Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 537–543

PHASE EQUILIBRIA IN THE SYSTEM V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ AND SOME PROPERTIES OF THE $Fe_8V_{10}W_{16}O_{85}$ PHASE

I. Rychlowska-Himmel and P. Tabero

Institute of Chemistry and Environmental Protection, Technical University of Szczecin,
Al. Piastów 42, 71-065 Szczecin, Poland

Abstract

A phase diagram of the V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system were carried out using XRD and DTA methods. In addition, an indexing of $Fe_8V_{10}W_{16}O_{85}$ powder diffraction pattern was made and its basic crystallographic parameters were determined. Finally, the phase was studied using IR spectroscopy.

Keywords: DTA, IR, phase equilibria, V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system, XRD

Introduction

The catalytic properties of transition metal oxides and their mixtures have induced many workers to undertake extensive studies on some multicomponent systems. Recently some studies on the not yet refined system Fe_2O_3–V_2O_5–WO_3 have been made. In the first rate, some investigations have been carried out to verify the divergent data available – pertaining to the system Fe_2O_3–WO_3 as one of the three two-component systems building the system of interest. The work done has pointed out that Fe_2WO_6, as the sole compound arising in the above system, forms not two, as it has hitherto been supposed [1, 2], but three polymorphic forms [3]. The discovered polymorph, β-Fe_2WO_6, crystallizes in a monoclinic system and is formed as a result of monotropic transformation of α-Fe_2WO_6, taking place during a long-term heating at 750–840°C [3]. At over 950°C, an enantiotropic transformation of β-Fe_2WO_6 into γ-Fe_2WO_6 takes place [3], the latter known as a high-temperature variety [1].

Further studies on the Fe_2O_3–V_2O_5–WO_3 system have led to the discovery of a new compound with an assigned formula $Fe_8V_{10}W_{16}O_{85}$ [5–9]. This compound is known to melt at 830±5°C with depositing two solid products, i.e. Fe_2WO_6 and WO_3 [4]. Besides, a solid solution of V_2O_5 in iron(III) tungstate has been found to occur in the three-component system [10].

This work shows the experimental results for the phase equilibria being established in the V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system in which one of its components is the discovered phase. The other component is vanadium(V) oxide, which crystallizes in an orthorhombic system [11], and melts at 675±5°C [12]. In addition, an indexing of

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

powder diffraction pattern of $Fe_8V_{10}W_{16}O_{85}$ was made and its basic crystallographic parameters were determined. Finally, the phase was studied using IR spectroscopy, although the interpretation of its IR spectrum can only be qualitative considering that the structure of the compound is unknown.

Experimental

The following reagents were used in the experiments: α-Fe_2O_3, p.a. (VEB, Germany), additionally calcinated at 1000°C in three 24-hour stages, V_2O_5, p.a., (POCh, Gliwice, Poland), WO_3, p.a., (Fluka AG, Switzerland), additionally calcinated at 700°C for 24 h and $Fe_8V_{10}W_{16}O_{85}$ – obtained according [5].

In order to determine phase equilibria being established in the title system, 23 samples with an increasing contents of $Fe_8V_{10}W_{16}O_{85}$ in terms of the system components were prepared from oxides – the components of the Fe_2O_3–V_2O_5–WO_3 system. All the samples were heated in the following way: 550°C (24 h)+600°C (24 h+96 h) +610°C (48 h×6). A detailed method of preparing samples considered as remaining in a state of equilibrium and a method of identification of the type of the phases coexisting in the samples have been given in work [4].

The DTA examinations were performed with the use of derivatograph (MOM, Hungary). The measurements were carried out in the air atmosphere in the temperature range 20–1050°C. The portions of 500 mg were heated in quartz crucibles at a rate of 10°C min^{-1}. The accuracy of reading the temperatures of the thermal effects on the DTA curves was equal to ±5°C as it was determined by repetitions.

