Processing of LaCrO_3 for Solid Oxide Fuel Cell Applications

Topical Report

Wayne Huebner
Harlan U. Anderson

September 1994

Work Performed Under Contract No.: DE-FG21-93MC29224

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Missouri-Rolla
Rolla, Missouri

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CONTRACT INFORMATION

Contract Number	DE-FG21-93MC29224
Contractor	University of Missouri - Rolla Ceramic Engineering Department 222 McNutt Hall Rolla, MO 65401 (314) 341-6129
Contractor Project Manager	Wayne Huebner
Principal Investigators	Wayne Huebner Harlan U. Anderson
METC Project Manager	Bruce Harrington
Period of Performance	April 16, 1994 to April 15, 1995
Schedule and Milestones	

FY94 Program Schedule

	A	M	J	J	A	S	O	N	D	J	F	M
Spray Pyrolysis of the Organometallic Precursors	←-----→											
Construction of sintering and wetting study furnace			←-----→									
Wettability of alkaline earth chromate liquids on LaCrO_3						←-----→						
Solubility of alkaline earth chromate in LaCrO_3								←-----→				
Effect of Stoichiometry of the Sintering Behavior of LaCrO_3		←-----→										
Fuel Cell Measurement System Construction	←-----→											
Processing of Planar SOFC's	←-----→											
Electrical Characterization of Planar SOFC's						←-----→						

OBJECTIVES

The University of Missouri-Rolla is performing a 5 year research program dedicated towards the development of LaCrO_3 -based interconnect powders which densify when in contact with anode and cathode materials for solid oxide fuel cells (SOFC). During a previous DOE-METC program (DE-FG21-89MC26015) we developed and characterized potential cathode and interconnect materials.¹ During the course of this program we investigated compositions within the pseudo-ternary LaCrO_3 - LaMnO_3 - LaCoO_3 system. Results indicated that some of the compositions in this system exhibited the requisite electrical conductivity and stability towards reduction, and could be sintered in air at temperatures less than 1450°C.

In this research program we have expanded our studies on the processing and sintering of LaCrO_3 to make dense interconnects using LaCrO_3 -based oxides at temperatures less than 1500°C in an air atmosphere and in contact with both anode and cathode oxides. The specific objectives of this research program are to:

- ♦ Develop a novel technique which reproducibly yields LaCrO_3 -based powders with the desired particle characteristics
- ♦ Fully understand the liquid phase sintering mechanism
- ♦ Clearly identify the reason why LaCrO_3 does not densify in the presence of electrolyte and cathode materials
- ♦ Systematically solve this problem through judicious control over the liquid phase.
- ♦ Incorporate materials developed in this program into planar cells and measure their performance.

BACKGROUND INFORMATION

One of the primary factors limiting the commercialization of SOFC's is the inability to fabricate LaCrO_3 -based interconnects cheaply, and

in contact with other SOFC components. The very properties which make LaCrO_3 a good interconnect material, also make it very difficult to sinter. Microstructural evolution $\leftrightarrow$ property relationships of the LaCrO_3 -based interconnect need to be understood. This was recently confirmed again at a DOE-sponsored SOFC workshop held May 11, 1994 in Oak Ridge, TN. At this meeting the densification behavior of LaCrO_3 was identified as the top "show-stopper" limiting the development of SOFC's. Indeed, the inability to co-sinter LaCrO_3 -based compounds in air at $T < 1550^\circ\text{C}$ with other SOFC components leads to unacceptable interfacial reactions, and resultant losses in efficiency. Many researchers have addressed this problem, yet progress has been hindered due to recognized difficulties in repeatable processing. Phase development, stoichiometry, particle size/distribution, agglomerate/ aggregate formation, volatility of components, and their dependence on dopant levels and sintering temperature, time and atmosphere are very difficult to systematically take into account.

The results of our work and other investigators²⁻¹⁰ have lead us to the conclusion that the densification of LaCrO_3 -based oxides is controlled by the ability for mass transport (sintering) to occur under conditions which minimize Cr oxide volatilization (Cr activity, a_{Cr}). We demonstrated that this could be accomplished by sintering at temperatures $> 1750^\circ\text{C}$ and oxygen activities of about 10^{-10} atm^2 but clearly these sintering conditions are not compatible with the stability of other SOFC components. Another approach to reduce a_{Cr} is to lower the sintering temperature with liquid fluxes, which was initially pursued by Argonne National Labs⁸. Although the high mobility of the fluoride fluxes detrimentally affected the other cell components, their work showed that liquid phase sintering with a more compatible transient phase would be an attractive approach.

