ANTICORROSIVE COATINGS, PROCESSES AND USES THEREOF

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ABSTRACT

The invention provides novel methods for anticorrosive protection of iron or steel surfaces, such as on embedded iron or steel reinforcement components in composite materials and on steel surfaces of piles and vessels. The unique siderite coating formed during a carbonation curing possesses excellent anticorrosive properties and is suitable for improving the overall service life of coated objects.
FIG. 1

PRIOR ART
FIG. 2

PRIOR ART
FIG. 3

PRIOR ART
FIG. 4

PRIOR ART
FIG. 5

PRIOR ART
FIG. 6

PRIOR ART
FIG. 7
PRIOR ART
FIG. 8
PRIOR ART
FIG. 11 (a)

Fine particles

Fiber Core

Amorphous or crystalline layer

FIG. 11 (b)

Elliptical Core

Fine particles

Amorphous or crystalline layer

FIG. 11 (c)

Equiaxed Core

Fine particles

Amorphous or crystalline layer
Plain Carbon steel (1/2” diameter)

Ingredients to form composite material

FIG. 13
FIG 15
FIG. 20
ANTICORROSIVE COATINGS, PROCESSES AND USES THEREOF

PRIORITY CLAIMS AND RELATED PATENT APPLICATIONS

[0001] This application claims the benefit of priority from U.S. Provisional Application Ser. No. 61/922,059 filed on Dec. 30, 2013, the entire content of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention generally relates to anticorrosive coatings for metal surfaces and processes and uses thereof. More particularly, the invention relates to formation of anticorrosive coatings on iron or steel surfaces, such as on embedded iron or steel reinforcement components in composite materials and on surfaces of iron or steel piles and vessels. The unique siderite coating possesses excellent anticorrosive properties, can be formed alongside curing of the bulk composite material, and can significantly improve the service life of coated objects.

BACKGROUND OF THE INVENTION

[0003] Precast concrete objects, such as pre-stressed concrete girders, beams and railway ties, are elongated beams typically with plain carbon steel as reinforcement. In addition, cast-in-place concretes such as bridge deck slabs and pavements are often reinforced with steel. For example, reinforcing bars (rebar) are common steel bars or meshes of steel wires regularly used as tension devices in reinforced concrete and reinforced masonry structures to strengthen as well as to hold the concrete in compression.

[0004] Most of the precast concrete elements or cast-in-place concretes are manufactured from conventional concrete. The common rebar is made of unfinished tempered steel, making it susceptible to rusting. The concrete cover typically provides a pH value higher than 12, helping the rebar avoid or slow the corrosion process. However, too little concrete cover or loss of coverage over time can compromise this guard through carbonation from the surface and salt penetration. While the high pH of the concrete may protect reinforcing steel from corroding, the concrete is affected by chloride penetration from salts during winter season or carbonation reaction with atmospheric carbon dioxide (CO₂), which reduces the pH of concrete. This breaks the passivation layer on the rebar leading to corrosion of steel. As rust takes up greater volume than the steel from which it was formed, it causes severe internal pressure on the surrounding concrete, leading to cracking, spalling, and ultimately, structural failure.

[0005] Recently, a novel composite material was developed that exhibit excellent performance characteristics, including toughness, flexibility, abrasion resistance and durability, which match or exceed that of conventional concrete. The novel composite material can be readily produced from widely available, low cost raw materials by a process suitable for large-scale production with reduced equipment need, improved energy consumption, and more desirable carbon footprint. The raw materials include inexpensive calcium silicate materials, for example, ground wollastonite. Carbon dioxide is consumed in the production as a reactive species and ends up sequestered in the final product. (See, e.g., U.S. Pat. No. 8,114,567; U.S. Pub. Nos. 2009/0142211A1, 2011/0104469A1, 20090142578, 2013012267A1, and 20120312194A1; PCT publications WO 2009/102360, WO 2011/053598, and WO 2011/09067).

[0006] During production of this novel composite material and over its service life, a carbonation process takes place that leads to its pH of about 7 or 8 inside the composite material. Such level of pH makes it highly desirable for a method that prevents corrosion of steel components in the composite material. One way to improve anticorrosion performance is to use components made of stainless steel, which significantly increases the product cost. Another approach would be to pre-treat the steel components before embedment to form a protective coatings, which could add to the manufacturing complexity including additional steps for protective treatment and coating formation as well as increased cost for related materials and energy consumption.

