42. The Effectiveness of Alkali Halide Media for the Process of MgFe_2O_4 , MgAl_2O_4 and MgCr_2O_4 Formation

By

Hiroaki YANAGIDA and Masao ATUMI

(Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo)

A number of reactions involving solid phase are influenced by some mineralizers. Alkali halides, alkali tungstates, etc. are used as good mineralizers for the processes such as crystal growth, polymorphic transformation of solid phases, solid state reactions and so on. However, we are not always able to assign the best mineralizer for the process of a given system. It has hardly been tried at all to relate the effectiveness of mineralizers to their properties such as their melting point, their lattice dimension, etc.

In the presenst work, the authors will show a fairly good correlation between the effectiveness of alkali halide media, which are often called mineralizers when the amount is only a little in the system, for the process of MgFe_2O_4 formation, a spinel with $a=8.366 \text{ \AA}$, $z=8$, and the value $|a_{\text{MgO}} - a_{\text{alkali halide}}|$, where a is the unit cell dimension of the cubic lattice. The correlation will be found also in the processes of MgAl_2O_4 and MgCr_2O_4 formation. Although alkali halides are usually regarded as flux mineralizer, it will be readily shown that the melting point is hardly related at all to their effectiveness for the process of those spinel formation.

Experimental

Starting Materials

Magnesium oxide (periclase) was prepared from pure $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ by heating it at 1200°C in air. Ferric oxide (haematite) was obtained from ferric oxyhydroxide (goethite) by heating it at 800°C in air. Chromic oxide (corundum structure) was prepared by heating chromic hydroxide at 800°C in air. Aluminium oxide (corundum) was prepared by heating aluminium hydroxide (gibbsite) at 1400°C in air.

Alkali Halides

Chemically pure LiF , LiCl , KF , NaCl , NaBr , KCl and KBr were used as media for the processes of MgFe_2O_4 , MgAl_2O_4 and MgCr_2O_4 formation.

Procedures

Powders of MgO , R_2O_3 (Fe_2O_3 , Al_2O_3 or Cr_2O_3) and AX (an alkali halide) were mixed well in the molar ratio 1:1:6 or 1:1:0. They were heated in a platinum crucible at the predetermined temperature in the range of 500° to 1100°C for 1 or 3 hours, and then quenched to room temperature. The products were washed by dilute hydrochloric acid and then by pure water. Residues without contamination by alkali halide mineralizer were obtained by this washing treatment. The residues were dried at 110°C in air.

The amounts of MgO , R_2O_3 (Fe_2O_3 , Al_2O_3 or Cr_2O_3) and of spinel phase (MgFe_2O_4 , MgAl_2O_4 or MgCr_2O_4) in the residues were determined by measuring the intensities of powder X-ray diffraction peaks. Mn filtered FeK_α radiation was applied. The peaks used for the determination were (111) of spinel structure near $2\theta=38^\circ$, (104) near $2\theta=42^\circ$ and (024) near $2\theta=64^\circ$ of the corundum structure (Fe_2O_3 , Al_2O_3 or Cr_2O_3) and (200) near $55^\circ 2\theta$ of periclase. However, the peaks arising from periclase could not be detected in the product obtained from the starting materials with an addition of alkali halide medium. In this case, peaks arising from brucite were found in stead of those from periclase.

Results and Discussions

1) Preliminary Investigation into the Effects of Alkali Halide Media

The processes of MgFe_2O_4 formation from MgO

Fig. 1. The role of NaCl medium for the process of MgFe_2O_4 formation.

Table 1. Colors of products at various temperatures with and without NaCl medium.

(The starting material: 1 mol MgO; 1 mol Fe₂O₃; 1 or 0 mol NaCl)

Temperatures (°C)	Color and the amount of MgFe ₂ O ₄ formed(%)	
	With NaCl mineralizer	Without NaCl mineralizer
600	Brownish red (0)	Brownish red (0)
700	Pale brown (15)	Brownish red (0)
800	Pale brown (50)	Brownish red (5)
900	Brown (80)	Pale brown (15)
1000	Brownish black (100)	Pale brown (30)
1100	Brownish black (100)	Pale brown (50)

Brownish red color is of haematite.

Brownish black color if of MgFe₂O₄.

Pale brown color transformed into brownish red if the product was ground.

and Fe₂O₃ with and without the medium of NaCl were studied. The amounts of spinel formed at temperatures of 500° to 1100°C were plotted in the Figure 1. A change of heating period, 1 to 3 hours, caused only a negligible change in the amount of spinel formed at each temperature. It can be easily concluded that NaCl is very effective for the process of MgFe₂O₄ formation. And it should be noted that NaCl has the effectiveness even below its melting point of about 800°C.

