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Sintering behaviour of lithium ferrites containing Nb_2O_5 and V_2O_5

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Lithium ferrite toroids with various compositions and with various amounts of Nb_2O_5 or V_2O_5 have been prepared by a powder compacting method, and their sintering behaviours, microstructures and weight-loss characteristics have been investigated. The rate of sintering is higher in an Fe_2O_3-deficient lithium ferrite than in an Fe_2O_3-excess lithium ferrite due to the presence of excess oxygen vacancy in the Fe_2O_3-deficient lithium ferrite during sintering. The presence of $LiNbO_3$ or $LiVO_3$, which is formed by Nb_2O_5 or V_2O_5, on the surface of lithium ferrite grains causes an increase in oxygen activity of the lithium ferrite and a decrease in the rate of lithium evaporation during sintering, resulting in a strong enhancement in the sintering rate. The enhancing effect of V_2O_5 in the sintering of lithium ferrite is stronger than that of Nb_2O_5 due to the possible formation of liquid V_2O_5 before the formation of $LiVO_3$.

1. Introduction

The ferrite toroids used as magnetic amplifiers or information storage elements (memory cores) in computers must exhibit rectangular magnetic hysteresis loops. "Square-loop cores" are today fabricated from materials chosen from a few ferrite solid-solution systems which include lithium manganese ferrite and cobalt-substituted lithium ferrites [1, 2]. The magnetic properties of ferrite strongly depend on the microstructure, which is determined by the sintering behaviour. It is reported that the rectangularity of B–H loops increases when there are numerous defects that hinder magnetic domain wall motion in the grains [3].

There are a number of reports concerning the effects of sintering aids on the magnetic properties of ferrites. The effects of Bi_2O_3 [4, 5], V_2O_5 [6, 7] and Nb_2O_5 [5, 8] on the memory-core characteristics of substituted lithium ferrites are reported. The effects of Bi_2O_3 (melting temperature: 820° C) on the sintering and microstructure of substituted lithium ferrites have been explained in terms of the formation of a liquid phase [4]. The enhancing effects of V_2O_5 (melting temperature: 690° C) on the sintering of the substituted lithium ferrites were explained in terms of a liquid phase [4, 9] of V_2O_5 or in terms of enhanced volume diffusion due to the solubility of vanadium in the lithium ferrite [7]. However, the enhancing effect of Nb_2O_5 (melting temperature: 1460° C) on the sintering of lithium ferrites has never been explained. It is reported that V_2O_5 and Nb_2O_5 forms $LiVO_3$ and $LiNbO_3$, respectively, below 600° C when mixed with lithium ferrite and their melting temperature are higher than 1000° C, and that the effects of $LiVO_3$ on the sintering and magnetic properties of lithium ferrites are almost identical to those of V_2O_5 and Nb_2O_5 respectively [5, 6].

The present study was directed towards determining the sintering behaviours and microstructures of lithium ferrites containing Nb_2O_5 or V_2O_5, and investigating the possible sintering mechanisms involved in these ferrites. Additions of Nb_2O_5 or V_2O_5 were made to non-stoichiometric as well as stoichiometric lithium ferrites, and the effects of the atmosphere on the sintering of these ferrites and thermogravimetric analysis have also been investigated.

2. Experimental procedure

A number of materials in the systems $Li_{0.5}Fe_{2.5-x}O_4 + yNb_2O_5$ and $Li_{0.5}Fe_{2.5-x}O_4 + zV_2O_5$ have been investigated. A conventional ceramic powder compacting method was used for sample preparation. Each powder with a basic composition of $Li_{0.5}Fe_{2.5-x}O_4$ was prepared by mixing lithium carbonate and iron oxide in a rubber-lined ball-mill with stainless steel balls and isopropyl alcohol. After drying each slurry, the mixed powder was calcined at 900° C for 2 h in air, and was then ball-milled again to grind and mix after the addition of an appropriate amount of Nb_2O_5 ro V_2O_5. Toroids with o.d. 14 mm, i.d. 8.5 mm and height 3 mm were obtained using a press and die set. Toroid samples were sintered for 2 h at various temperatures in oxygen, nitrogen or air atmosphere.

