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RAPIDLY SOLIDIFIED CERAMICS:
PROCESSING, STRUCTURE, AND MAGNETIC PROPERTIES

Progress Report for the period
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Since its initiation in September 1984, work under this contract has progressed in two areas: construction of a gas atomizer for rapid solidification of ceramics; and characterization of rapidly solidified materials in the $\text{SrO-Fe}_2\text{O}_3$, $\text{BaO-Fe}_2\text{O}_3$, $\text{MnFe}_2\text{O}_4\text{-SiO}_2$, and $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ systems. The following sections summarize this work.

Construction of Gas Atomizer

Construction of a rapid solidification chamber, intended for gas atomization and twin roller quenching of small (up to about 100 grams) batches of ceramics and metals, is one of the preliminary goals of this work. The existing chamber was prepared for gas atomization by the addition of an atomization die, solenoid valves, a feed-through for induction heating, a vacuum pump and gauges, a temperature read-out, and an external frame and cart. Runs can be conducted in vacuum (5 millitorr), inert gas, or oxygen. Pressurized ejection of the melt and atomization will be controlled by toggle switches on the front of the unit.

No attempt has been made in this first die design to attain ultrasonic gas velocities or shock pulses. The present die is made of 304 stainless steel, is 1.75" in diameter with a 0.375" orifice, and has 18, 1/64" diameter holes oriented at 60° off of vertical.

Characterization of rapidly solidified $\text{SrO-Fe}_2\text{O}_3$ compositions

In previous work by this research group, the composition 54 mole% Fe_2O_3 46% SrO was rapidly solidified by single-wheel melt spinning. This composition, with melting point 1210° C, is the eutectic between $\text{SrFe}_{12}\text{O}_{19}$ and a phase that has been variously identified as $\text{Sr}_7\text{Fe}_{10}\text{O}_{22}$ (Batti, 1962) and $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ (Vogel and Evans, 1979). The quenched materials ranged from nearly

entirely glassy ribbons to (in order of decreasing cooling rate) powder, fibers, and pellets. Characterization of these materials continues under the present project.

XRD of the ribbons showed five faint rings, indicating the presence of a trace crystalline phase. This corroborates previous TEM results. The crystallites must be smaller than about 200 Å, since no hyperfine splitting appeared in the Mossbauer spectrum of this material, and the width of the quadrupole doublet indicated that most of the Fe was in a glassy (rather than paramagnetic crystalline) phase.

The five spacings obtained from the XRD film correspond to the weaker lines in Fe_3O_4 , but this identification must be regarded as tentative since the four strongest Fe_3O_4 lines are absent.

XRD of more slowly solidified material of the same composition shows that they contain the 5:7 (4:6) composition as a major phase. These films also contain most of the lines for $\text{SrFe}_{12}\text{O}_{19}$, though some are shifted and their low intensity indicates a small concentration of the hexaferrite is present. The presence of Fe_3O_4 in the powder cannot be ruled out, but it is absent from the more slowly cooled pellets.

The Mossbauer spectra of ribbons, powder, and fibers indicate an increasing degree of crystallinity and magnetic ordering, and a decreasing proportion of glassy phase, with decreasing quenching rate. The phases present in materials of intermediate quench rate, while clearly not the equilibrium ones, remain to be identified. Monteil, et al. (1978) found that a metastable crystalline phase, which they identified as SrFe_2O_4 , formed before the equilibrium phases when splat-quenched material of the present composition was reheated. Their interplanar spacings, however, do not match those found in this work.

Pellets of this composition have been sintered to obtain their equilibrium phases. Comparing their Mossbauer spectra, x-ray patterns, and magnetic properties will provide a basis for a better understanding of the phases found in the rapidly solidified material.

Other compositions

The following compositions have been splat-cooled with a hammer-and-anvil device in a solar furnace:

<u>Sample</u>	<u>Composition</u>	<u>Liquidus Temperature</u>
BF6	BaFe ₁₂ O ₁₉	1500 °C
SF6	SrFe ₁₂ O ₁₉	1500 °C
CFS40	30CoO, 30Fe ₂ O ₃ , 40SiO ₂	1465 °C
MFS20	40MnO, 40Fe ₂ O ₃ , 20SiO ₂	1495 °C
MFS43	28.5MnO, 28.5Fe ₂ O ₃ , 43SiO ₂	1375 °C

The yield from this apparatus was much higher than from melt spinning; starting batches were smaller (a few grams) and just under a gram of well-quenched material was obtained from each composition. Because of a lack of temperature control in the solar furnace, these compositions were melted well above their liquidus, and in air, so appreciable Fe²⁺ is expected.