[0007] In the oil and gas industry, corrosion remains a major impediment to long service life of the pipelines used to transport oil, gas and hazardous liquids. Corrosion is one of the leading causes of failures in onshore transmission pipelines in the United States. It is a threat to gas distribution mains and services as well as oil and gas gathering systems. Corrosion is also responsible for a significant portion of incidents involving pipelines. (Pipeline Corrosion Final Report 2008, U.S. Department of Transportation.)


[0009] Thus, there is an on-going need for anticorrosive methods to protect iron or steel surfaces, such as that of embedded iron or steel reinforcement components in composite materials and steel surfaces of oil and gas pipelines and vessels. In particular, the desired method should be inexpensive to adopt and preferably with improved energy consumption and desirable carbon footprint.

SUMMARY OF THE INVENTION

[0010] The invention is based in part on the unexpected discovery of novel coating methods to protect iron or steel surfaces against corrosion. The methods of the invention can be used in a wide range of applications, for example, to protect iron or steel reinforcement components embedded in composite materials as well as steel surfaces of oil and gas pipelines and vessels. In particular, the unconventional process is inexpensive and with desirable carbon footprint. The formed coating exhibits strong bonding to both iron or steel reinforcement components and to the composite material they are embedded in.

[0011] The anticorrosive coating of the invention can be readily produced from widely available, low cost raw materials by a process suitable for large-scale processing with lower energy consumption. The necessary conditions are aqueous environment with saturated carbon dioxide.

[0012] The anticorrosive coating of the invention may be used to protect metal objects. It may also be used to protect metal objects embedded in a composite material. In this context, the anticorrosive coating may be formed during the
carbonation curing of a composite material containing inexpensive calcium silicate and aggregates (e.g., filler materials such as trap rock, sand, perlite or vermiculite). A fluid component is provided as a reaction medium, comprising liquid water and/or water vapor, and a reagent, comprising carbon dioxide (CO₂), which is consumed in the production as a reactive species and ends up sequestered in the final product.

[0013] Depending on the application, various additives can be used to improve mixture consistency and flow and to fine-tune the physical appearance and mechanical properties of the resulting composite material. These additives may include chemical admixtures, rheology modifying admixtures, and pigments. Additive materials may also include natural, synthetic or recycled materials, as well as additives to the fluid component, such as a water-soluble dispersant.

[0014] In one aspect, the invention generally relates to a process for forming an anticorrosive coating on a metal surface. The process includes contacting the metal surface with an aqueous atmosphere of CO₂ and water vapor at a temperature and for a time period sufficient to form an anticorrosive coating on the metal surface.

[0015] In another aspect, the invention generally relates to a process for passivating iron or steel reinforcement wires or bars for corrosion resistance. The process includes contacting the iron or steel reinforcement wires, cables or bars with an aqueous suspension of particulate calcium silicate under an atmosphere of CO₂ and water vapor at a pH from about 3.5 to about 14 to form an anticorrosive coating of iron carbonate covering the surface of iron or steel reinforcement wires, cables or bars. The step of contacting the iron or steel surface with an aqueous suspension of particulate calcium silicate is conducted at a temperature in the range from about 10⁰ C. to about 150⁰ C., for a time period from about 1 hour to about 150 hours, and under an atmosphere of water and CO₂ having a pressure in the range from ambient atmospheric pressure to about 150 psi above ambient and having a CO₂ concentration ranging from about 10% to about 90%. The particulate calcium silicate having a median particle size in the range from about 500 nm to about 100 μm.

[0016] In yet another aspect, the invention generally relates to an article of manufacture having a body prepared from a composite material. The body is embedded with one or more reinforcement metal wires, cables or bars. Each of the one or more reinforcement metal wires, cables or bars is coated with an anticorrosive coating. The composite material includes: a plurality of bonding elements, wherein each bonding element comprises: a core comprising primarily calcium silicate, a silica-rich first or inner layer, and a calcium carbonate-rich second or outer layer, and filler particles comprising coarse filler particles and/or fine filler particles, wherein the plurality of bonding elements and the plurality of filler particles together form one or more bonding matrices and the bonding elements and the filler particles are substantially evenly dispersed therein and bonded together.

[0017] In yet another aspect, the invention generally relates to an article of manufacture comprising a metal surface coated with an anticorrosive coating comprising metal carbonate.

