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Phase equilibrium relations in the V_2O_3–La_2O_3 system

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Phase equilibrium relations in the V_2O_3–La_2O_3 system were investigated by X-ray powder diffraction and metallographic techniques. Binary mixtures, prepared from high-purity V_2O_3 and La_2O_3 powders, were equilibrated at 1600° C and then arc-melted under a partial pressure of argon. The specimens were heat-treated at various predetermined temperatures for prolonged periods and the phases present were identified by reflected-light microscopy and X-ray powder diffraction. The system consists of only one binary compound $LaVO_3$. A eutectic between V_2O_3 and $LaVO_3$ was established at 1750° C and 19 mol % La_2O_3 and also between $LaVO_3$ and La_2O_3 at 1765° C and 75 mol % La_2O_3. No appreciable solid solubility was detected in the system.

1. Introduction

The anomalous temperature-induced metal to insulator transition exhibited by vanadium sesquioxide, V_2O_3 at about 170 K, which is accompanied by a change in resistivity of several orders of magnitude, has drawn considerable interest to the potential use of this oxide for electronic switching devices. However, the transition temperature is too low for any practical purpose and the synthesis of V_2O_3 single crystals is a tedious as well as an expensive process. Thus, attempts have been made to prepare polycrystalline V_2O_3 ceramics with additions of various oxides which can be incorporated, at least, partly, into the host V_2O_3 lattice to bring about a change in the transition temperature. To obtain an understanding of the behaviour of V_2O_3 in the presence of the additive oxides, it is apparent that there should be a knowledge of the phase equilibria involved between these materials. In the present investigation, compound formation and phase equilibrium relations existing in the V_2O_3–La_2O_3 system have been investigated and the data obtained were used to construct a pseudo-binary phase diagram. The data available from literature in this particular system are limited to the existence of a compound $LaVO_3$ and its crystal structure [1–5]. The compound is known to melt congruently at about 2080° C [6]. No further data in the system are known.

2. Experimental procedure

Vanadium sesquioxide, V_2O_3 was prepared by the decomposition of ammonium metavanadate, NH_4VO_3, at 500° C and subsequent reduction in an atmosphere of purified hydrogen at 1000° C for about 10 h. The La_2O_3 used was of 99.99% purity and was obtained from Alfa Products Division, Ventron Corporation. Powdered mixtures containing variable proportions of V_2O_3 and La_2O_3 were weighed to the nearest milligram, mixed thoroughly under alcohol, dried in an oven and then pressed into cylindrical pellets which were wrapped in Pt envelopes and fired at 1600° C for 20 h in an argon atmosphere with intermittent cooling, crushing, mixing and pressing to ensure homogeneity and to attain equilibrium. Solid-state reaction, intended to achieve complete equilibrium, was often very sluggish and required longer periods of firing. The sintered pellets were cooled inside the furnace and then arc-melted on a water-cooled copper hearth in an argon atmosphere using a non-consumable W-electrode. Melting was repeated several times, the samples being turned over between each melting. The melted samples were heat-treated at

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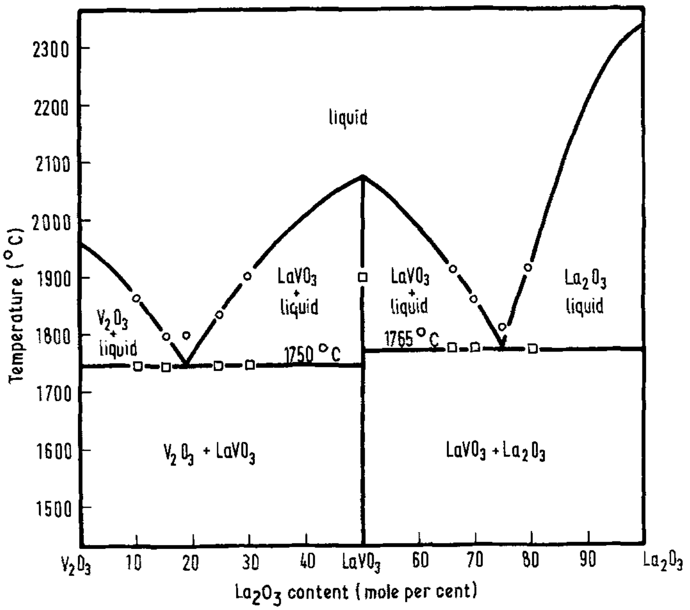

Figure 1 Phase diagram of the V_2O_3–La_2O_3 system.

various predetermined temperatures in an argon atmosphere for periods ranging from 5 to 30 h.