In our earlier DOE-METC program we showed that additions of Ca and Co to LaCrO_3 and YCrO_3 allowed densification to take place in air at temperatures below 1450°C. However further studies showed that interactions during cofiring

between the transient liquid phase (mixture of CaO-CoO and Cr₂O₃) and the electrolyte and cathode prevent densification of the LaCrO₃.

Recent sintering studies on Ca- and Sr-doped LaCrO₃ suggest that the ability to densify these compounds in air at $T < 1550^{\circ}\text{C}$ may be related to the presence of a transient liquid phase formed from the melting of chromates (CaO-CoO-Cr₂O₃ system)^{1,12}. If this is true, then in order to co-sinter this system with other SOFC components, detailed knowledge concerning the composition, source, stability range, and wetting behavior of the liquid phase is required. With this information we can vary the parameters which will allow for the densification of the interconnect when cofired with the other SOFC components. Successful completion of the proposed objectives will be a major step towards the commercialization of SOFC.

PROJECT DESCRIPTION

This project is divided into four primary objectives:

- #1 Reproducible Synthesis of LaCrO₃ Powders
- #2 Sintering of LaCrO₃-based Powders
- #3 Co-sintering of LaCrO₃-based Powders with Cathode and Electrolyte Materials
- #4 Characterization of Planar SOFC's

Results from these studies are presented in the following sections.

LaCrO₃ SINTERING STUDIES

RESULTS

Studies over the past year have focused on understanding the role CaCrO₄ plays in the densification behavior of (La,Ca)CrO₃. A-site excess and deficient materials were compared through the use of SEM, EDS, XRD and DTA.

Experimental Procedure

Powder specimens were prepared having the compositions: $(\text{La}_{0.6}\text{Ca}_{0.4})_x\text{CrO}_4$, where $x = 0.95, 0.98, 0.99, 1.00, 1.01, 1.02$ and 1.05 . A large amount of Ca (≈ 40 at%) was added into the system so that $\text{Ca}_m(\text{CrO}_4)_n$ could be easily observed and analyzed. Samples were synthesized and processed in the low temperature monazite-type form to control the distribution of secondary phases. Above 700°C , $(\text{La,Ca})\text{CrO}_4$ transforms into LaCrO₃, CaCrO₄ and other unidentified minor phases which, at higher temperatures for a $(\text{La,Ca})\text{CrO}_3$ solid solution and a $\text{Ca}_m(\text{CrO}_4)_n$ liquid phase¹³.

Powder synthesis was performed using a modified liquid mix process¹⁴ which is schematically illustrated in Figure 1. This process is identical to the procedure we are using to prepare organometallic precursors for spray pyrolysis (SP). This study was not performed on powders prepared using spray pyrolysis as it was initiated prior to completion of the SP system. Drying was

Figure 1. Experimental Overview

performed in an oven at 120°C, which initiated charring. Prior to calcination the char was milled in ethyl alcohol for 8 h to reduce agglomeration. Calcination took place in flowing argon for 8 h at 550°C. Phase analysis was performed using XRD (Scintag, Model 2000).

Calcined powders were uniaxially pressed into 12.7 mm x 3.2 mm disks at 500 MPa. Bulk green and sintered densities were determined using geometric and liquid displacement techniques. For the sintering studies, disks were heated at 5°C/min to temperatures ranging between 1300 and 1450°C for 2 -100 h.

Several specimens with compositions of $(La_{0.6}Ca_{0.4})_{0.99}CrO_3$ (LC99) and $(La_{0.6}Ca_{0.4})_{1.02}CrO_3$ (LC102) were air-quenched to room temperature from various temperatures during a sintering run. The furnace heating rate was 4°C/min, and isothermal holds were made at 1030°C and 1350°C for 2 h. Microanalysis on quenched and sintered samples was performed by SEM and EDS.

The melting characteristics of the liquid phase in LC99 and LC102 were compared with $CaCrO_4$ using DTA (STA Model 409, Netzsch).