[0018] In yet another aspect, the invention generally relates to an article of manufacture having a body prepared from Portland cement, the body being embedded with one or more reinforcement metal wires, cables or bars, wherein each of the one or more reinforcement metal wires, cables or bars is coated with an anticorrosive coating comprising metal carbonate.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0019] The objects and features of the invention can be better understood with reference to the drawings described below, and the claims. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the drawings, like numerals are used to indicate like parts throughout the various views.

[0020] FIG. 1 is a pressure-temperature phase diagram showing the phases present in the reversible reaction CaCO₃ + SiO₂ + CaSiO₃ (calcium silicate)+CO₂.

[0021] FIG. 2 is a pressure-temperature phase diagram showing the phases present in the reversible reaction 3CaCO₃ + 2CaSiO₃ + 2Ca₃Si₂O₆CaCO₃ + CO₂.

[0022] FIG. 3 is a phase diagram of the CaO—SiO₂—CO₂ system at a pressure of 1 kilobar.

[0023] FIG. 4 is a pressure-temperature phase diagram showing the phases present in the reversible reaction MgO + CO₂ + MgCO₃.

[0024] FIG. 5 is a pressure-temperature phase diagram showing the equilibrium curves for the reversible reaction MgO + CO₂ + MgCO₃ as a function of the proportion of CO₂ in an inert gas.

[0025] FIG. 6 is a temperature-composition phase diagram that illustrates the stability regions for various phases in the CaO—MgCO₃ system.

[0026] FIG. 7 is a tetrahedron diagram illustrating the phase relationships among the compounds CaO, MgO, SiO₂ and CO₂, and showing the CO₂ deficient region below the Ce—Di—Wo and the Ce—Wo—Mo planes (shaded), where Cc denotes calcite, Wo denotes wollastonite, Ak denotes akermanite, Di denotes diopside, and Mo denotes monticellite (CaMgSiO₄).

[0027] FIG. 8 is a pressure-temperature phase diagram illustrating the phase relationships among the compounds CaO, MgO, SiO₂ and CO₂ with univariant curves emanating from the quaternary invariant point involving the phases calcite (Cc), diopside (Di), forsterite (Fo), monticellite (Mo), akermanite (Ak), and CO₂. The inset is the phase diagram for the three compound systems of CaCO₃, MgO and SiO₂.

[0028] FIG. 9 is a schematic diagram of a CO₂ composite material curing chamber that provides humidification according to principles of the invention.

[0029] FIG. 10 is a schematic diagram of a curing chamber with multiple methods of humidity control as well as ability to control and replenish CO₂ using constant flow or pressure regulation and that can control the temperature according to principles of the invention.

[0030] FIGS. 11(a)-11(c) are schematic illustrations of cross-sections of bonding elements according to exemplary embodiments of the present invention, including three exemplary core morphologies: FIG. 11(a) fibrous, FIG. 11(b) ellipsoidal, and FIG. 11(c) equiaxed.

[0031] FIGS. 12(a)-12(f) are schematic illustrations of side view and cross section views of composite materials according to exemplary embodiments of the present invention, illustrating FIG. 12(a) 1D oriented fiber-shaped bonding elements in a dilute bonding matrix (bonding elements are not touching), FIG. 12(b) 2D oriented platelet shaped bonding elements in a dilute bonding matrix (bonding elements are not touching).
touching), FIG. 12(c) 3D oriented platelet shaped bonding elements in a dilute bonding matrix (bonding elements are not touching), and FIG. 12(d) randomly oriented platelet shaped bonding elements in a dilute bonding matrix (bonding elements are not touching), wherein the composite materials include the bonding matrix and filler components such as polymers, metals, inorganic particles, aggregates etc., FIG. 12(e) a concentrated bonding matrix (with a volume fraction sufficient to establish a percolation network) of bonding elements where the matrix is 3D oriented, and FIG. 12(f) a concentrated bonding matrix (with a volume fraction sufficient to establish a percolation network) of randomly oriented bonding elements, wherein filler components such as polymers, metals, inorganic particles, aggregates etc. may be included.

[0032] FIG. 13 is a schematic illustration of an exemplary system for forming anticorrosive coating on embedded rebar.

[0033] FIG. 14 shows an exemplary micrograph showing anticorrosive coating on embedded rebar during carbonation curing of composite material at 60°C.

[0034] FIG. 15 shows an exemplary EDX analysis for the coating formed on embedded rebar during carbonation curing of composite material at 60°C.

