Journal of the European Ceramic Society **16** (1996) 579–581
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0955-2219/96/$15.00

0955-2219(95)00167-0

Sintering Capability of V_2O_5/Nb_2O_5 System Treated by Sol–Gel Technique

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(Received 21 July 1994; revised version received 18 July 1995; accepted 27 August 1995)

Abstract

Consideration of the X-ray diffraction patterns for the sintered products of V_2O_5/Nb_2O_5 mixtures, with molecular ratio 1/9, has indicated that oxide mixtures prepared by sol–gel technique show improved sintering capability compared with simply homogenized mixtures. The stable sintered product VNb_9O_{25} was produced faster, and in a better crystallized form, in the case of the sol–gel treated oxide mixtures. It was also shown that sol–gel procedures reduce the size of agglomerates in the precipitate and improve its homogeneity.

1 Introduction

Previous investigations of the V_2O_5/Nb_2O_5 system[1,2] (one of them based on the sol-gel technique[1]) have led to the conclusion that the only stable product of this system at temperatures higher than 800°C is the compound VNb_9O_{25}. The aim of the present investigation is to study the effect of the sol–gel procedure, when applied to this system, on the sintering capability, as well as to determine the grain size distribution and homogeneity of the green oxide mixtures, factors which in turn influence the sintering capability.[3]

The production of the compound VNb_9O_{25} in a well crystallized form is also desired, so that the physical and chemical characteristics of the compound can be investigated more intensively. Multicomponent oxides such as VNb_9O_{25} commonly have electronic applications.[4,5] It is also known that transition metal oxides can present superionic conduction capabilities.[6,7]

2 Experimental and Discussion

The oxide mixtures used had a molecular ratio of V_2O_5/Nb_2O_5 of 1/9, which corresponds to the compound VNb_9O_{25}. The oxide mixtures, after having been homogenized, were converted to alkoxides. Absolute ethanol was used together with benzene, which was used as the solvent. Both of the oxides were transformed to alkoxides according to the following chemical reactions:

$$V_2O_5 + 10\ EtOH \leftrightarrow 2\ V(OEt)_5 + 10\ H_2O \quad (1)$$

$$Nb_2O_5 + 10\ EtOH \leftrightarrow 2Nb(OEt)_5 + 10\ H_2O \quad (2)$$

Standard air humidity contains enough water to hydrolyse the alkoxides rapidly,[8] so the reactions were performed under high vacuum. The water produced by the reaction forms an azeotropic mixture with benzene, and is extracted from the system by fully controlled distillation at a temperature of 69·25°C.

As soon as the reactions were completed, the alkoxides were hydrolysed with an appropriate amount of water. The resulting oxide mixtures were first dried under vacuum for 2 h, and then sintered simultaneously with control samples prepared by co-grinding oxide mixtures. The reaction occurring during sintering is:[9]

$$V_2O_5 + 9\ Nb_2O_5 \leftrightarrow 2\ VNb_9O_{25} \quad (3)$$

According to our experiments, which confirm data given in the literature,[1,2] the formation of the compound VNb_9O_{25} for any mixing ratio of the oxide mixture, starts just above 600°C. The eutectic line for the quasi-binary system V_2O_5–Nb_2O_5 lies at 648°C. Especially for the 1/9 mixture, at 648°C only the non-melting product VNb_9O_{25} appears.

Using differential scanning calorimetry (DSC) analysis of the oxide mixture, it was found that at 650°C an endothermic peak appears, attributed to the melting of V_2O_5 (this was confirmed by DSC analysis of pure V_2O_5). This melting reaction promotes the formation of the non-melting product VNb_9O_{25}. The above observations led to the selection of 650°C as the sintering temperature.

An X-ray diffraction (XRD) pattern for the

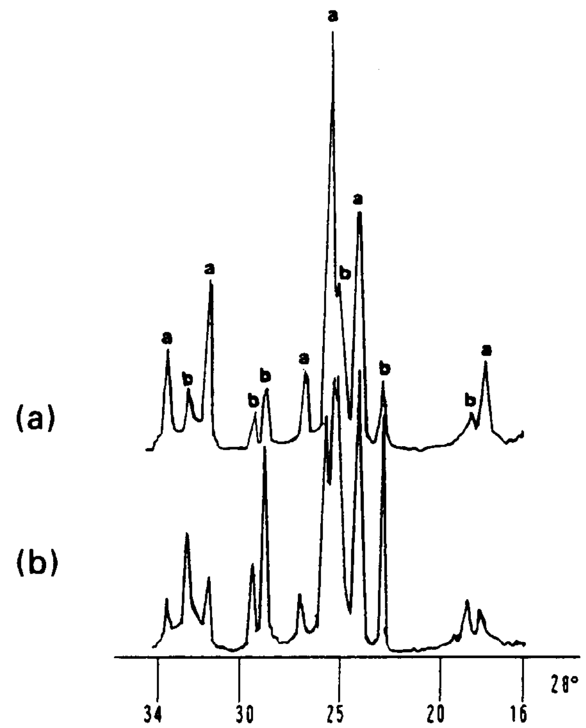

Fig. 1. XRD pattern of sintered products of V_2O_5/Nb_2O_5 1/9 sol–gel (A) and non sol–gel (B) treated mixtures, sintered for 3 h at 650°C. The peak marked (a) and (b) represent the compounds VNb_9O_{25} and Nb_2O_5, respectively.

sintered products from the sol–gel system is compared with one from the co-grinding process in Fig. 1, this showing the comparison after 3 h of firing. It is observed that the peaks corresponding to VNb_9O_{25} have a greater relative intensity for the sol–gel treated mixtures, while the peaks corresponding to Nb_2O_5 are less evident. This finding indicates that sol–gel samples can be transformed to the equilibrium product more easily, as well as in a shorter sintering time. Clear differences remain until the firing time reaches 12 h (Fig. 2), by which time the ground powders are also reacted.