Results and Discussion

Porosity and Shrinkage

The sintering behavior of $(La_{0.6}Ca_{0.4})_xCrO_3$ compositions were studied by measuring the shrinkage, density and porosity of the samples sintered under various temperature/time profiles. A plot of shrinkage with respect to the $(La+Ca)/Cr$ cation ratio under the sintering conditions of 1400°C/2h is shown in Figure 2. The total shrinkage increases rapidly as $(La+Ca)/Cr$ increases from 0.95 to 0.99. The maximum shrinkage is obtained when the cation ratio is between 0.99 and 1.01.

Density measurements were difficult to correlate, because the amount of exsolved $Ca_m(CrO_4)_n$ changed throughout the process, making the theoretical density difficult to track. However, the open porosity, shown in Figure 3, directly correlates to the densification behavior. We see the open porosity decreases steadily as

$(La+Ca)/Cr$ increases from 0.95 to 1.0., and approaches zero between 1.01 and 1.05.

Figure 2: Percent total shrinkage vs $(La+Ca)/Cr$ ratio of $(La_{0.6}Ca_{0.4})_xO_3$

Figure 3: Percent open porosity vs $(La+Ca)/Cr$ ratio of $(La_{0.6}Ca_{0.4})_xO_3$

Sintering Behavior

Evidence of the liquid phase was readily observed in quenched specimens. Figure 4 is an SEM micrograph showing the recrystallized liquid as a dark, glass-like mass enveloping the lighter $(\text{La,Ca})\text{CrO}_3$ particles. Similar microstructures were common in all of the bulk $(\text{La}_{0.6}\text{Ca}_{0.4})\text{CrO}_3$ compositions under similar conditions. According to EDS, the bulk quenched liquid is composed of Ca, Cr and O. XRD confirmed the presence of mainly CaCrO_4 and sometimes other $\text{Ca}_m(\text{CrO}_4)_n$ phases.

The sintering of LC99 and LC102 were compared by SEM analysis on a series of quenched samples. Figures 5-7 show SEM micrographs of fracture surfaces which show the behavior of the two compositions. Each specimen pair was air-quenched from similar temperatures during the sintering process.

Figure 8 is a cross section of LC102, which shows a dark layer which has formed on the free surface. The liquid has spread into a uniform layer along the free surface after being squeezed out of the grain boundaries as the grains coalesced. The surface layer was identified by XRD as $\text{Ca}_5(\text{CrO}_4)_3\text{OH}$. Figure 9 shows a back-scatter image of the cross section of $\text{Ca}_m(\text{CrO}_4)_n$ crystals on the surface of LC99 and Figure 10 is a top view of a polished specimen. Surrounding this mass is a large porous region with a radius of $\geq 100\text{ }\mu\text{m}$. EDS indicated that these crystals are Ca-poor, although XRD only showed the presence of CaCrO_4 .

Annealing experiments demonstrated the difficulty in dissolving large amounts of Ca into $(\text{La,Ca})\text{CrO}_3$. Specimens containing 40at% Ca with $(\text{La}+\text{Ca})/\text{Cr}$ cation ratios of 0.95 to 1.05 contained residual, re-crystallized liquid in the grain boundaries after long term annealing. For example, Figure 11 is a back scatter image of LC105 sintered and annealed at 1300°C for 100 h. According to EDS, the dark cubic phase contains Ca and O.

Melting Behavior

The characteristic of liquid phase formation with respect to stoichiometry, are further illustrated by comparing the DTA curves of CaCrO_4 , LC102 and LC99, as shown in Figure 12. In the upper set

Figure 4: Polished surface of LC95 heated to 1350°C

of curves, the onset of melting takes place at nearly the same temperature for each composition. In particular, the CaCrO_4 and LC99 curves display a similar, single-step melting process. The double peaks corresponding to LC102 indicate that the associated liquid phase melts in two stages.

The crystallization peaks in the lower section occur at lower temperatures which reflects supercooling of the liquid. The CaCrO_4 composition crystallizes first, and the other two liquids crystallize $\approx 10^\circ\text{C}$ lower. The liquid in LC102 again shows a double peak which suggests a two step recrystallization process.