For microstructure study, photographs of fractured as well as etched surfaces were taken using a scanning electron microscope (SEM). X-ray powder diffraction patterns and X-ray diffraction patterns of the surfaces of sintered samples were taken to analyse structure and phases. Thermogravimetric analysis (TGA) data were also taken in an attempt to characterize the material-loss behaviour which is possibly related to changes in the defect structure of the sintered ferrites.

3. Results and discussion

Since the samples were prepared by mixing and grinding in a ball-mill with stainless steel balls, which is the

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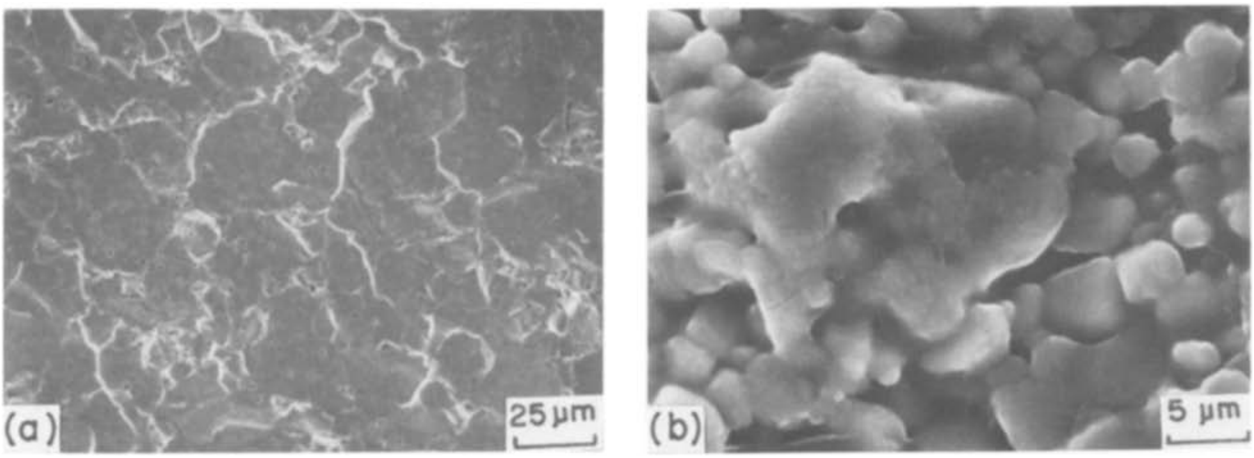


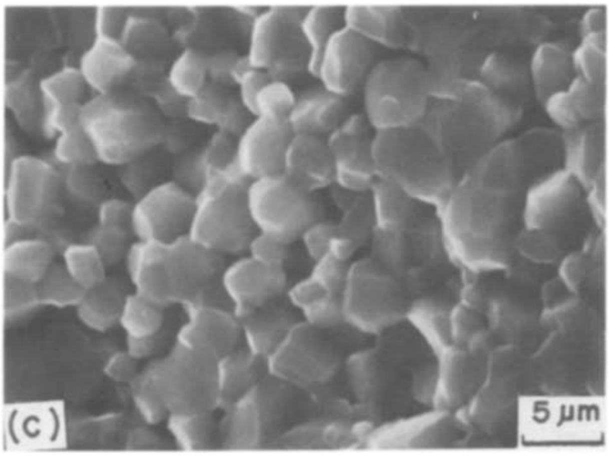


Figure 1 Microstructures of $Li_{0.5}Fe_{2.5-x}O_4$ with various weigh-in values of x sintered at 1025° C for 2 h in 1 atm O_2. (a) $x = 0.08$; (b) $x = 0.04$; (c) $x = 0.00$.

method widely used in the mass-production of ferrites, the composition of final specimen differs from the starting weigh-in composition due to the pick-up of iron during the ball-mill process and the possible loss of oxygen and lithium during sintering. To determine the stoichiometry of sintered lithium ferrites, a number of compositions in $Li_{0.5}Fe_{2.5-x}O_4$ with weigh-in values of x equal to 0, 0.02, 0.04, 0.06 and 0.08 were prepared. When the ferrite specimens with these compositions were sintered at 1100° C for 2 h in nitrogen or in air, all the specimens showed a density of over 95% of the theoretical density with microstructures that indicated the occurrence of abnormal grain growth.