The phases present, both in the melted and heat-treated specimens, were identified by X-ray powder diffraction using a Guinier-type focusing camera with Ni-filtered Cu*Kα* radiation. Reflected-light microscopy was extensively used to determine various phase fields in the system. For metallographic examination, the specimens were prepared by grinding on silicon carbide papers followed by polishing with diamond pastes. The polished specimens were etched with dilute nitric acid. One inherent problem with compositions lying in the La_2O_3-rich portion of the system in which free La_2O_3 occurred was the rapid hydrolysis of the rare-earth oxide in air at room temperature. This behaviour made it increasingly difficult for the petrographic examination of the fired mixtures containing more than 70 mol% La_2O_3. However, the problem was partially solved by quickly mounting the specimens in a fast setting resin followed by polishing, using paraffin oil as a vehicle. The temperatures at which the specimens were heat-treated for various lengths of time and which were used to delineate the phase boundaries were determined with an optical pyrometer, which was periodically calibrated at the melting point of several pure metals. The solidus lines were established by reflected-light microscopy within a narrow temperature region at which the first sign of liquid formation was detected. This method, however, was not very accurate since the amount of liquid which formed in a given composition at or just above the solidus temperature may be insufficient to be readily detected under the microscope.

3. Results and discussion

X-ray powder diffraction analysis of the equilibrated specimens containing variable proportions of V_2O_3 and La_2O_3 indicated that there was only one stable binary compound existing in the system and this was identified as $LaVO_3$. The X-ray powder diffraction pattern for the compound agreed with the previously reported powder data for the tetragonal form of $LaVO_3$. Solid solution of either V_2O_3 or La_2O_3 in $LaVO_3$ is very limited, as observed by the constancy of the cell parameters of $LaVO_3$ in the binary assemblages. No attempt has been made in this investigation to determine the melting point of $LaVO_3$ which has previously been reported as 2080° C. However, a composition containing an equimolecular mixture of V_2O_3 and La_2O_3, on arc-melting, yielded an X-ray diffraction pattern which was identical to that of the product obtained by solid-state reaction at 1600° C. This indicates that $LaVO_3$ melts congruently. Petrographic examination of the arc-melted specimen supplemented this finding.

The phase equilibrium relations in the V_2O_3–La_2O_3 system showing the datum points used for the determination of the solidus and liquidus temperatures and various phase-fields are shown in Fig. 1. Additional compositions studied but not

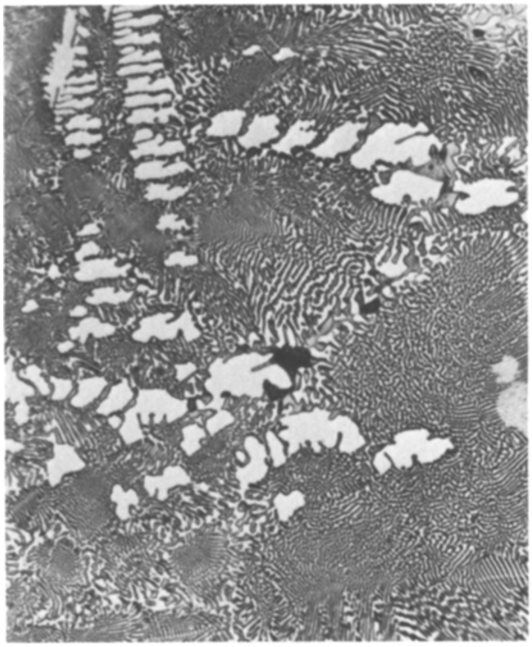

Figure 2 Composition 10 mol% La_2O_3, heat-treated at 1850° C showing primary dendrites of V_2O_3 in a eutectic matrix containing V_2O_3 and $LaVO_3$.

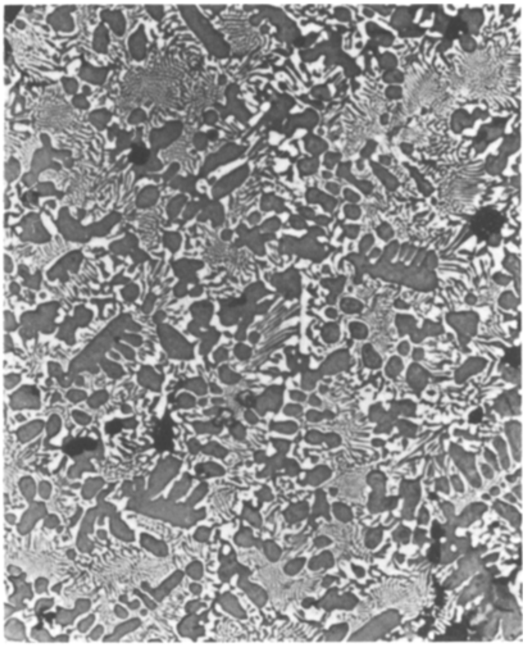

Figure 3 Composition 25 mol% La_2O_3, heat-treated at 1825° C showing primary dendrites of $LaVO_3$ in a eutectic matrix containing V_2O_3 and $LaVO_3$.

