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Phase diagram of the system: ZrO_2–Cr_2O_3

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Abstract

The ZrO_2–Cr_2O_3 system was studied by differential thermal analysis in the composition range from 0 to 40 mass% Cr_2O_3. The formation of extensive solid solutions (25 mass% Cr_2O_3 in cubic zirconia and 40 mass% ZrO_2 in Cr_2O_3 at the eutectic temperature) and the eutectic point coordinate: 1950°C and 50 mass% of ZrO_2 are reported. Cubic zirconia solid solution decomposes at 1840°C, 25 mass% Cr_2O_3, by eutectoid reaction forming tetragonal zirconia solid solution with 9 mass% Cr_2O_3. This phase transforms at 1115°C to monoclinic zirconia solid solution. The enthalpies of these transformations are: 610±60 J/g for eutectic fusion, 110±10 J/g for eutectoid at 1840°C, 25 mass% Cr_2O_3, 22±5 J/g for eutectoid at 1115°C, 9 mass% Cr_2O_3 and 42±5 J/g for pure zirconia at 1165°C.

Keywords: Phase diagram; ZrO_2–Cr_2O_3 system

1. Introduction

The ZrO_2–Cr_2O_3 system could be involved in practical applications in refractories industry and metallurgy, in high temperature fuel cells and in theoretical analysis of the products of oxidation of Fe–Cr–Zr alloys. The phase diagram of this system was studied partially [1–9], but results of investigations differ. In agreement with previous results [1–7] the components form a simple eutectic. The published eutectic point coordinates are 58 mass% Cr_2O_3 and 1850±10°C [7], 59 mass% Cr_2O_3 and 1880°C [2,3], 50 mass% Cr_2O_3 and 2100°C [1], 55 mass% Cr_2O_3 and 2320°C [4].

Some researchers [1,5] find slight solubility of ZrO_2 in Cr_2O_3 while results of [2,3] claim 38 mass% ZrO_2 in Cr_2O_3 solid solution (SS). The authors [2,3] find linear increase of optical refractive index of Cr_2O_3 SS in melted samples with increasing ZrO_2 contents. In spite of the reported low solubility of Cr_2O_3 in ZrO_2 [1,5,6], results of [8] confirm some Cr_2O_3 (0.5–3 mass%) in zirconia in sintered material of (mass%): 45 Al_2O_3, 35 ZrO_2, 15 Cr_2O_3, 5 SiO_2. Data in [7] report the first appearance of Cr_2O_3 X-ray reflections in samples annealed at 1700°C at 4.5 mass% Cr_2O_3 and the first appearance of DTA peaks at 1850±10°C at 8.5 mass% Cr_2O_3. Moreover, X-ray analysis of co-precipitated hydroxides sintered at 900°C found SS in monoclinic ZrO_2 up to 34.5 mass% Cr_2O_3 [9].

2. Experimental

Samples were prepared from chemical grade oxides calcined 1 h at 1000°C with compositions of 0, 10, 20, 30 and 40 mass% Cr_2O_3. Both crucibles and furnace heater were made from molybdenum, that permits experiments to 2100°C. To minimize reaction between Mo and Cr_2O_3 all experiments were carried in argon at 1.3 atm.

Temperature and enthalpy data were recorded by DTA. All signals were carried through a low noise amplifier, then converted by 15-bit analogue-digital device and stored on hard disk drive. Experiments were carried using a high temperature differential thermal analyser with three-crucible cell. The third crucible contains pure alumina that permits calibration of the thermocouple (tungsten–rhenium 5/20) in situ by melting of Al_2O_3 at the same time as measurement of the sample in the adjacent crucible. The method, in combination with heating rate variation, has an accuracy of temperature determination better than ±10°C at 1700–2100°C. Heating rates were 10, 20, 60 and 100°C/min. Every sample (40–100 mg) was heated 2–4 times up to 2080–2100°C. Preliminary calibrating of the cell was done

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using enthalpies of melting of 13 pure substances from In and Sn to Pt and Al_2O_3 so that uncertainties in heat determination were less than 10%. After each sample treatment the cell was calibrated with pure copper to correct temperature and heat effect data of α–β polymorph transition of ZrO_2 SS.