To observe the differences in sintering rate and microstructure between ferrites with various compositions, specimens were sintered at lower temperatures. Fig. 1 shows SEM photographs of fractured surfaces of lithium ferrites, which had various weigh-in value of x and were sintered at 1025° C for 2 h in 1 atm O_2 atmosphere. It is seen that no significant sintering took place in the sample whose starting composition was $x = 0$ (stoichiometric), abnormal grain growth began in the sample with $x = 0.04$ and complete abnormal grain growth occurred in the sample with $x = 0.08$. It is reported that the diffusion of the oxygen ion, which has a larger diameter than the cations, is the rate-determining step in the sintering of ferrites. Thus the vacancy concentration of oxygen is an important parameter in the sintering process of spinel ferrites. Applying Reijnen's theory [10] in the present lithium ferrite system, the effect of the addition of excess Fe_2O_3 to pure lithium ferrite can be expressed by

$$\tfrac{8}{3}Fe_2O_3 \xrightarrow{Li_{0.5}Fe_{2.5}O_4} \tfrac{1}{3}Fe^{3+} + 5Fe^{3+} + 8O^{2-} + \tfrac{2}{3}V_c \quad (1)$$

where V_c is the cation vacancy. Thus we see that ferrite powder with excess Fe_2O_3 tends to form cation vacancies. The formation of excess cation vacancy reduces the concentration of anion (oxygen) vacancy which results in a decrease in oxygen ion diffusion and sintering rate. Thus it appears that the ferrite specimens of Figs. 1b and c had a slower sintering rate due to the presence of excess Fe_2O_3.

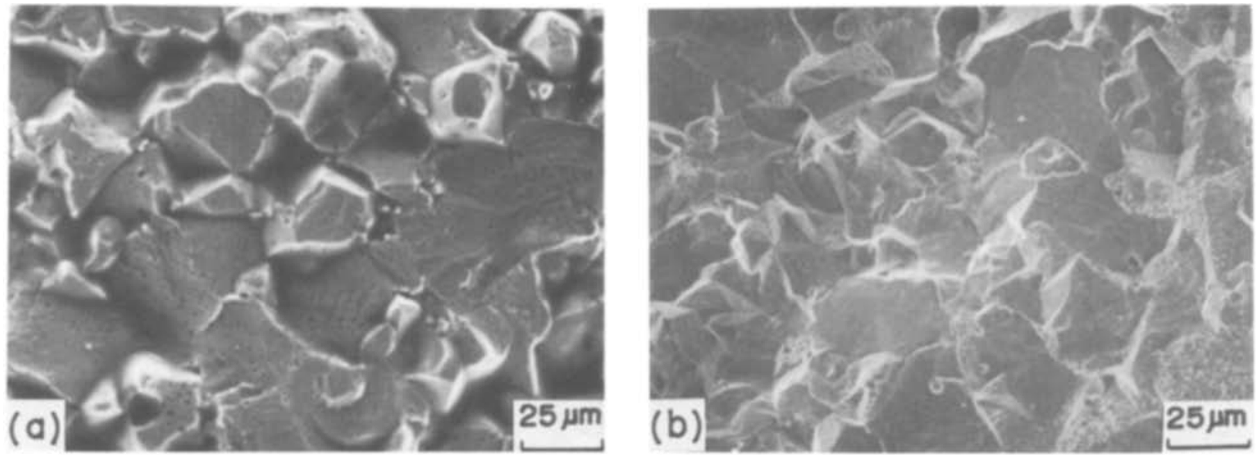
It has also been reported that a loss of oxygen and lithium occurs when the lithium ferrites were sintered at high temperature [11]. According to Salmon and Marcus [11], the reactions involving the loss of oxygen and lithium in a lithium ferrite can be expressed by

$$6Li_{0.5}Fe_{2.5}O_4(s) \rightleftharpoons 3LiFeO_2(s) + 4Fe_3O_4(s) + O_2(g) \quad (2)$$

$$6LiFeO_2(s) \rightleftharpoons 2Fe_3O_4(s) + 3Li_2O(g) + \tfrac{1}{2}O_2(g) \quad (3)$$