shown merely corroborate those given in the diagram. Two invariant points, both defined as simple eutectics, were established in the systems. These are between V_2O_3 and $LaVO_3$, at 1750° C and 19 mol% La_2O_3, and between $LaVO_3$ and La_2O_3, at 1765° C and 75 mol% La_2O_3. The solidus lines were located by detecting the first sign of liquid formation in the system and are probably not better than ± 20° C of the temperatures shown in the diagram. The liquidus temperature for a given composition was ascertained by examining the microstructure of the specimen which was quenched from various predetermined temperatures. It was observed that the quenching procedure used was insufficiently rapid to prevent some crystallization of the primary phase during cooling. This effect was utilized in determining the liquidus lines in the system. In general, the primary phase always appeared in the form of dendrites, when quenched from temperatures above the liquidus. However, the primary phase appeared as massive grains with sharp corners when quenched from temperatures below the liquidus, indicating that the grains were not completely melted. Specimens lying in the primary phase fields of both V_2O_3 and $LaVO_3$ on quenching from the melt, yielded microstructures in which the characteristic dendrites of V_2O_3 and $LaVO_3$ could be easily distinguished, but those lying in the primary phase field of La_2O_3 appeared in the form of long needles. The variations in the microstructures as observed in the melted and heat-treated specimens were used in the delineation of the phase boundaries in the system and are illustrated by the following micrographs.

The microstructure of a composition lying in the primary phase field of V_2O_3 is shown in Fig. 2 which exhibits the primary dendrites of V_2O_3 in equilibrium with the eutectic liquid. This is typical of the microstructure resulting from quenching above the liquidus temperature, the primary phase being present always as dendrites. The microstructure of a composition lying in the primary phase field of $LaVO_3$ is shown in Fig. 3 which exhibits the different forms of dendrites of $LaVO_3$ in equilibrium with the eutectic liquid. The eutectic composition between V_2O_3 and $LaVO_3$ was located at 19 mol% La_2O_3, the microstructure of which is shown in Fig. 4. The characteristic fine-grained structure, with partial separation of V_2O_3 in a few isolated areas, can be seen in the microstructure. Specimens containing more than 50 mol% La_2O_3, in which $LaVO_3$ co-exists with free La_2O_3, were difficult to examine under the

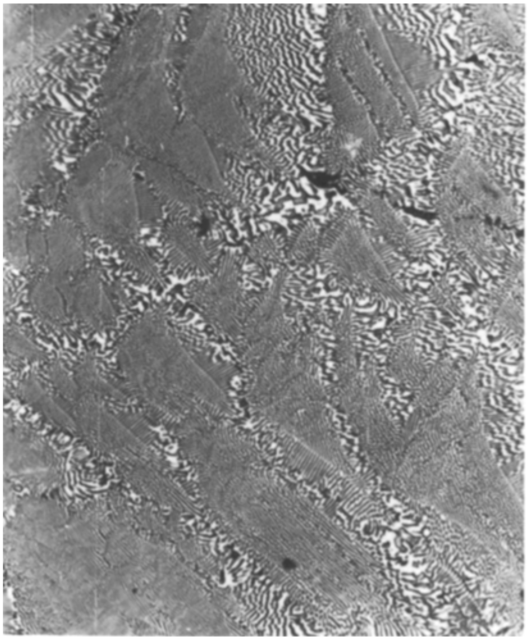

Figure 4 Composition 19 mol% La_2O_3, quenched from liquid exhibiting a complete eutectic structure between V_2O_3 and $LaVO_3$.