Discussion

The large amount of exsolved $\text{Ca}_m(\text{CrO}_4)_n$ in the system made it difficult to correlate the sinterability of $(\text{La}_{0.6}\text{Ca}_{0.4})_x\text{CrO}_3$ compositions directly by shrinkage or density measurements. For example LC99 had a shrinkage comparable to LC101, which contradicts the results of Sakai¹⁵ and Chick¹⁶. Possibly, enough liquid was present to overcome some of the effects of stoichiometry. Obviously, the amount of total Ca added to these

Figure 5a: Fracture surface of LC99 heated to 740°C

Figure 6a: Fracture surface of LC99 heated to 1030°C

Figure 5b: Fracture surface of LC102 heated to 740°C

Figure 6b: Fracture surface of LC99 heated to 1030°C

Figure 7a: Fracture surface of LC99 heated to 1350°C

Figure 8: Fracture surface of LC102 heated to 1350°C

Figure 7b: Fracture surface of LC102 heated to 1350°C

Figure 9: Fracture surface of LC102 heated to 1350°C

Figure 10: Top surface of LC102 heated to 1400°C

Figure 11: Polished surface of LC105 heated at 1300°C-100h

Figure 12: DTA comparison of various compositions.

compositions exceeded optimum values and should be reduced if these compositions are to be used as an interconnect. This is evident from the annealing experiment. A former study⁹ suggested that < 25at% Ca in (La,Ca)CrO₃ approaches an optimal composition.

Notable differences in the densification became evident from porosity measurements. The A-site deficient compositions show a higher open porosity than their A-site excess counterparts.

Microscopic analysis of a series of quenched specimens provided a visual investigation of the sintering. Initially, specimen pairs of A-site excess and deficient compositions followed the same general steps of densification. Both transformed to the perovskite structure below 740°C as evidenced by XRD. Grain growth has occurred so that the primary particles can be resolved.

From previous work it is known that CaCrO₄ loses oxygen and begins to form a solid solution with LaCrO₃. Excess Ca which is not incorporated into solid solution segregates along with Cr and O to the free-surface in both A-site excess and A-site deficient materials.

Upon melting Ca_m(CrO₄)_n, all compositions experienced rapid grain growth. The recrystallized

liquid is identified in either the figures as darker, irregular masses; the lighter equiaxed grains are $(\text{La,Ca})\text{CrO}_3$. It appears that $\text{Ca}_m(\text{CrO}_4)_n$ segregates from $(\text{La,Ca})\text{CrO}_3$. Continued heating was accompanied with further grain growth and spreading of the liquid.

From these series of micrographs, the sinterability of the two compositions appear to be quite similar. In both cases a liquid phase forms and spreads, grain growth occurs at similar rates, and the final grains sizes are comparable. This did not allow any explanation to the observed differences in shrinkage and porosity. However, differences became apparent by examination of the specimen free surfaces.

A comparison of Figures 8 and 9 illustrate the difference between the liquid phases in the final sintering stages of A-site excess and deficient compositions. The liquid on the free surface of the A-site excess specimen has spread into a uniform 3 μm layer, demonstrating good wetting characteristics. This is desirable for optimum liquid phase sintering. In contrast, the $\text{Ca}_m(\text{CrO}_4)_n$ phase in the A-site deficient material formed a 100 μm diameter island on the surface. The large volume of porosity surrounding this island is a result of the segregation of the liquid from the matrix. This $\text{Ca}_m(\text{CrO}_4)_n$ phase appears to be more crystalline, and it is believed that it contained Ca-Cr-O solids throughout sintering, because CaCr_2O_4 whiskers were observed to grow from some of the A-site deficient compositions while at the sintering temperature.

The divergent behavior of the $\text{Ca}_m(\text{CrO}_4)_n$ compositions towards densification may be understood by reference to the CaO- Cr_2O_3 phase diagram shown in Figure 13. Assuming $(\text{La,Ca})\text{CrO}_3$ retains its stoichiometry with respect to the A and B cations, any nonstoichiometry within a given system is presumed to appear in second phases. Therefore, when Ca dissolves into the $(\text{La,Ca})\text{CrO}_3$ matrix, it is accompanied with stoichiometric amounts of Cr and O. This process of dissolution consequently induces a change in composition of the $\text{Ca}_m(\text{CrO}_4)_n$ phase in nonstoichiometric systems.