Concentrations determined by DTA peak analysis were elaborated by X-ray fluorescence microanalysis (XFM). The method permits determination of the relative concentration of Zr and Cr in two phases after their electron microscope observation in a cut and polished sample. For instance, in a sample annealed at 900°C

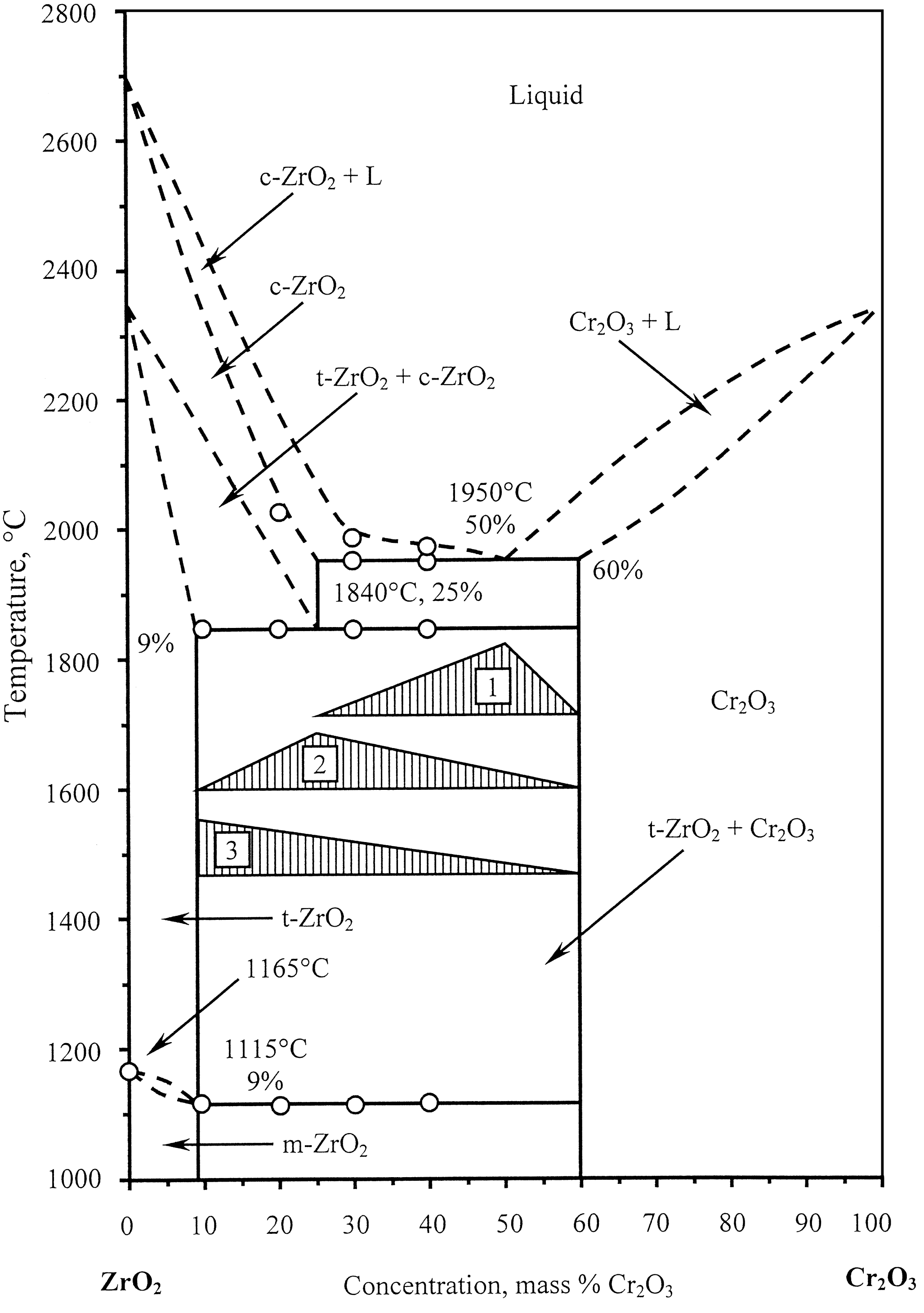

Fig. 1. Phase diagram of ZrO_2–Cr_2O_3 system. Triangles express the expected peak areas of the eutectic at 1950°C (1) and eutectoids at 1840°C (2) and 1115°C (3).

with a total 30 mass% Cr_2O_3 the Zr fluorescence intensity ratio in two phases (p1 and p2) was Zr(p1)/Zr(p2) = 2.34 and Cr ratio Cr(p1)/Cr(p2) = 0.143. From these data and concentration normalization ($[ZrO_2(p1)] + [Cr_2O_3(p1)] = 100$ mass% and $[ZrO_2(p2)] + [Cr_2O_3(p2)] = 100$ mass%) the concentrations of Cr_2O_3 in two phases are $[Cr_2O_3(p1)] = 8.7$ mass% and $[Cr_2O_3(p2)] = 61.0$ mass%.

3. Results and discussion

The main result is the stability of cubic zirconia SS below the eutectic temperature (Fig. 1). The eutectoid decomposition of this SS occurs at 1840±7°C and 25±5 mass% Cr_2O_3 forming Cr_2O_3 SS with 60±7 mass% Cr_2O_3 and tetragonal ZrO_2 SS with 9±2 mass% Cr_2O_3. The small size of the sample (100–150 mg) allowed resolution of two peaks on DTA curves of samples at 30 and 40 mass% Cr_2O_3 and revealed a little hump on the second peak (Fig. 2). Investigators using 1.5 g samples found a single humped peak starting at 1850°C which was correlated with the eutectic [7].

