO_2 + spinel and c-ZrO_2 + spinel, so that three three-phase fields appear. At a $MgO:Cr_2O_3$ ratio of 1 (i.e. on the join $ZrO_2-MgCr_2O_4$) only u-ZrO_2 and a stoichiometric spinel can coexist, whereas formation of c-ZrO_2 requires an excess of MgO over Cr_2O_3. It should be noted that the assemblage spinel + u-ZrO_2 + c-ZrO_2 is stable only over a very narrow range of $MgO:Cr_2O_3$ ratio.

Upon increasing temperature from 1600 to 1900° C the solid solution ranges of both the c-ZrO_2 and spinel phase increase slightly and consequently the two-phase fields widen systematically.

4.3. The system $MgO-Al_2O_3-ZrO_2$

At 1600° C no ternary compound has been observed, and the topology of the system is identical to that found for the $MgO-Cr_2O_3-ZrO_2$ system (Table III). The only difference is the larger solubility of the Mg-Al-spinel, particularly towards Al_2O_3 (Fig. 2a). Again, when $MgO:Al_2O_3$ = 1, u-ZrO_2 coexists with a nearly stoichiometric $MgAl_2O_4$ spinel. The c-ZrO_2 + u-ZrO_2 + spinel assemblage is restricted, at 26.6 mol % ZrO_2 component, to $MgO:Al_2O_3$ ratios above 1 and less than 1.14.

In the temperature range 1600 to 1700° C a ternary compound becomes stable in the MgO-rich part of the system [8, 15] which seems to be identical to that reported independently by [7]. Its composition depends slightly on the bulk composition,

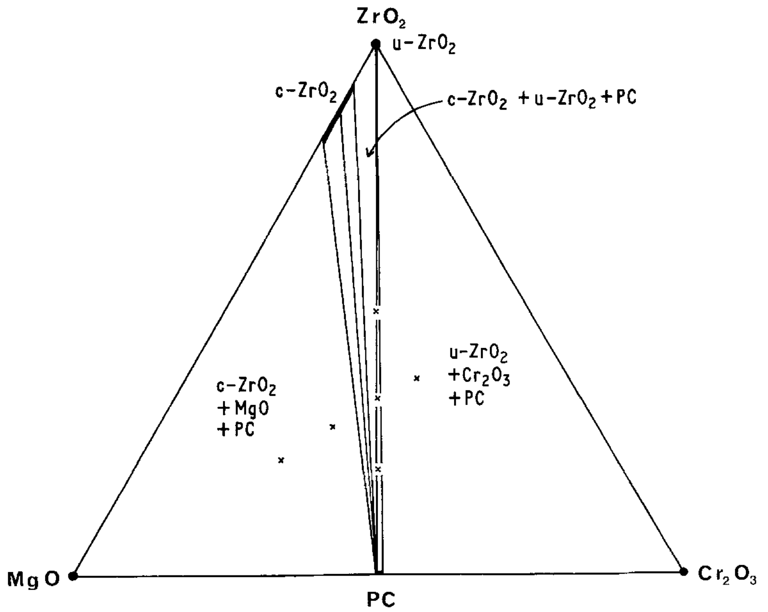

Figure 1 Section through the system $MgO-Cr_2O_3-ZrO_2$ at 1800° C. Abbreviations: u-ZrO_2 = unstabilized ZrO_2, c-ZrO_2 = cubic (stabilized) ZrO_2, PC = picochromite, close to $MgCr_2O_4$. Bulk compositions investigated are indicated by crosses. Two-phase fields originating from the small solid solubilities of u-ZrO_2, MgO, and Cr_2O_3 are omitted for simplicity.

TABLE III Representative results on the system $MgO-Al_2O_3-ZrO_2$ at 1600 and 1800°C

Bulk composition	Products	
	1600°C	1800°C
36.5/36.5/27.0	Sp (a = 0.80830 (6)), m-ZrO_2	Sp (a = 0.80823 (8)), m-ZrO_2
23.0/47.0/30.0	Sp (a = 0.80081 (9)), m-ZrO_2, Cor	Sp (a = 0.80065 (8)), m-ZrO_2
50.0/26.0/24.0	Sp (a = 0.80889 (7)), c-ZrO_2 (a = 0.5079 (1)), MgO	Sp (a = 0.80876 (5)), c-ZrO_2 (a = 0.5083 (1)), MgO, X
57.8/10.6/31.6	Sp, c-ZrO_2, MgO	Sp, c-ZrO_2, MgO, X
38.4/35.0/26.6	Sp, c-ZrO_2, m-ZrO_2	Sp, c-ZrO_2, m-ZrO_2
39.1/34.3/26.6	Sp, c-ZrO_2	Sp, c-ZrO_2
36.0/35.5/28.5	Sp, c-ZrO_2, m-ZrO_2	Sp, c-ZrO_2, m-ZrO_2

*Chemical compositions (in mol %) are given in the form $MgO/Al_2O_3/ZrO_2$. Sp = spinel, Cor = corundum. X = ternary Mg–Al–Zr oxide. a = lattice constants (in nm), with their estimated standard deviations.