To inhibit the evaporation of Li_2O and oxygen during sintering, a set of toroid specimens with various values of x were buried within lithium ferrite powder in the sintering boat and were sintered at 1025° C for 2 h in 1 atm O_2, and their microstructures after the sintering are shown in Fig. 2. It can be seen that complete abnormal grain growth has taken place in the specimen of Fig. 2b as well as in that of Fig. 2a, indicating that both samples were Fe_2O_3-deficient under above the sintering conditions. Thus it may be reasonable to say that the specimens with initial weigh-in values $x = 0$, 0.04 and 0.08 resulted in samples with compositions of $Li_{0.5}Fe_{2.54}O_4$ (Fe_2O_3-excess), $Li_{0.5}Fe_{2.5}O_4$ (stoichiometric) and $Li_{0.5}Fe_{2.46}O_4$ (Fe_2O_3-deficient), respectively, after the ball-mill process and sintering in an oxygen atmosphere.

To investigate the effects of Nb_2O_5 and V_2O_5 on the sintering behaviours of lithium ferrites, 0.005 formula unit (f.u.) of Nb_2O_5, or 0.005 or 0.01 f.u. of V_2O_5, was



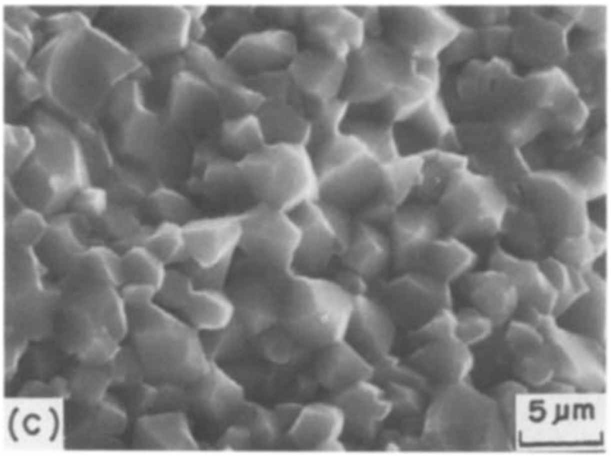


Figure 2 Microstructures of $Li_{0.5}Fe_{2.5-x}O_4$ with various weigh-in values of x sintered at 1025° C for 2 h in O_2 + packing powder atmosphere. (a) $x = 0.08$; (b) $x = 0.04$; (c) $x = 0.00$.

added to both the Fe_2O_3-deficient and Fe_2O_3-excess lithium ferrite powders. The sintering densities of lithium ferrites with these compositions, after the sintering of 2 h in 1 atm O_2, as a function of sintering temperature are shown in Fig. 3. As can be seen in the figure, densification of Fe_2O_3-excess lithium ferrite (filled circles) takes place at a higher sintering temperature than the Fe_2O_3-deficient lithium ferrite (open circles) due to the decrease in the concentration of oxygen vacancy which is caused by Reaction 1. For the lithium ferrites with Nb_2O_5, the densification takes place at temperatures approximately 100° C below the sintering temperatures of the lithium ferrites with no addition of a sintering aid, and the difference between the sintering temperatures for the iron-deficient (open squares) and iron-excess (closed squares) lithium ferrites is small. It should be pointed out that the sintering behaviours of lithium ferrite with 0.01 Nb_2O_5 were almost identical to those of lithium ferrite with 0.005 Nb_2O_5 shown in the figure. For the lithium ferrites with 0.005 f.u. V_2O_5, significant densification has taken place at the sintering temperatures approximately 300° C below those for "pure lithium ferrites" (with no sintering aid). In all three cases, the densification begins at a lower temperature for iron-deficient lithium ferrites but the highest density was observed in iron-excess lithium ferrites.