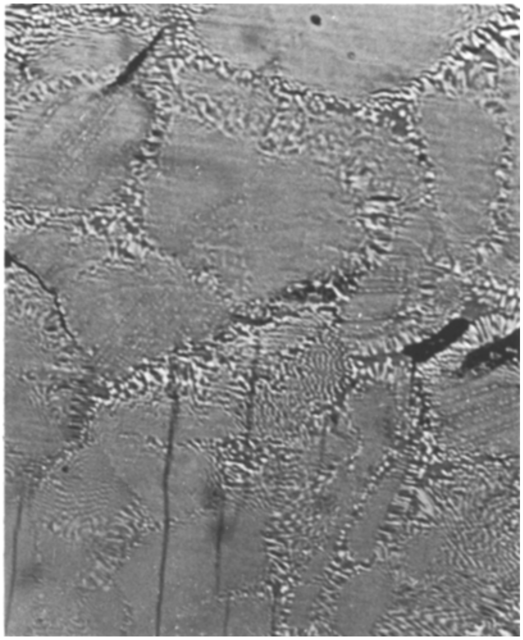

Figure 6 Composition 75 mol% La_2O_3, quenched from liquid exhibiting a complete eutectic structure between $LaVO_3$ and La_2O_3.

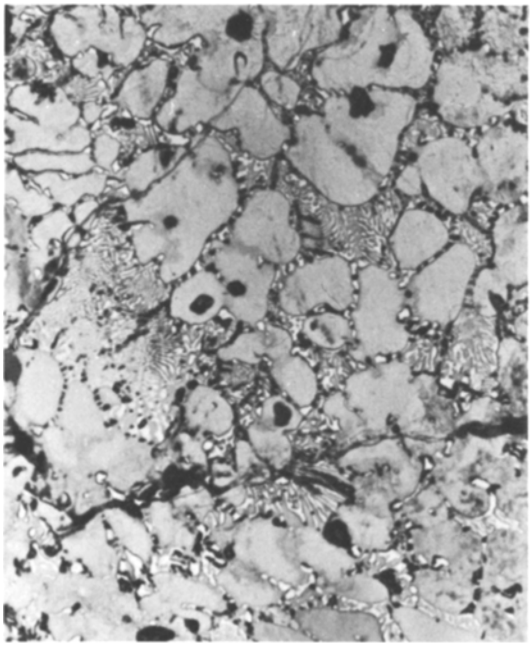

Figure 5 Composition 60 mol% La_2O_3, heat-treated at 1900° C, showing predominantly $LaVO_3$ with a small amount of eutectic liquid containing $LaVO_3$ and La_2O_3.

microscope because of the rapid hydration of La_2O_3 in air. The difficulty became most pronounced as the La_2O_3 content in the mixtures was gradually increased. The microstructure of a composition showing predominantly $LaVO_3$ with a small amount of eutectic liquid of $LaVO_3$ and La_2O_3 is exhibited in Fig. 5. The appearance of the primary phase as rounded massive grains indicated that the composition had not melted completely at the firing temperature used. The eutectic composition between $LaVO_3$ and La_2O_3 as established at 75 mol% La_2O_3 is shown in Fig. 6. As can be seen, the sharpness of the microstructure was affected due to partial hydration of free La_2O_3 in air. Fig. 7 shows the microstructure of a composition lying in the primary phase field of La_2O_3 in which the characteristic long needles of La_2O_3, partially hydrolyzed at the edges, co-exist with the eutectic liquid. X-ray powder diffraction analysis of the fired specimens showed no appreciable shift in the characteristic lines of either V_2O_3 or La_2O_3. Petrographic examination of selected compositions located at both ends of the system indicated that the extent of solid solubility is very small and limited to less than 3 mol %.

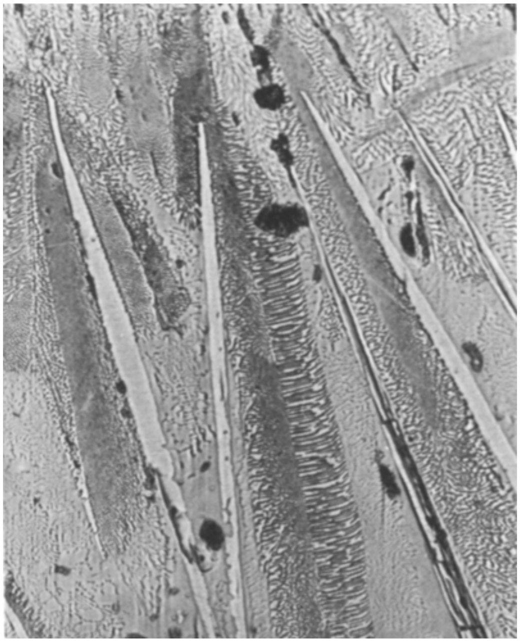

Figure 7 Composition 80 mol% La_2O_3, quenched from liquid showing crystallization of primary needles of La_2O_3 in a eutectic matrix containing $LaVO_3$ and La_2O_3.

Acknowledgements

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