The change in composition of $\text{Ca}_m(\text{CrO}_4)_n$ while heating is indicated by the dashed lines on the phase diagram. The lines are estimated and their curvature will depend upon the kinetics of dissolution of CaCrO_4 into $(\text{La,Ca})\text{CrO}_3$. The initial composition of $\text{Ca}_m(\text{CrO}_4)_n$ at low

Figure 13: Phase diagram of the CaO - Cr_2O_3 system.

temperature depends upon the A/B ratio and the amount of exsolved CaCrO_4 . A different A/B ratio in $(\text{La,Ca})\text{CrO}_3$, or mole fraction of CaCrO_4 will shift the initial composition of the secondary phase along the composition axis. For example if $(\text{La,Ca})\text{CrO}_3$ was initially prepared as A-site excess, and no CaCrO_4 was exsolved, the secondary phase would be CaO.

Upon heating of A-site excess $(\text{La,Ca})\text{CrO}_3$, the initial composition of the exsolved phase starts to the left of the CaCrO_4 composition line. As the temperature is increased the Ca solubility also increases, and Ca, Cr and O begin to dissolve into the perovskite matrix. The Ca content of $\text{Ca}_m(\text{CrO}_4)_n$ will increase towards the CaO end member. At 1022°C, a liquid phase forms with some amount of solid $\beta\text{-CaCr}_2\text{O}_4$. As heating continues, the liquid composition changes towards CaO and the solid $\beta\text{-CaCr}_2\text{O}_4$ disappears. At some point the melt becomes 100% liquid. The SEM study showed that good wetting behavior is exhibited by this liquid phase system throughout the sintering process.

In A-site deficient $(\text{La,Ca})\text{CrO}_3$, the Ca content of $\text{Ca}_m(\text{CrO}_4)_n$ decreases towards the

Cr₂O₃ end member with increasing temperature and Ca solubility. At some point, a solid network is formed between β -CaCr₂O₄ and the (La,Ca)CrO₃ grains and densification by particle rearrangement stops. The remaining liquid eventually segregates from the matrix, forming islands on the free surface. Regions surrounding these areas are typically porous.

DTA results also indicated deviating behavior in the opposing liquid phases. The phase diagram indicates two melting peaks should be exhibited, one near 1022°C, the eutectic temperature, and one at a higher temperature upon complete melting of the liquid. Conversely, the DTA curve of Cr-rich Ca_m(CrO₄)_n would contain only one broad peak, beginning at the eutectic temperature since there would be no other reaction expected.

Conclusion

The present results from our studies on the densification behavior of LaCrO₃-based interconnects has clearly delineated the effects of stoichiometry. A liquid phase forms in both A-site excess and deficient compositions, however the final stages of sintering differ due to changes in the composition and resultant wetting behavior. The melt in the A-site excess material becomes 100% liquid, and retains its wetting behavior, while the A-site deficient material does the opposite.

SOFC PERFORMANCE STUDIES

In this portion of the research we are focusing on the microstructure $\leftrightarrow$ property relations in solid oxide fuel cells (SOFC's) to better understand the mechanisms involved in cell performance. The aim is to fabricate SOFC's with controlled microstructures utilizing La_{1-x}Sr_xMnO₃ (LSM), yttria stabilized zirconia (YSZ), and Ni-YSZ composites as the cathode, electrolyte, and anode, respectively. The specific objectives of this research project are to:

- Fabricate SOFC components with controlled microstructures (i.e. grain size and porosity of the cathode/anode).
- Gain a better understanding of the mechanisms involved in improving cell

performance via electrochemical and impedance techniques, and correlate these results to the microstructure.

This aspect of the project is divided into three phases:

- I. Construct a system for measuring planar SOFC's
- II. Processing and forming of trilayer structures of anode/electrolyte/cathode
- III. Electrical characterization of single cells by electrochemical and impedance techniques.

Phase I has been completed whereas Phase II and III are presently ongoing and will overlap during the course of this research.

I. System Construction

The system built for measuring cell performance is completed and shown in Figure 14. The apparatus is a two tube design capable of operating at temperatures up to 1100°C. The oxygen activity of the oxidant and fuel is controlled by mass flow controllers and the pO₂ is monitored using a ZrO₂ sensor. The electrical characterization, I-V, current density, and interfacial characterization, will be carried out using a computer controlled Schlumberger Impedance/Gain-Phase Analyzer (1286) and Electrochemical Interface (1260).