[0035] FIG. 16 shows an exemplary micrograph showing anticorrosive coating on embedded rebar during carbonation curing of composite material at 90°C.

[0036] FIG. 17 shows an exemplary EDX analysis for the coating formed on embedded rebar during carbonation curing of composite material at 90°C.

[0037] FIG. 18 shows an exemplary X-Ray diffraction pattern for an exemplary coating formed on plain carbon steel.

[0038] FIG. 19 shows XRD pattern for ductile cast iron exposed to 1M sodium bicarbonate solution for 24 hours at 90°C.

[0039] FIG. 20 shows Scanning electron micrograph for ductile cast iron exposed to 1M sodium bicarbonate solution for 24 hours at 90°C.

DETAILED DESCRIPTION OF THE INVENTION

[0040] The invention provides novel anticorrosive methods for the protection of iron or steel surfaces against corrosion. The methods are suitable for forming a protective coating on various iron or steel objects (e.g., reinforcement components embedded in composite materials as well as steel surfaces of oil and gas pipelines and vessels). The unconventional approach disclosed herein is easy and inexpensive to apply and greatly helps with service life of the underlying iron or steel components.

[0041] The novel, reinforced objects can be readily produced from widely available, low cost raw materials by a process suitable for large-scale production with improved energy consumption, reduced production cycle (e.g., less curing time), and more desirable carbon footprint. The production method of the invention consumes large quantities of CO₂, resulting in a CO₂ sequestered product thereby making it carbon-neutral and environmentally friendly. For example, the anticorrosive coating can be formed on plain carbon steel embedded in the composite material during curing of the composite material without the need for a separate/additional coating-forming process.

[0042] The novel objects manufactured from the composite material embedded with iron or steel reinforcement components with anticorrosive coating exhibit excellent physical and performance characteristics matching or exceeding existing precast and cast-in-place objects made from conventional concrete. These novel objects also possess excellent durability and performance characteristics, including toughness, flexibility, abrasion resistance, and chemical resistance. As used herein, the term “iron” refers to the metal iron in solid state in any size, shape, weight or environment of presence. The term “steel” refers to an alloy of iron and a small amount of carbon, in solid state in any size, shape, weight or environment of presence. Additional elements may also present in steel, for example, small to trace amounts of manganese, phosphorus, sulfur, silicon, oxygen, nitrogen and aluminum. Examples of iron include ductile cast iron and examples of steel include plain carbon steel.

[0043] The reinforced objects of the invention can be used in a wide range of applications such as building and construction components including, for example, hollow core slabs, railroad ties, wall panels, floor panels, roof panels, bridges, frames, pathways, Jersey barriers, linings, foundations, blocks, beams, pipes, culverts utility vaults, septic tanks, and storm drains.

[0044] For example, the one or more reinforcement elements may be bars, wires or cables or combinations thereof. In certain embodiments, the one or more reinforcement bars are made of iron, steel, polymeric materials, glass, or a combination thereof. In certain preferred embodiments, the one or more reinforcement elements are pre-stressed.

[0045] Reinforcement elements may be solid bars, wires or cables. The reinforcement elements may take any suitable physical dimensions, for example, as a solid bar having a cross section from about 1/4 inch to 3 inches in diameter and up to about 40 feet or more in length, as a flexible cable with a cross section from about 1/8 inch to 4 inches in diameter and up to about 100 feet or more in length. A cable may be a plurality of wires or filaments bundled together. The reinforcement elements may be made with materials of desired characteristics, for example, iron, steel, polymeric materials, glass, or a combination thereof. In certain preferred embodiments, the reinforcement elements are steel bars. In certain preferred embodiments, the reinforcement elements are steel cables. In certain preferred embodiments, the reinforcement elements are steel wires.

[0046] A key feature of the anticorrosive approach of the invention is that the coating can be readily formed on embedded reinforcement components directly during the curing process of the underlying object. There is no pre-treatment or post-reaction. There is also no requirement of additional agents or ingredients in addition to the raw materials used to form the bulk of the underlying objects.

[0047] In regard to protecting non-embedded components such as iron or steel pipes or vessels, the invention provides a process for directly forming an anticorrosive coating on the surfaces of the pipes and vessels using inexpensive materials and simple processes. The thickness of the coatings may be controlled to meet specific needs depending on the application.