A detailed analysis of the microstructures indicated that the abnormal grain growth always occurs at a lower sintering temperature in the iron-deficient lithium ferrites than in the iron-excess lithium ferrites. Once the abnormal grain growth takes place through the whole sample, further sintering and densification hardly occur because it takes quite a long sintering time to decrease the voids in the grains. The sintering behaviour of lithium ferrite which contained 0.01 f.u. of V_2O_5 is unique, i.e. the sintering temperature is much lower than for the other ferrites and there is not much difference between the iron-deficient and the iron-excess cases. From the sintering data of Fig. 3 and analysis of microstructures, and from the consideration of the reported fact that the sintering behaviours of lithium ferrites with $LiNbO_3$ or $LiVO_3$ are identical to those of lithium ferrites with Nb_2O_5 or V_2O_5, respectively [5], it appears that sintering mechanisms for the lithium ferrites with 0.005 Nb_2O_5 or 0.005 V_2O_5 involve some kinds of solid-state reaction and that a liquid-phase sintering mechanism operates, at least in the early stages of sintering, in the lithium ferrite with 0.01 V_2O_5.

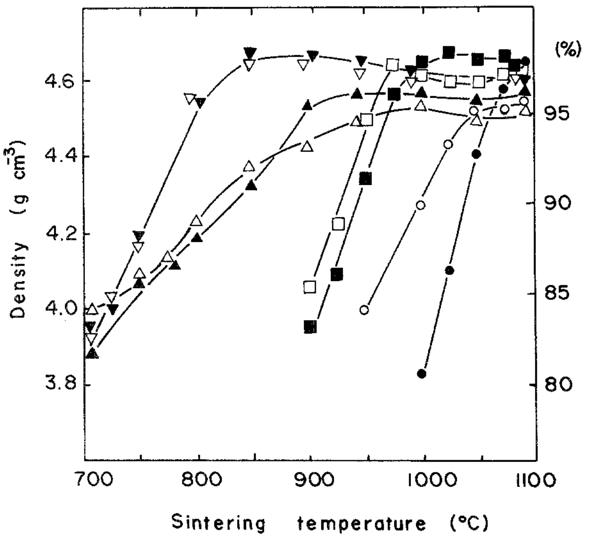


Figure 3 Sintered density against sintering temperature of lithium ferrite with various compositions and additives. (○) $Li_{0.5}Fe_{2.46}O_4$; (●) $Li_{0.5}Fe_{2.54}O_4$; (□) $Li_{0.5}Fe_{2.46}O_4$ + 0.005 Nb_2O_5; (■) $Li_{0.5}Fe_{2.54}O_4$ + 0.005 Nb_2O_5; (△) $Li_{0.5}Fe_{2.46}O_4$ + 0.005 V_2O_5; (▲) $Li_{0.5}Fe_{2.54}O_4$ + 0.005 V_2O_5; (▽) $Li_{0.5}Fe_{2.46}O_4$ + 0.01 V_2O_5; (▼) $Li_{0.5}Fe_{2.54}O_4$ + 0.01 V_2O_5.

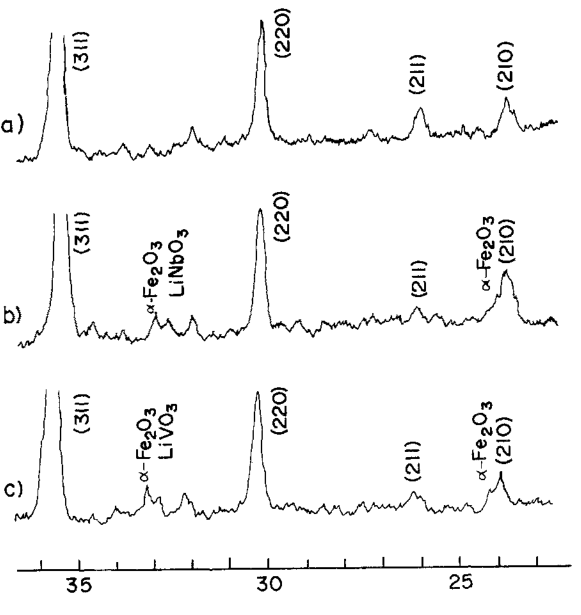


Figure 4 X-ray powder diffraction patterns for lithium ferrites with additives sintered at 1100° C for 2 h in O_2. (a) Pure; (b) 0.04 Nb_2O_5; (c) 0.02 V_2O_5.