The powder diffraction pattern of the phase under study was obtained with the aid of a diffractometer DRON-3 (Bourevestnik, St. Petersburg, Russia) and a cobalt lamp with a Fe filter as source of radiation. Because of a strong tendency of a powdered $Fe_8V_{10}W_{16}O_{85}$ for texturing, its diffraction pattern was prepared using a technique of spraying the sieved powder (a 200-mesh sieve) on a glass plate covered with a silicon oil. The internal reference was α-Al_2O_3.

Indexing of a powder diffraction pattern of the $Fe_8V_{10}W_{16}O_{85}$ phase was made using a DICVOL programme [13].

Density of the compound was determined by the method described [14].

Spectroscopic studies were carried out by a spectrometer SPECORD M 80 (Carl Zeiss, Jena, Germany) at a range of 1100–300 cm^{-1} using a technique of pellets with KBr at a ratio by mass of 1:300.

Results and discussion

A diagram of phase equilibria of the V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system

Figure 1 shows a phase diagram of the V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system at the whole component concentration range, up to 1000°C. The diagram was prepared on the basis of DTA curves and XRD results obtained for all the samples. The solidus line temperature was determined depending on the onset temperature of the first endothermic ef-

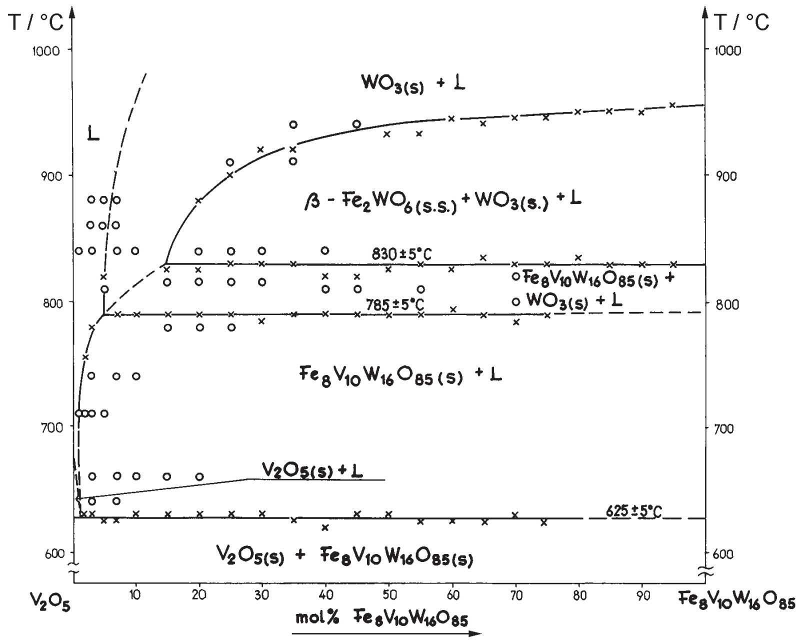

Fig. 1 Phase diagram of the V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system

fect, noticed on the DTA curves of all samples being in equilibrium. In samples, the initial mixtures of which contain less than 80 mol% of V_2O_5 (in terms of the system components), the effect has been recorded as residual. The liquidus lines were drawn reading maximum temperatures of the endothermic peaks noticed as terminal on DTA curves of the same samples. The DTA results of samples being in equilibrium made a ground for the ranges of solid phases coexisting with liquid, the types of the phases have been qualified depending on the XRD analysis of samples ‘frozen’ at suitable temperatures (dotted lines). The content of the samples and temperatures of ‘freezing’ have been marked in the figure.

The phase diagram implies that components of V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system remain in equilibrium up to the solidus line temperature, and at the 98 mol% V_2O_5 content they form a eutectic mixture melting at 625±5°C. However, above the eutectic temperature the system is not a real two-component system and its components are in equilibrium with liquid. In the system, at temperature 785°C upwards, solid phases that coexist in equilibrium with liquid, i.e. WO_3 and β-Fe_2WO_6 phases, have not been found in the subsolidus area. The phases appear in the system owing to peritectic melting of $Fe_8V_{10}W_{16}O_{85}$ [4] described by reaction:

$$Fe_8V_{10}W_{16}O_{85(s)}\xrightarrow{830\pm 5^\circ C}WO_{3(s)}+\beta\text{-}Fe_2WO_{6(s)}+\text{liquid}$$

(the formation of a low-concentration solid solution of V_2O_5 in β-Fe_2WO_6 was observed too).