[0048] In one aspect, the invention generally relates to a process for forming an anticorrosive coating on a metal surface. The process includes contacting the metal surface with an aqueous atmosphere of CO₂ and water vapor at a temperature and for a time period sufficient to form an anticorrosive coating on the metal surface.

[0049] In certain preferred embodiments, the metal surface is a surface of a metal selected from iron and steel. In certain preferred embodiments, the object is selected from iron or
steel bars, wires, cables, shards, filaments, tubings, pipes, containers, vessels and equipment.

0050 In certain preferred embodiments, the aereal suspension of particulate calcium silicate under an atmosphere of CO₂ and water vapor is characterized by a pH value between about 3.5 to about 14 (e.g., between about 4.0 to about 13.0, between about 4.0 to about 12.0, between about 4.0 to about 11.0, between about 4.0 to about 10.0, between about 5.0 to about 14.0, between about 5.0 to about 13.0, between about 5.0 to about 12.0, between about 5.0 to about 11.0, between about 6.0 to about 14.0, between about 6.0 to about 13.0, between about 6.0 to about 12.0, between about 6.0 to about 11.0, between about 7.0 to about 14.0, between about 7.0 to about 13.0, between about 7.0 to about 12.0, between about 7.0 to about 11.0, between about 7.0 to about 9.0, between about 7.0 to about 8.0, between about 8.0 to about 12.9, between about 9.0 to about 12.9, between about 10.0 to about 12.9, between about 11.0 to about 12.9).

0051 In certain embodiments, the anticorrosive coating comprises metal carbonate, e.g., iron carbonate (FeCO₃), also referred to as siderite. In certain preferred embodiments, the anticorrosive coating consists essentially of iron carbonate.

0052 While not wishing to be bound by the theory, the following reaction may be representative of the underline chemical reaction that resulted in the formation of the protective coating. The CO₃⁻ in presence of aqueous environment reacts with iron to form iron carbonate as shown in reaction. This depends on temperature, pressure, pH, solution chemistry, steel type and others.

Fe²⁺+CO₃⁻→FeCO₃

0053 It is noted that the above equation reflects the net reaction for the formation of siderite and does not require or is not limited to a reaction exactly as shown. For example, the follow transformations may occur at appropriate pH.

CO₃(aq)+H₂O→HCO₃⁻+H⁺(aq)

2H⁺(aq)+Fe(s)→Fe²⁺(aq)+H₂(g) xAZ

CO₃(aq)+H₂O→Fe⁺(aq)+FeCO₃(s)+2H⁺(aq)

0054 Thus, in the formation of anticorrosive coating for an object such as a pipe or a vessel, where the iron or steel part is not embedded as reinforcement of a composite material, the anticorrosive coating may be generated in an environment comprising CO₂ and having an appropriate pH without calcium silicate.

0055 In certain embodiments, the anticorrosive coating has a thickness in the range from about 1 µm to about 50 µm (e.g., from about 1 µm to about 40 µm, from about 1 µm to about 30 µm, from about 1 µm to about 20 µm, from about 5 µm to about 50 µm, from about 10 µm to about 50 µm, from about 20 µm to about 50 µm, from about 30 µm to about 50 µm, from about 5 µm to about 40 µm, from about 10 µm to about 40 µm, from about 20 µm to about 40 µm, from about 30 µm to about 40 µm, from about 5 µm to about 30 µm, from about 10 µm to about 30 µm, from about 20 µm to about 30 µm).

0056 In certain embodiments, the anticorrosive coating has a surface coverage of about 90% or greater (e.g., about 95% or greater, about 97% or greater, about 98% or greater, about 99% or greater).

0057 In certain embodiments, the anticorrosive coating has a porosity of about 2.5x10⁻² or less (e.g., about 2.0x10⁻² or less, about 1.5x10⁻² or less, about 1.0x10⁻² or less, about 5.0x10⁻² or less).

0058 In another aspect, the invention generally relates to a process for passivating iron or steel reinforcement wires or bars for corrosion resistance. The process includes contacting the iron or steel reinforcement wires, cables or bars with an aqueous suspension of particulate calcium silicate under an atmosphere of CO₂ and water vapor at a pH from about 3.5 to about 14 to form an anticorrosive coating of iron carbonate covering the surface of iron or steel reinforcement wires, cables or bars. The step of contacting the iron or steel surface with an aqueous suspension of particulate calcium silicate is conducted at a temperature in the range from about 10°C. to about 150°C., for a time period from about 1 hour to about 150 hours, and under an atmosphere of water and CO₂ having a pressure in the range from ambient atmospheric pressure to about 150 psi above ambient and having a CO₂ concentration ranging from about 10% to about 99%. The particulate calcium silicate having a median particle size in the range from about 500 nm to about 100 µm.

