

Chapter-7

(Summary and conclusions)

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The synthesis of nanostructured materials has generated great expectations to develop newer technological products in the past few years. It is reported that the high alumina cements prepared through solid-state reaction require intermediate grinding and prolonged calcination periods at elevated temperatures. It shows poor sinterability with some impurity phases. Wet chemical methods are preferred for ceramic materials preparation as they show high sinterability and high surface area with required stoichiometry. Therefore present thesis work addresses four different, fast and effective methods for producing fine and nano-sized high alumina cement powders. Furthermore, all the fabricated cements were used as hydraulic binders to formulate bauxite based low cement castables.

The first method described was a gel-trapped co-precipitation process which yielded fine and thermally reactive HAC powders. Desired mineralogy, having high refractoriness, was achieved by synthesizing cementing phases. CA, CA₂, C₁₂A₇, CA₆ and C₄A₃SO₄ began to form in the temperature range of 1200–1350°C. One advantage of this process was to exclude silicate phases which plays a major role in eutectic formations in such cements. Although these samples have high initial and final setting, better CCS values at different curing times were obtained than their commercial counterparts. Castables prepared by HAC80 cements have better physical and cementing properties than the HAC70 containing castables. The XRD patterns of the formulated castables confirmed the formation of corundum and mullite phases. This mullite, formed at high temperatures, also acted as a bonding phase due to its interlocking structure and was accounted for the high CCS values. The mechanical and refractory properties showed a remarkable increment with 10 wt% zirconia. This study also establishes a range limit of microfine inclusions. Excessive micro-fines resulted in high flow values, high water demand and as a consequence strength degradation which were the causes behind low mechanical strength of 15 wt% zirconia containing castable.

Second method of high alumina cement preparation was termed as novel co-melting process. Using this technique, high alumina cements were successfully prepared having small crystallite size in the range 20–35 nm. Desired cementing phases (CA, CA₂ and C₁₂A₇), which have high refractoriness, were successfully formed at 1000°C. The XRD patterns of castables showed corundum and mullite formations, which were responsible for superior thermo-mechanical and physical properties. Additive such as silicon carbide acted as a reinforcing agent. This helped in improvement of bulk densities and in turn diminution of apparent porosities. Acicular mullite formation occurred at high temperatures due to oxidation derived silica from silicon carbide and added silica. Microstructure revealed liquid phase formation, which at high temperature accommodated thermal stresses and helped in improving mechanical properties. Hence, it was concluded that addition of microsilica although improves mechanical and thermal properties, its addition must be appropriately optimized in order to ensure a suitable blend of properties. Its addition up to 3 wt% was optimum in bauxite based castables. For steelmaking applications, microsilica containing materials must be restricted for areas in which the resistance to slag attack is an essential requirement.

An auto combustion process was employed as a third technique to produce pure and crystalline calcium aluminates with good compositional control. All the desired cementing phases such as CA, CA₂, and C₁₂A₇ were formed even at 1000°C with small crystallite size in the range 18-38 nm. The XRD patterns of castables showed corundum and spinel as major phases present. Trigonal corundum and cubic spinel formed at high temperatures facilitated ceramic bonding providing high CCS and CMOR. Large grains of corundum improved spalling resistance. This study revealed that dispersion of in-situ formed spinel was present in fine grained alumina as a part of castable matrix and promoted its ductile elongation at high temperatures. These results were responsible for high temperature strengths of castables.

In the fourth portion of the study, high alumina cements were mechanochemically synthesized at temperatures starting from 1000°C. Prepared cements had an

average particle size of 40nm as evaluated from TEM microplots. Formation of CA, CA₂, and CA₆ cementing phases was confirmed through XRD patterns. The XRD patterns of castables showed corundum, mullite formation along with pre-existing zirconia and SiC. The formation of CA₆ and absence of silicate phases in cement were responsible for superior thermo-mechanical and physical properties when compared with commercial cement containing castables. The strengthening of castables was also attributed due to formation of needles like mullite structures. The mechanical strength was a close analogy to porosity and bulk density, where suppressed porosity caused a substantial improvement in crushing and bending values. The maximum in-situ mullite formation enabled the castables Q6 to achieve highest residual bending strength amongst all other formulations. This work also re-established that addition of micronized zirconia up to 10 wt% was found to be optimum for castable matrix as proved in first method of preparation of HAC and their castable formulations.

These approaches may be successfully applied for the commercial preparation of HACs at relatively lower temperatures than existing industrial productions with better control over particle size as well as cement mineralogy. These excellent properties of such castables enable their use in various refractory applications such as steelmaking, aluminum, copper, glass, cement, petro-chemicals and other ceramic industries.