The color of the products are shown in the Table 1. The brownish red color was of the starting material of haematite and the brownish black was of spinel MgFe₂O₄. Although an X-ray diffraction pattern showed an existence of haematite in the pale brown product, the brownish red color of haematite was masked there. The color of haematite itself appeared when the pale brown product was ground. In the product, if NaCl medium was used, X-ray diffraction peaks of periclase could not be found but those of brucite were able to be detected. Since the starting material of periclase in the present work was hardly rehydrated into brucite in water near 25°C, the media seems to have made magnesium oxide into the pale brown product which is reactive with water. The color of masking phase does not arise from iron oxide material but from magnesium oxide material.

These may lead us to consider that magnesium oxide is dissolved in a sodium chloride flux and then is transported to the surface of haematite grains through the flux.

2) Comparison of Effectiveness of Some Alkali Halide Media with the That of NaCl for the Process of MgFe₂O₄ Formation

Such a medium as LiF, LiCl, KF, NaBr, KCl or KBr was mixed well with MgO and Fe₂O₃ in the molar ratio of 6:1:1. The mixture was heated at the temperatures of 750° to 800°C for 2

hours, where a reference mixture with the NaCl medium was also treated at the same time. The both amounts of MgFe₂O₄ thus formed from the former mixture and from the reference mixture were determined by the X-ray diffraction methods. When each of the amount was in the range of 10 to 90 percent, the ratio of the amount of spinel formed with some alkali halide media to that with NaCl was calculated. The ratio could not be exactly calculated if not within the range. The ratio will indicate the ratio of the effectiveness of some alkali halide media to that of NaCl. The ratios of the effectiveness are summarized in the Table 2.

Table 2. Comparison of effectiveness of alkali halide media for the process of MgFe₂O₄ formation.

Medium (750°~800°C)	Relative Effectiveness
LiF	2.29±0.30
LiCl	1.73±0.20
NaCl	1.00
NaBr	0.72±0.07
KCl	0.61±0.05
KBr	0.55±0.07
KF	0.00?

If KF was used, an amorphous phase was obtained.

Fig. 2. The relationship between melting point and relative effectiveness for the process of MgFe₂O₄ formation.

The effectiveness of the alkali halide media vs. their melting point is plotted in Figure 2. Although alkali halides are called flux-mineralizers, the Figure 2 does not show any good correlation between their melting point and their effectiveness. Then the authors tried to correlate their effectiveness to a property of the alkali halides and found a fairly good correlation between their effectiveness and the difference of their lattice dimension from that of MgO [$a_{\text{MgO}} - a_{\text{AX}}$], where AX means alkali halide and a the cubic lattice dimension. The plot of the logarithm of their effectiveness vs. the difference of their lattice dimension from that of MgO is shown in the

Fig. 3. The relationship between the value $|a_{\text{MgO}} - a_{\text{AX}}|$ and the logarithm of relative effectiveness of alkali halide media for MgFe_2O_4 formation.

Figure 3. Since the correlation has been quantitatively established, it may be the best way of many methods that the effectiveness of alkali halide media is correlated to the value $|a_{\text{MgO}} - a_{\text{AX}}|$. Only an exception was noticed when KF was used as the medium, where the product was amorphous.

3) Confirmation of the Correlation between the Effectiveness of Alkali Halide Media and the Values $|a_{\text{MgO}} - a_{\text{AX}}|$ in the Processes of MgAl_2O_4 and MgCr_2O_4 Formation

Media such as LiF, LiCl, KF, NaBr, KCl or KBr was mixed well with MgO and Al_2O_3 in the molar ratio of 6:1:1. The mixture was heated at the temperatures of 900° to 950°C for 2 hours, where a reference mixture with the NaCl medium was also treated at the same time. The amounts of MgAl_2O_4 thus formed in both of the mixtures were determined by the X-ray diffraction method. When either of the amounts was within the range of 10 to 90 percent, the ratio of the amount with some alkali halide media to that with NaCl was calculated. The ratio will mean the ratio of effectiveness of some alkali halide media to that of NaCl for the process of MgAl_2O_4 formation. The ratios vs. the values $|a_{\text{MgO}} - a_{\text{AX}}|$ were plotted in Figure 4. A fairly good correlation between them can be seen as well as in the case of MgFe_2O_4 formation with these media, while an amorphous phase was obtained if KF was used as the medium.

The correlation was examined also for the process of MgCr_2O_4 formation. The heating temperatures were 700° to 750°C and the procedures and the analytical methods were almost the same as the

Fig. 4. The relationship between the value $|a_{\text{MgO}} - a_{\text{AX}}|$ and the logarithm of relative effectiveness of alkali halide media for MgAl_2O_4 and MgCr_2O_4 formation.

former two processes. An amorphous phase was obtained with the system of KF-MgO- Cr_2O_3 as well as with the systems of KF-MgO- Fe_2O_3 and KF-MgO- Al_2O_3 . The ratio of the amount of MgCr_2O_4 formed with some alkali halide media to that formed with NaCl vs. the value $|a_{\text{MgO}} - a_{\text{AX}}|$ was plotted in Figure 4. There can be seen also a fairly good correlation between them except for the plot of LiF. The heating temperatures were below 750°C. The reason why the amount of MgCr_2O_4 formed with LiF mineralizer was so little may be because MgO in the LiF medium was not so easily transported at that temperature to the surface of haematite grains.