Table 1 X-ray diffraction pattern of the phase $Fe_8V_{10}W_{16}O_{85}$

No.	$d_{obs.}$/nm	$d_{calc.}$/nm	h k l	I/%
1	1.39459	1.39677	1 1 0	1
2	0.69874	0.69838	2 2 0	4
3	0.46660	0.46559	3 3 0	44
4	0.36539	0.36533	1 0 1	14
5	0.34891	0.34919	4 4 0	100
6	0.33922	0.33877	5 3 0	2
7	0.32967	0.32922	6 0 0	2
8	0.30773	0.30761	3 2 1	1
9	0.27947	0.27935	5 5 0	6
		0.27935	7 1 0	
10	0.27089	0.27073	4 3 1	20
		0.27073	5 0 1	
		0.27133	7 2 0	
11	0.26121	0.26110	5 2 1	1
12	0.24675	0.24692	8 0 0	10
13	0.23731	0.23740	5 4 1	1
14	0.23282	0.23279	6 6 0	1
15	0.22484	0.22477	7 0 1	6
16	0.20455	0.20457	7 4 1	1
16	0.20455	0.20457	8 1 1	1
17	0.19966	0.19954	7 7 0	30
18	0.18592	0.18582	8 7 0	4
		0.18587	0 0 2	
19	0.18353	0.18340	10 4 0	3
20	0.17440	0.17444	8 6 1	2
		0.17444	10 0 1	
21	0.17324	0.17325	9 7 0	7
		0.17325	11 3 0	
22	0.16609	0.16621	8 7 1	6
23	0.16400	0.16408	4 4 2	4
		0.16404	9 8 0	
		0.16404	12 1 0	
24	0.15615	0.15616	12 4 0	1
25	0.15469	0.15475	5 5 2	1
		0.15475	7 1 2	
26	0.15362	0.15367	11 4 1	7
27	0.14836	0.14838	10 7 1	1
28	0.14110	0.14109	14 0 0	3

Indexing of the $Fe_8V_{10}W_{16}O_{85}$ diffraction pattern and parameters of its unit cell

The study of the $Fe_8V_{10}W_{16}O_{85}$ phase has resolved itself into the determination of density of this phase, made by indexing of its X-ray powder diffraction pattern (Table 1), and establishment of the spatial parameters for the unit cell. For indexing purposes, 28 reflexions were chosen from the 7–80° region of the 2θ angle (CoK_α). The best agreement with the experimental data was shown by the tetragonal unit cell with the parameters: $a=b=1.9753(3)$ nm, $c=0.3717(2)$ nm. The number of molecules in the unit cell $Z=1$. The unit cell volume: $V=1.45052$ nm^3. The density measured $\sigma_{obs.}=5.94\div0.05$ g cm^{-3} and is in good agreement with the calculated $\sigma_{rtg}=6.02$ g cm^{-3}.

IR spectrum of the $Fe_8V_{10}W_{16}O_{85}$ phase

Figure 2 shows a spectra of the α-Fe_2O_3 (curve a), WO_3 (curve b), V_2O_5 (curve c), α-Fe_2WO_6 (curve d), $FeVO_4$ (curve e) confronted with spectrum of $Fe_8V_{10}W_{16}O_{85}$ phase (curve f).