The areas of peaks, marked on Fig. 1, are shown on Fig. 3 from which a maximum heat effect at 1840°C is encountered at ~25, not 58 mass% Cr_2O_3 as should follow from [7] which supposed the eutectic at this point. Simultaneously from Fig. 3 one can see that peak areas at 1840 and 1115°C decrease with increasing Cr_2O_3 content from 30 to 40 mass%. These peaks correspond to relative amount of ZrO_2 SS in the sample. By extrapolation to zero peak area it could be estimated that solubility of zirconia in Cr_2O_3 is 45±10 mass%, not far from XFM data printed on phase diagram.

The solubility of Cr_2O_3 in ZrO_2 at the eutectic temperature is about 25±5 mass% Cr_2O_3. Moreover, the sample contained 10 mass% Cr_2O_3 remained solid even at 2200°C and the sample containing 20 mass% Cr_2O_3 at 2100°C was only partially melted. The transformation at 1840°C of ZrO_2 SS with 25 mass% Cr_2O_3 was accompanied by a 110±10 J/g heat effect. This value is close to enthalpy of the β–γ transformation of pure ZrO_2: 105 J/g [10] so it indirectly confirms that the transformation at 1840°C is due to eutectoid decomposition of cubic zirconia SS. Below this temperature the stable phases are tetragonal zirconia SS with 9±2 mass% Cr_2O_3 and Cr_2O_3 SS with 40±7 mass% ZrO_2, as measured by XFM: the latter value in fact is equal to [2,3].

A eutectic occurs at 1950±10°C and 50±5 mass% Cr_2O_3 (measured by XFM) by mentioned SS. The heat of eutectic fusion was found to be 610±60 J/g by extrapolation of data in Fig. 3. The fusion enthalpy of pure ZrO_2 (720 J/g [10–13]) and Cr_2O_3 (690 [12] or 820 J/g [13]) is larger, according to its higher melting temperatures.