Room temperature Mossbauer spectra of these materials and of commercial strontium hexaferrite powder have been measured and fit using a least squares technique (Figures 1-6). The Mossbauer parameters obtained from these fits are listed in Table I.

Figure 1, the spectrum of commercial strontium hexaferrite powder, reflects the complexity of the compound's magnetoplumbite structure, in which Fe resides in five distinct magnetically ordered sites, with three coordination

Figure 1. Room temperature Mossbauer spectrum of commercial $\text{SrFe}_{12}\text{O}_{19}$ powder.

Figure 2. Room temperature Mossbauer spectrum of splat-quenched $\text{SrFe}_{12}\text{O}_{19}$.

Figure 3. Room temperature Mossbauer spectrum of splat-quenched $\text{BaFe}_{12}\text{O}_{19}$.

Figure 4. Room temperature Mossbauer spectrum of splat-quenched 40 mole% MnO , 40% Fe_2O_3 , 20% SiO_2 .

Figure 5. Room temperature Mossbauer spectrum of splat-quenched 28.5 mole% MnO, 28.5% Fe₂O₃, 43% SiO₂.

Figure 6. Room temperature Mossbauer spectrum of splat-quenched 30 mole% CoO, 30% Fe₂O₃, 40% SiO₂.

CFS40 RSP'D FERRITE-SILICATE 3/4 RT 10-SEP-84 MCFS40.DAT (C4615)

TABLE I. Room temperature Mossbauer parameters, relative to Fe Foil, from the spectra shown in Figures 1-6.

<u>sample</u>	<u>spectral feature</u>	<u>IS [mm/sec]</u>	<u>QS [mm/sec]</u>	<u>MHF [kOe]</u>	<u>Interpretation</u>
unquenched	sextet	0.379	-0.478	407	sym. Fe ³⁺ oct.
SrFe ₁₂ O ₁₉	sextet	0.298	-0.181	497	4 unres. sextets
QSF6	sextet	0.346	-0.200	487	sym. Fe ³⁺ oct.
	sextet	0.653	0.028	454	unres. Fe ²⁺ , Fe ³⁺
BF6	sextet	0.360	-0.231	486	sym. Fe ³⁺ oct.
	sextet	0.666	-0.084	451	unres. Fe ²⁺ , Fe ³⁺
MFS20	sextet	0.458	-0.685	486	Fe ³⁺ oct.
	sextet	0.568	-0.186	451	
MFS43	doublet	1.025	1.995	---	dist. Fe ²⁺ oct.
CFS40	doublet	1.185	2.593	---	sym. Fe ²⁺ oct.
	doublet	1.056	1.620	---	dist. Fe ²⁺ oct.
	doublet	0.368	1.081	---	dist. Fe ³⁺ oct.

numbers (4, 5, and 6). The spectra of the quenched hexaferrites (Figures 2 and 3) show no signs of a magnetoplumbite phase; identification of the phases present is under way. Although $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$ are isostructural, the strong similarities between Figures 2 and 3 are noteworthy, considering that the equilibrium crystalline phases in the BaO - and $\text{SrO-Fe}_2\text{O}_3$ systems are otherwise quite different (Batti, 1962; Vogel and Evans, 1979).

The remaining three compositions lie along the joins $\text{MFe}_2\text{O}_4\text{-SiO}_2$. MFS20 lies in the Mn-Fe spinel primary phase field. MFS43 and CFS40 lie on the spinel-silica phase boundaries.

The spectrum of MFS20 (Figure 4) indicates at least two magnetically ordered Fe sites. The symmetric Fe^{3+} site is consistent with MnFe_2O_4 , an almost completely normal spinel. The misfit in the center peaks suggests that the spectrum also contains at least one quadrupole split.

The spectrum of MFS43 (Figure 5) resembles that of a rapidly solidified 35.5 mole% CoO , 35.5% Fe_2O_3 , 29% P_2O_5 glass (Sugimoto and Hiratsuka, 1982). The CFS40 spectrum, however, indicates three Fe sites and traces of hyperfine splitting in the baseline.

Summary

The equipment under construction will provide those rapid solidification techniques which we feel are the most promising for ceramic materials. The small size of the rapid solidification chamber will enable rapid turnaround after each run and easy adaptability to the wide range of magnetic and non-magnetic materials covered in the original proposal.

In the meantime, preliminary but detailed investigations of melt-spun and splat-quenched materials continue. Several familiar capabilities of rapid solidification have been realized, including new amorphous phases, metastable

crystalline phases, and extremely fine-scale microstructure. Understanding the atomistic mechanisms leading to these phases, and the role these phases might play in the development of materials with outstanding properties, will be the goals of future work.

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