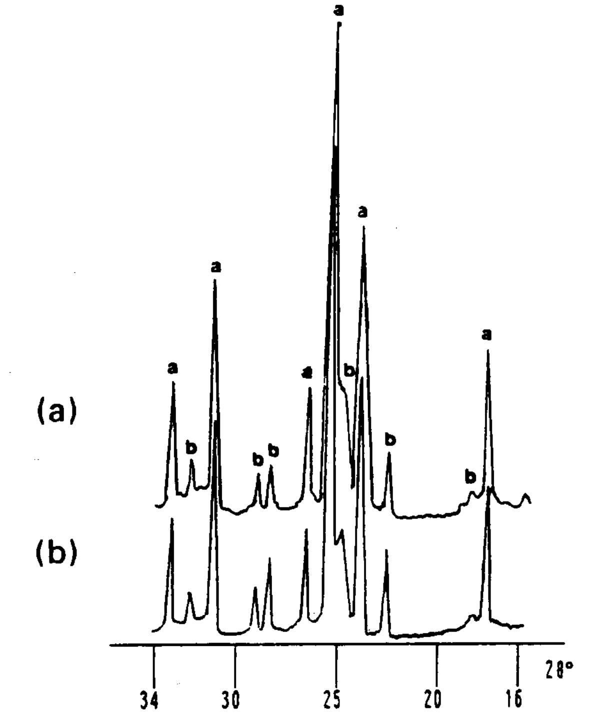

Fig. 2. XRD pattern of sintered products of V_2O_5/Nb_2O_5 1/9 sol–gel (A) and non sol–gel (B) treated mixtures, sintered for 12 h at 650°C. The peak marked (a) and (b) represent the compounds VNb_9O_{25} and Nb_2O_5, respectively.

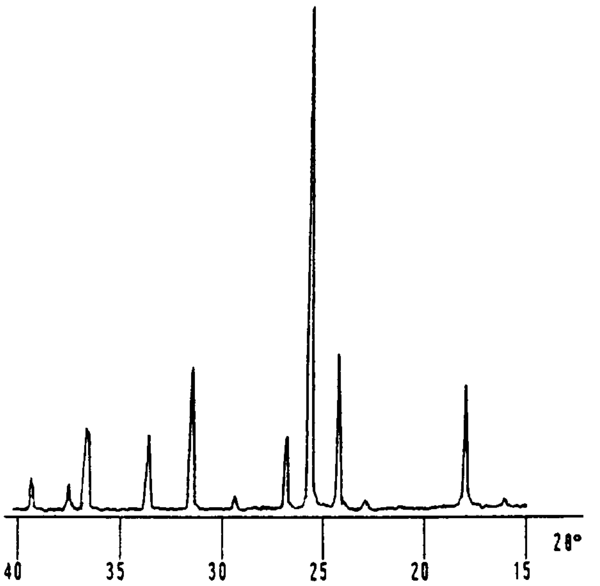

Fig. 3. XRD pattern of sintered products of V_2O_5/Nb_2O_5 1/9 sol–gel treated mixtures, sintered for 100 h at 650°C. The transformation of the initial oxide mixture to the compound VNb_9O_{25} is complete.

The XRD pattern for a sol–gel treated 1/9 oxide mixture sintered at 650°C for 100 h is presented in Fig 3. In this diagram it is observed that the starting oxide mixture has been fully transformed into the mixed compound VNb_9O_{25}, which has been produced in a well crystallized form. The crystalline form of this product is shown in Fig. 4.

The sol–gel treated oxide mixtures were also compared with co-ground mixtures, in respect to

Fig. 4. The compound VNb_9O_{25} produced from a sol–gel treated oxide mixture, sintered for 100 h at 650°C. The shape of the crystals suggests that the compound is crystallized in the orthorhombic system.

Fig. 5. The grains and agglomerates of the initial oxide mixture. The biggest agglomerate has a maximum diameter of 180 μm.

grain size distribution, by means of optical microscopy. Taking into consideration the fact that the starting oxides consisted of very small particles (< 1 μm), it was expected that the sol–gel process may not further reduce the size. Nevertheless, it was observed that the size of the agglomerates was considerably reduced: the size in the starting material (~180 μm) is shown in Fig. 5; in contrast, that in the sol–gel product has a maximum diameter of 25 μm (Fig. 6).

The homogeneity of the sol–gel treated oxide mixtures was also compared with that of the co-ground mixtures, by using electron probe microanalysis (EPMA). All the former samples showed the expected atomic ratio, as shown in Table 1.

Fig. 6. The grains and agglomerates of the sol–gel treated initial oxide mixture. The agglomerate in the centre has a diameter of 25 μm.

Table 1. Results of the EPMA analysis of sol–gel and non sol–gel treated mixtures

	Non sol–gel		*Sol–gel*	
	Weight	*Atoms*	*Weight*	*Atoms*
% V	5·29	9·25	5·74	10·00
	5·02	8·79	5·74	10·00
	3·38	11·05	5·74	10·00
% Nb	94·71	90·75	94·26	90·00
	94·98	91·21	94·26	90·00
	93·62	88·95	94·26	90·00

3 Conclusions

Sol–gel procedures have a positive effect on the sintering capability of ceramic powders. The desired sintering products are produced in a better crystallized form, after a shorter sintering period, as a result of the refined grain size and the improved homogeneity of the green powder mixtures. It was observed that these procedures reduce the size of the agglomerates and enhance the chemical homogeneity of the ceramic powder.

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