The influence of Cr_2O_3 on the α–β polymorph transition of ZrO_2 was also determined: pure ZrO_2 transforms at 1165±7°C and ZrO_2 saturated SS with 9±2 mass% Cr_2O_3 transforms at 1115±5°C. The reverse transitions occur with hysteresis at 1055±5 and 945±5°C respectively.

The heat of the α–β transformation of pure ZrO_2 is found as 42±5 J/g and ZrO_2 saturated SS with 9±2 mass% Cr_2O_3 transforms with 22±5 J/g heat effect but it should be noted that by X-ray data [7] not all ZrO_2 SS transforms from tetragonal to monoclinic polymorph.

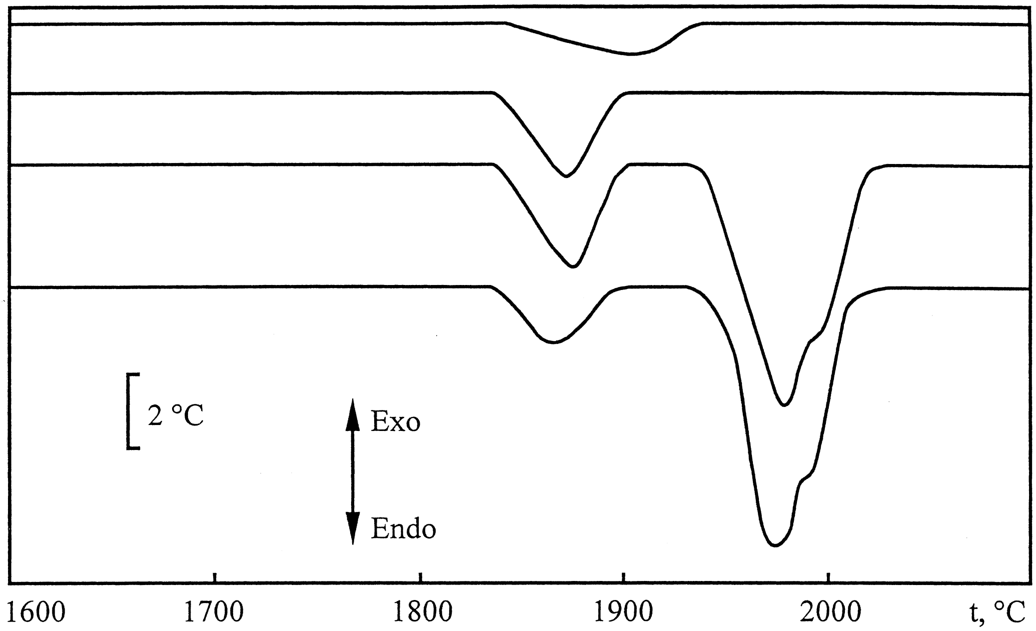

Fig. 2. DTA curves of the samples with (from top to bottom): 10, 20, 30 and 40 mass% Cr_2O_3. Heating rate 60°C/min, argon atmosphere.