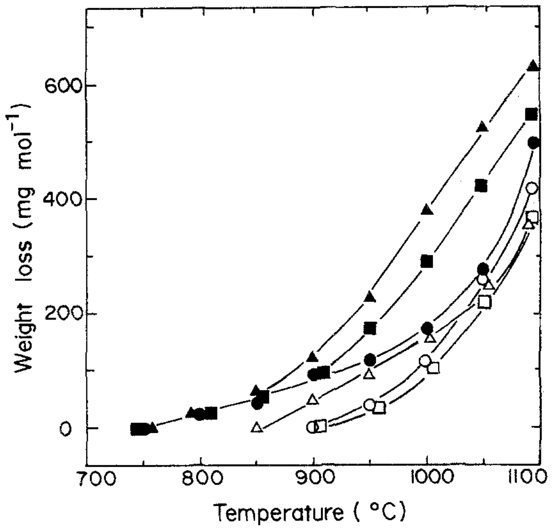


Figure 5 Weight loss against temperature of lithium ferrite with various compositions and additives. (○) $Li_{0.5}Fe_{2.46}O_4$ (P-2.46); (●) $Li_{0.5}Fe_{2.54}O_4$ (P-2.54); (□) $Li_{0.5}Fe_{2.46}O_4$ + 0.005 Nb_2O_5 (Nb-2.46); (■) $Li_{0.5}Fe_{2.54}O_4$ + 0.005 Nb_2O_5 (Nb-2.54); (△) $Li_{0.5}Fe_{2.46}O_4$ + 0.005 V_2O_5 (V-2.46); (▲) $Li_{0.5}Fe_{2.54}O_4$ + 0.005 V_2O_5 (V-2.54).

It is well known that pure lithium ferrite has a superstructure due to the long-range ordering of Li^+ ions and Fe^{3+} ions in octahedral sites [12]. Fig. 4 shows the X-ray powder diffraction patterns of lithium ferrites which contained Nb_2O_5 or V_2O_5 before sintering and were sintered at 1100° C in an oxygen atmosphere. It shows that the intensity of the superlattice peak (2 1 1) decreases for both lithium ferrites with 0.04 Nb_2O_5 or 0.02 V_2O_5. Similar phenomena have been observed for lithium ferrites with V_2O_5 [7] and Nb_2O_5 [8], and it was concluded that V^{5+} and Nb^{5+} ions substitute for Fe^{3+} ions in the octahedral sites resulting in the formation of α-Fe_2O_3, i.e. V^{5+} and Nb^{5+} are soluble in lithium ferrite to a certain degree.

It should be noted that the peaks due to $LiVO_3$ and $LiNbO_3$ are observed instead of V_2O_5 and Nb_2O_5 in the X-ray powder diffraction patterns. It has been suggested that the substitute of V^{5+} or Nb^{5+} into lithium ferrite might cause the formation of excess vacancy and hence enhance the sintering of lithium ferrites by an enhanced volume-diffusion mechanism [7, 8]. However, if excess vacancy is formed it would be cation vacancy rather than anion vacancy since the V^{5+} and Nb^{5+} ions have a higher charge than the Fe^{3+} ion, and this would retard the sintering. It appears that this kind of mechanism may explain the decrease in the difference between the sintering temperatures for iron-deficient and iron-excess lithium ferrites with either 0.005 f.u. V_2O_5 or Nb_2O_5 (Fig. 3), and that it is difficult to explain the difference of more than 100° C in the sintering temperature, for both iron-deficient and iron- excess cases, between the "pure lithium ferrite" and lithium ferrites with either Nb_2O_5 or V_2O_5.

To investigate the possible changes in the defect structure, which, in turn, influences the sinterability, weight-change characteristics of the lithium ferrites have been investigated. Fig. 5 shows the weight-loss data from constant-heating-rate runs for the lithium ferrites with various compositions. The constant heating rate used was 5° C min^{-1}, and weight loss was measured in air. The general features of the curves are similar to those observed by Bandyopadhyay *et al.* [13] for compositions in the system $LiFeO_2-Fe_2O_3$, i.e. the weight loss is larger for the lithium ferrite in the Fe_2O_3-excess case than in the Fe_2O_3-deficient case. This result could be explained in terms of Reaction 1, which states that the excess Fe_2O_3 in lithium ferrite tends to form cation vacancy (V_c), and of the reaction [14]

$$Fe^{3+} + \tfrac{3}{8}V_c + \tfrac{1}{2}O^{2-} = Fe^{2+} + \tfrac{1}{4}O_2(g) \quad (4)$$

Fig. 5 also shows that the weight loss for lithium ferrites with V_2O_5 or Nb_2O_5 is, in general, larger than for "pure" lithium ferrite indicating that the activity of oxygen is increased in the lithium ferrites when V_2O_5 or Nb_2O_5 is added.