The apparatus was calibrated using a YSZ electrolyte with Pt anode/cathode. Results of open circuit potential were in good agreement with theoretical values.

II. Cell Fabrication

At present, powder preparation and forming techniques are underway to fabricate planar cells. Various powder preparation techniques have been investigated, Pechini liquid mix, Glycine - Nitrate, and mixed oxide, to vary the starting powder characteristics. A tape casting, laminating, and

Figure 14: Cell measurement system.

screen printing fabrication scheme is currently being used to prepare trilayer structures.

The YSZ electrolyte and Ni-YSZ anode are currently co-fired at 1400°C. Commercially available YSZ can be sintered to near theoretical density and has a final grain size of approximately 5 μm . The anode is deposited by screen printing and is made porous by introducing a fugitive phase which is burnt out during densification. The final microstructure (i.e. Ni grain size, pore size, pore size distribution, and % porosity) is dictated by the powder and fugitive phase characteristics and amount of fugitive phase added. A typical fracture surface of a YSZ/ Ni-YSZ couple is shown in Figure 15.

After co-firing the electrolyte and anode, a LSM paste is screen printed onto the electrolyte followed by a 1100°C heat treatment. Different powder preparation techniques enable various LSM microstructures to be fabricated. Distinctly different microstructures have been attained as shown in LSM/YSZ couples, Figures 16 and 17.

The overall goal in fabricating planar cells is to systematically vary the microstructure (i.e. grain size, % porosity) of the cathode and anode to better

Figure 15: YSZ: Anode couple.

Figure 16: LSM anode - fine scale, high TPB.

Figure 17: LSM anode - fine scale, low TPB.

understand the factors effecting cell performance. Some questions which should be answered are:

- What effect does the triple phase boundary (pore, YSZ, LSM) have on performance?
- Can a dense cathode be used if there is sufficient ionic conductivity at a low overpotential?
- Is long term stability sensitive to the microstructure of the electrodes?
- Is there a critical thickness for the anode and cathode?
- Would a composite structure of fine grain material next to the electrolyte with coarse grain structure composing the remainder of the electrode be more efficient?
- Can results be reproduced?

III. Electrical Characterization

A Pt/YSZ/Pt cell has been used to calibrate the system with results that correlate well with theoretical values. At present electrochemical and impedance techniques are being explored through literature review and experimental studies.

Some typical experimental studies which will be performed include:

- I - V, current density and open circuit potential as a function of temperature, time and pO_2
- Impedance spectra as a function of temperature, time and pO_2

FUTURE WORK

With respect to the major thrusts of this program:

Sintering of $LaCrO_3$ -based Powders

Specific Tasks:

A. Reproducible Green State Synthesis via Tape Casting

- ◆ Develop the tape casting system & characterize the dispersive behavior of the spray-pyrolyzed powders in the binder system.

B. Further Characterization of the Chromate Liquid Phase

- ◆ Composition
- ◆ Volume fraction
- ◆ Viscosity as a $f(T, \text{composition})$
- ◆ Temperature stability
- ◆ Wettability on $LaCrO_3$ -based powders (contact angle measurements)

Co-sintering of $LaCrO_3$ -based Powders with Cathode and Electrolyte Materials

Goal: Understand why LCC and YCC do not densify when in contact with ZrO_2 or LSM

Specific Tasks:

A. Identify the Underlying Cause

- ◆ Contact angle measurements of liquid phase on LSM and ZrO₂
- ◆ Diffusion couples
 - dense & porous specimens
 - microstructural analysis of the interface (microprobe)

B. Develop Approaches to Solve the Co-Sintering Problem

- ◆ If Ca²⁺ segregation (surface diffusion, preferential migration):
 - decrease the Ca activity gradient (Δa_{Ca}) by using Ca-doped LaMnO₃ and ZrO₂
- ◆ If wicking:
 - alter pore size distributions to diminish the driving force - this knowledge will come out of consideration of the viscosity of the melt & the contact angles - the pore size needed to prevent wicking can then be calculated.
 - alter wetting behavior via dopants to the liquid phase (changes in viscosity - incorporation of ions that bond well to Cr³⁺ compared to Mn³⁺ or Zr⁴⁺)

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