temperature and run duration. 100% yields of this phase could not be achieved, it always coexisted with minor amounts of relic c-ZrO_2, MgO, and spinel. The microprobe analyses define a chemical variation of the phase that may be described by a formula $Mg_{5+x}Al_{2.4-x}Zr_{1.7+0.25x}O_{12}$ with $-0.4 \lesssim x \lesssim 0.4$ (Fig. 3). Through the existence of this phase, the c-ZrO_2 + MgO + spinel three-phase field in the 1600°C section is further subdivided under equilibrium conditions into three different three-phase fields involving the ternary compound at temperatures of and above 1700°C. When the ternary compound is hot annealed at or slightly below 1600°C, it decomposes within about 2h to the metastable assemblage MgO + c-ZrO_2 + Al_2O_3 (corundum) which only subsequently is transformed to MgO + $MgAl_2O_4$ + c-ZrO_2. Temperature increase beyond 1700°C leads to an expansion of the two-phase fields c-ZrO_2 + spinel and u-ZrO_2 + spinel (Fig. 2b).

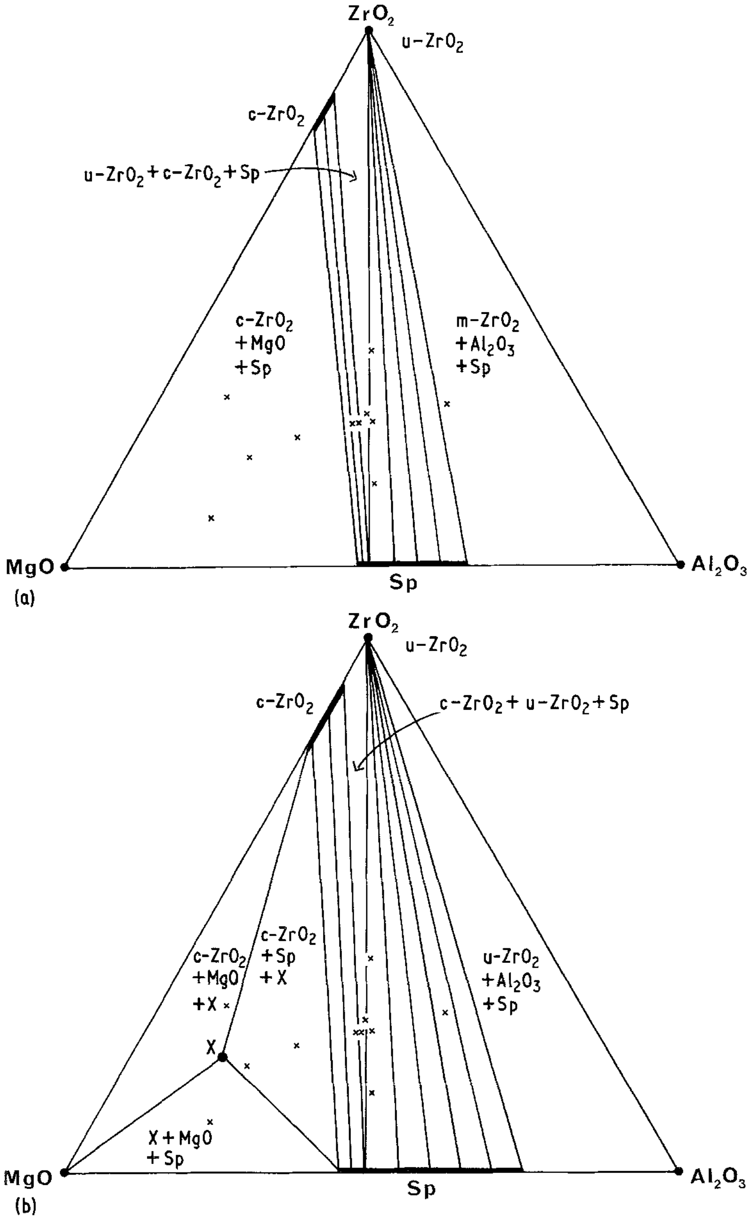

Figure 2 Sections through the system $MgO-Al_2O_3-ZrO_2$ at (a) 1600°C and (b) 1800°C. Abbreviations: u-ZrO_2 = unstabilized ZrO_2, c-ZrO_2 = cubic (stabilized) ZrO_2, Sp = magnesium aluminate spinel, X = ternary Mg–Al–Zr–oxide (cf. text). Compositions investigated are indicated by crosses. Two-phase fields originating from the small solid solubilities of u-ZrO_2, MgO, X, and Al_2O_3 are omitted for simplicity.