As pointed out before, the evaporation of lithium also occurs in lithium ferrite by Reactions 2 and 3. To separate the weight loss due to evaporation of lithium, which is an irreversible process, weight loss during heating to 1100° C plus heating at 1100° C for 2 h and weight gain during the cooling were measured. Table I shows the weight losses and weight gains of lithium

TABLE I Weight change of lithium ferrites with various compositions and additives during heat treatment in air

Sample	Weight loss (mg mol^{-1})*		
	ΔW_1	ΔW_2	ΔW_3
P-2.46	−774.2	+77.4	−696.8
P-2.54	−703.8	+122.8	−581.0
Nb-2.46	−546.6	+192.4	−352.2
Nb-2.54	−658.0	+250.7	−407.3
V-2.46	−593.5	+237.4	−356.1
V-2.54	−749.2	+287.1	−462.1

*ΔW_1: weight loss during heating,
ΔW_2: weight loss during cooling,
ΔW_3: net weight loss.

ferrites with various compositions and additives. It can be seen that net weight loss (ΔW_3) which is associated with the lithium loss, of Fe_2O_3-deficient lithium ferrite (P-2.46) is larger than that of Fe_2O_3-excess lithium ferrite (P-2.54) since it contained excess Li_2O. It is interesting to note that the net weight loss for the lithium ferrites with V_2O_5 or Nb_2O_5 is much smaller than that of "pure" lithium ferrites. The reason is not quite clear but it appears that the formation of $LiVO_3$ or $LiNbO_3$ on the surface of grains inhibits the evaporation of lithium from the lithium ferrites. Thus if we assume that the activity of oxygen around grain boundaries is increased and the evaporation of lithium is retarded by the presence of $LiVO_3$ or $LiNbO_3$ on the surface of lithium ferrite grains, the observed facts that small amounts of vanadium and niobium enhance the sintering of lithium ferrite and that the effect of the addition of V_2O_5 or Nb_2O_5 is almost identical to that of $LiVO_3$ or $LiNbO_3$ can be explained. The effect of V_2O_5 is stronger than that of Nb_2O_5 because the V_2O_5 can possibly be in the liquid phase, coating the grains more effectively, before $LiVO_3$ is formed. It should be pointed out that sintered lithium ferrites which contained these additives before sintering are much weaker in mechanical properties [15].

4. Conclusions

Based on the results of analyses of sintering behaviours and weight-loss characteristics of Fe_2O_3-excess and Fe_2O_3-deficient lithium ferrites which contained various amounts of V_2O_5 or Nb_2O_5 before sintering, the following conclusions can be drawn:

1. The sintering rate for Fe_2O_3-deficient lithium ferrite is larger than that of Fe_2O_3-excess lithium ferrite, due probably to the presence of excess oxygen vacancy in the Fe_2O_3-deficient lithium ferrite during sintering.
2. The presence of $LiVO_3$ or $LiNbO_3$, which was formed by V_2O_5 or Nb_2O_5, in lithium ferrite enhances the sintering.
3. The presence of $LiVO_3$ or $LiNbO_3$ in lithium ferrite also causes an increase in oxygen activity and a decrease in lithium evaporation during sintering.
4. The enhancement of sintering by the presence of $LiVO_3$ or $LiNbO_3$ in lithium ferrite appears to be caused by the increase in oxygen activity and by the retardation of lithium evaporation, which, in turn, increases the concentration of oxygen vacancy and the diffusion rate of oxygen ions during sintering.
5. The enhancing effect of V_2O_5 is stronger than that of Nb_2O_5, due probably to the presence of liquid V_2O_5 in the early stages of sintering.

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