A broad absorption band lying at the range of wave numbers 1050–830 cm^{-1}, with a maximum of 922 and a shoulder at 960 cm^{-1} in IR spectrum of the $Fe_8V_{10}W_{16}O_{85}$ phase can almost certainly be attributed to stretching vibrations of V–O links in VO_4 tetrahedra [15–18]. Another very broad band lying in the wavenumber range of 930–550 cm^{-1}, with a 660 maximum and a shoulder at 724 cm^{-1} is believed to be corresponding to stretching vibrations of WO_6 octahedra. A similar absorption band with a 670 cm^{-1} maximum noticed in an IR spectrum of α-Fe_2WO_6 phase, comprising WO_6 octahedra in its structure, is presented for the first time in this work [19]. At this wavenumber range absorption bands can also occur corresponding to stretching vibrations of Fe–O links in FeO_5 polyhedra, which was observed in IR spectra of iron(III) orthovanadate(V) [15]. Another absorption band, recorded in the range of 550–430 cm^{-1}, contains two maxima lying at 516 and 490 cm^{-1}. The bands can also be most likely ascribed to stretching vibrations of Fe–O

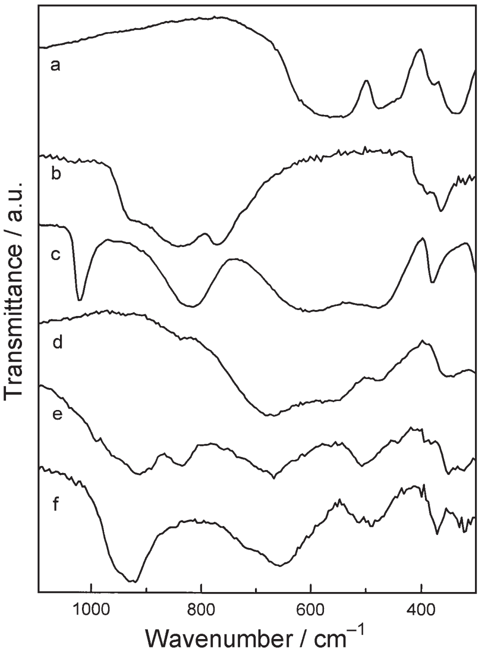

Fig. 2 IR spectra of the a – α-Fe_2O_3, b – WO_3, c – V_2O_5, d – α-Fe_2WO_6, e – $FeVO_4$ confronted with spectrum of f – $Fe_8V_{10}W_{16}O_{85}$ phase

links in FeO_6 octahedra [20, 21]. Interpretation of other bands, lying at the range of lower wave numbers, viz. those with maxima at 372 and 324 cm^{-1}, cannot be univocal in the light of the publications available. They may correspond to bending vibrations of M–O links in VO_4 tetrahedra and WO_6 octahedra, or be of a mixed character [15–18].

Analysis of the IR spectrum of $Fe_8V_{10}W_{16}O_{85}$ permits assumption, that the compound is built of VO_4 tetrahedra, and WO_6 and FeO_6 octahedra. One cannot also preclude occurrence of FeO_5 polyhedra. Lack, in the $Fe_8V_{10}W_{16}O_{85}$ phase, an absorption band with a maximum at 830 cm^{-1} – characteristic of VO_4 tetrahedra [22, 23] – implies that such polyhedra do not occur in the structure of the compound under study. Nevertheless, the mode of linking individual polyhedra involved in the structure of the $Fe_8V_{10}W_{16}O_{85}$ phase is difficult to refine on the basis of IR spectrum.

Conclusions

The V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system remains in equilibrium up to the solidus line temperature, and at the 98 mol% V_2O_5 content they form a eutectic mixture melting at 625±5°C. However, above the eutectic temperature the system is not a real two-component system and its components are in equilibrium with liquid.

The $Fe_8V_{10}W_{16}O_{85}$ cry stallizes in the tetragonal system with the unit cell parameters: $a=b=1.9753(3)$ nm, $c=0.3717(2)$ nm. The number of molecules in the unit cell $Z=1$. The unit cell volume: $V=1.45052$ nm^3.

Analysis of the IR spectrum of $Fe_8V_{10}W_{16}O_{85}$ permits assumption, that the compound is built of VO_4 tetrahedra, and WO_6 and FeO_6 octahedra. One cannot also preclude occurrence of FeO_5 polyhedra.

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