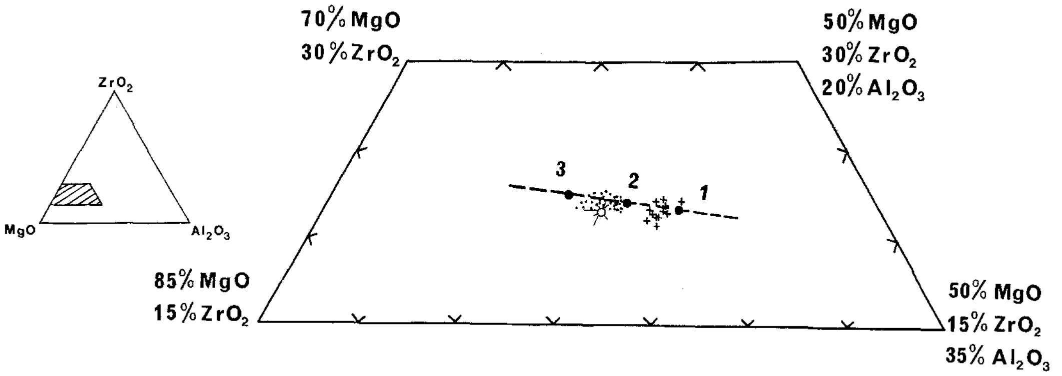

Figure 3 Results of microprobe analyses of the new ternary compound X in part of the system $MgO-Al_2O_3-ZrO_2$ (in mol %). Synthesis conditions: 1800° C, 24 h slow cooling (crosses); 1800° C, 48 h, fast quench (small dots). The dashed line indicates the chemical variability according to the formula $Mg_{5+x}Al_{2.4-x}Zr_{1.7+0.25x}O_{12}$. Specific compositions corresponding to $x = -0.4$, 0, and $+0.4$ are given by dots labelled 1, 2, 3, respectively. The open circle represents the composition of the phase reported by Firatli [7].

5. Discussion

In all the systems studied, solidus temperatures are above 1900° C which is one of the prerequisites for their usefulness as materials of refractories.

c-ZrO_2 can only be formed in the presence of excess MgO over Al_2O_3 or Cr_2O_3. For the binary systems $ZrO_2-Al_2O_3$ and $ZrO_2-Cr_2O_3$ the eutectoid temperature marking the decomposition of c-ZrO_2 into the respective oxides lies at too high temperatures (probably slightly below 2000° C [16]). We cannot exclude that in the 1900° C runs c-ZrO_2 has been present during sintering even when MgO:(Al_2O_3, Cr_2O_3) was below 1 but that this phase decomposed during cooling because of the rapid kinetics close to the high eutectoid temperature, and the rather poor thermal conductivity of ZrO_2. In the ZrO_2-MgO system the eutectoid temperature of the c-ZrO_2 decomposition is in the vicinity of 1400° C [16].

Refractories based only on spinel phases suffer from poor resistance to thermal shock. This property might be improved particularly through coexisting c-ZrO_2 + u-ZrO_2 (partially stabilized zirconia), and the phase relations obtained here indicate that a spinel + c-ZrO_2 + u-ZrO_2 assemblage can only be produced at MgO:(Al, Cr)$_2$O$_3$ ratios slightly above 1 (Figs 1 and 2). The ternary phase in the $MgO-Al_2O_3-ZrO_2$ system is about 10% less dense than c-ZrO_2 + $MgAl_2O_4$ + MgO, and its presence in a refractory would induce severe strain as soon as the lower stability limit of the phase (between 1600 and 1700° C) is reached.

References

1. P. TASSOT, dissertation, Universität Kiel (1983).
2. R. KLUTE, diplomarbeit, Technische Hochschule Aachen (1982).
3. S. G. SENNIKOV, G. E. REVZIN and M. V. CHISTYAKOVA, *Russ. J. Inorg. Chem.* **27** (1982) 1013.
4. R. F. MATHER, *J. Amer. Ceram. Soc.* **25** (1942) 93.
5. R. A. KORDYUK and N. V. GUL'KO, *Dokl. Akad. Nauk SSSR* **154** (1964) 1183.
6. P. G. HEROLD and W. J. SMOTHERS, *J. Amer. Ceram. Soc.* **37** (1954) 351.
7. A. C. FIRATLI, dissertation, Technische Hochschule Aachen (1981).
8. P. TASSOT, G. KÖNIG, F. LIEBAU and F. SEIFERT, *J. Appl. Cryst.* **16** (1983) 649.
9. H. U. VIERTEL and F. SEIFERT, *Neues Jahrbuch für Mineralogie Abhandlungen* **134** (1979) 167.
10. *Idem, ibid.* **140** (1980) 89.
11. O. SPIES, dissertation, Universität Frankfurt (1972).
12. A. M. ALPER, R. N. McNALLY, R. C. DOMAN and F. G. KEIHN, *J. Amer. Ceram. Soc.* **47** (1964) 30.
13. H. E. v. STEINWEHR, *Z. Krist.* **125** (1967) 377.
14. E. C. SUBBARAO, H. S. MATTI and K. K. SRIVASTAVA, *Phys. Status Solidi* **21** (1974) 41.
15. G. BISSERT and P. TASSOT, in preparation.
16. J. STÖCKER, *Ann. Chemie Serie* **13** (1960) 1459.

Received 1 November
and accepted 25 November 1985