4) The Role of Media Used in the Present Work

The results mentioned above may lead us to consider the role of alkali halide media for the processes of MgFe_2O_4 , MgAl_2O_4 and MgCr_2O_4 as follows: 1) Alkali halide and magnesium oxide make a kind of solution, no matter whether it is of solid or liquid. 2) Magnesium oxide is transported to surface of haematite, corundum or chromia grains and there forms spinel phase.

Summary

The effectiveness of an alkali halide media for the processes of MgFe_2O_4 , MgAl_2O_4 and MgCr_2O_4 formation is closely related to the value $|a_{\text{MgO}} - a_{\text{AX}}|$, where a is the cubic lattice dimension and AX an alkali halide. [Received June 12, 1967]

MgFe₂O₄, MgAl₂O₄ および MgCr₂O₄ スピネルの生成に 対するアルカリハライド媒体の活性

柳 田 博 明・渥 美 正 夫
(東京大学工学部)

固相を含む諸反応に対する鉍化剤などの媒体の活性と他の諸性質との間に定量的な関係を求めた研究は、従来おこなわれていない。これを行なうために、著者らは、MgFe₂O₄, MgAl₂O₄, MgCr₂O₄ の生成反応に対するハロゲン化アルカリ類媒体の活性をしらべ、それを、 $|a_{\text{MgO}}$

$-a_{\text{AX}}$ という値と関連づけることができた。ここで a は立方晶系の格子定数、AX はハロゲン化アルカリを示す。NaCl の活性を 1.00 として相対活性度とすると、相対活性の対数と格子定数の差の絶対値 $|a_{\text{MgO}} - a_{\text{AX}}|$ との間に、直線関係が成立した。(6/12/1967 受付)

PbO-V₂O₅ 系の相関係と系内生成化合物

下 平 高 次 郎・岩 井 津 一*・田 賀 井 秀 夫*
(群馬大学工学部, *東京工業大学)

43. Compound Formation and Phase Relation in the System PbO-V₂O₅

By

Takajiro SHIMOHIRA, Shinichi IWAI* and Hideo TAGAI*
(Gunma University, *Tokyo Institute of Technology)

Amadori's result of the phase diagram PbO-V₂O₅ are re-examined. Solidus and liquidus points of the various mixtures heated in a micro-furnace were determined with the naked eye through a binocular microscope.

In addition to 8PbO·V₂O₅, 3PbO·V₂O₅ and 2PbO·V₂O₅, they have already been reported, a new incongruent compound having a molecular formula of 4PbO·V₂O₅ was identified.

Four eutectic compositions occur at 7.3% (mole) V₂O₅ (761°C), 16.5% V₂O₅ (760°C) 31.7% V₂O₅ (725°C) and 50% V₂O₅ (502°C).

Although the 8PbO·V₂O₅ crystals might have pseudo tetragonal symmetry having unit cell dimensions of $a=5.31_6$ Å and $c=5.69_4$ Å tentatively, but unit cell dimension having $a=5.6_5$ Å, $b=10.7_1$ Å, $c=7.4_7$ Å and $\beta \approx 90^\circ$ with monoclinic symmetry are obtained by oscillation photographs of the single crystals.

The number of formula units in this monoclinic lattice were almost unity.

Although distorted hexagonal lattice having unit cell dimensions of $a=5.78$ Å, $c=20.47$ Å and $c/a=3.53$ are postulated for 3PbO·V₂O₅, unit cell dimensions of 4PbO·V₂O₅ and 2PbO·V₂O₅ are indeterminate yet.

[Received June 18, 1966]

1. 緒 言

金属または無機材質のオイルアッシュの堆積による損傷の問題を基礎的に解決するために V₂O₅ を含む相平衡図がかなり前から研究されている。また有機反応の触媒にも V₂O₅ およびその化合物が利用されているので、その方面の研究もおこなわれてきた。

最近では V₂O₅ と酸化鉛を含んだ低融フリット釉薬が研究され、そのすぐれた乳白性が報告されている¹⁾。それらの釉薬中に析出する結晶は直接この報告中にある化

合物と関係はないが、二、三の化合物が同定されている^{2), 3)}。

いっぽう、PbO-V₂O₅ 二成分系の報告⁴⁾ はかなり古く、またその後この系に関しての研究もほとんど見られない。この系の二元化合物は Amadori によると 8PbO·V₂O₅, 3PbO·V₂O₅ および 2PbO·V₂O₅ の3種類である。最近これらの化合物のうち 8PbO·V₂O₅ の存在を否定する報告⁵⁾ が見られる。これらの化合物のうち比較的良好に知られているのは 3PbO·V₂O₅ でその結晶構