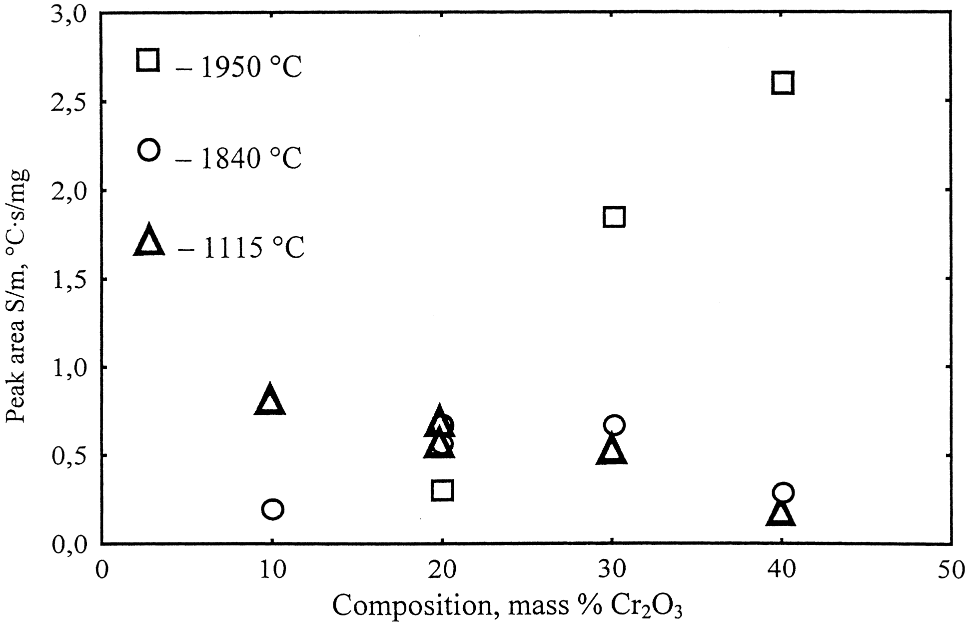

Fig. 3. Normalized peak areas versus sample composition.

Material of the crucible reacts slightly with Cr_2O_3. The molybdenum concentrations in the samples with 0, 10, 20, 30 and 40 mass% Cr_2O_3, measured by X-ray fluorescence microanalysis, are correspondingly <0.01, 0.3, 2, 3 and 4.5 mass% Mo. Moreover molybdenum was concentrated mainly in ZrO_2 phase. Such reactivity suggests that we should not use samples with higher Cr_2O_3 content owing to increasing reaction with the crucible.

References

[1] H. Wartenberg, H. Wert, Z. Anorg. Chem. T. 190 (1930) 178.
[2] V.F. Smachnaya, P.Ya Saldau, Zap. Len. Gorn. Inst. 24 (1950) 153 (in Russian).
[3] V.F. Smachnaya, Izv. vissh. uchebn. zaved., Chernaya Metallurgia 11 (1962) 191 (in Russian).
[4] S. Lang, R.S. Roth, C.L. Fillmore, J. Res. Nat. Bur. St. 53 (1954) 203.
[5] S.K. Rhee, M. Hoch, Trans. Metall. Soc. AIME 230 (1964) 1687.
[6] J. Stocker, R. Collongues, Compt. Rend. 245 (1958) 695.
[7] L.M. Lopato, V.A. Shevchenko, I.M. Maister, Izv. AN SSSR, Neorg. Materiali 13 (10) (1977) 1822–1824 (in Russian).
[8] I.A. Turkin, T.N. Maslova, Zhurn. prikl. himii AN SSSR, Leningrad (1984), No. 2797-84 Dep. (in Russian)
[9] J.F. Collins, J.F. Ferguson, J. Chem. Soc. A (1) (1968) 4–7.
[10] N.S. Zefirov, et al., Himicheskaya entsiklopedia, vol. 5. Bolshaya Rossiiskaya entsikl., Moscow, 1998, p. 783 (in Russian).
[11] V.A. Rabinovich, Z.Ya Havin, A.A. Potehin, A.I. Efimov (Eds.), Kratkii himicheskii spravochnik, 3rd edn. pererab. i dop.–L. Himia, 1991, p. 432 (in Russian).
[12] G.V. Samsonov, et al., Fiziko-himicheskie svoistva okislov. Spravochnik. Metallurgia (1969) 456 (in Russian).
[13] L.V. Gurvich, I.V. Veits, V.A. Medvedev, et al., Termodinamicheskie svoistva individualnih veschestv. Spravochnoe izdanie, vd. 4-h t, 3rd edn, pererab. i rasshiren, T.3. Kn.2. Nauka, Moscow, 1982, p. 560 (in Russian).