0059 Any suitable calcium silicate may be used as a precursor for the bonding elements. As used herein, the term “calcium silicate” refers to naturally-occurring minerals or synthetic materials that are comprised of one or more of a group of calcium-silicon-containing compounds including CaSiO₃ (also known as “wollastonite”) and pseudo-wollastonite, and sometimes formulated as CaO.SiO₂, Ca₃SiO₇ (also known as Rankinite and sometimes formulated as 3CaO.2SiO₂), Ca₃SiO₇ (also known as “Belite” and sometimes formulated as 2CaO.SiO₂), Ca₃SiO₇ (also known as “Alite” and sometimes formulated as 3CaO.SiO₂), which material may include one or more other metal ions and oxides (e.g., aluminum, magnesium, iron or manganese oxides), or blends thereof, or may include an amount of magnesium silicate in naturally-occurring or synthetic form(s) ranging from trace amount (1%) to about 50% or more by weight.

0060 It should be understood that, compositions and methods disclosed herein can be adopted to use magnesium silicate in place of or in addition to calcium silicate. As used herein, the term “magnesium silicate” refers to naturally-occurring minerals or synthetic materials that are comprised of one or more of a group of calcium-silicon-containing compounds including, for example, Mg₃SiO₇ (also known as “Fosterite”) and Mg₃SiO₇(OH₂) (also known as “Talc”), which material may include one or more other metal ions and oxides (e.g., calcium, aluminum, iron or manganese oxides), or blends thereof, or may include an amount of calcium silicate in naturally-occurring or synthetic form(s) ranging from trace amount (1%) to about 50% or more by weight.

0061 In certain preferred embodiments, the pH value is between about 3.5 to about 14 (e.g., between about 3.5 to about 12.0, between about 3.5 to about 11.0, between about 3.5 to about 10.0, between about 3.5 to about 9.0, between about 3.5 to about 8.0, between about 5.0 to about 14, between about 6.0 to about 14, between about 7.0 to about 14, between about 8.0 to about 14, between about 9.0 to about 14, between about 10.0 to about 14, between about 11.0 to about 14).

0062 In certain preferred embodiments, the temperature is in the range from about 10°C. to about 150°C. (e.g., from about 10°C. to about 130°C., from about 10°C. to about 120°C., from about 10°C. to about 110°C., from about 20°C. to about 130°C., from about 20°C. to about 120°C., from about 20°C. to about 110°C., from about 20°C. to about 100°C., from about 50°C. to about 120°C., from about 50°C. to about 110°C., from about 50°C. to about 100°C., from about 50°C. to about 90°C., from about 50°C. to about 50°C.)
to about 80°C, from about 50°C to about 70°C, from about 60°C to about 120°C, from about 70°C to about 120°C, from about 80°C to about 120°C, from about 90°C to about 120°C, from about 70°C to about 100°C.

Curing time may be adjusted according to the desired end product, for example, 1 hour to about 150 hours (e.g., from about 1 hour to about 120 hours, for about 1 hour to about 100 hours, for about 1 hour to about 90 hours, for about 1 hour to about 70 hours, for about 1 hour to about 60 hours, for about 6 hours to about 120 hours, for about 6 hours to about 100 hours, for about 6 hours to about 80 hours, for about 6 hours to about 70 hours, for about 6 hours to about 60 hours, for about 10 hours to about 80 hours, for about 10 hours to about 70 hours, for about 10 hours to about 60 hours, for about 15 hours to about 120 hours, for about 15 hours to about 100 hours, for about 15 hours to about 80 hours, for about 15 hours to about 60 hours, for about 15 hours to about 50 hours, for about 20 hours) under an atmosphere of water and CO₂. It is noted that, depending on the application, certain shortened or lengthened curing duration may be employed, for example, from about 1, 3, 5, 7 days to as long as 15, 20 or 28 days, or as short as less than 1 hour, 30 minutes, 20 minutes to 10 minutes.

In certain preferred embodiments, the atmosphere of water and CO₂ has a pressure in the range from ambient atmospheric pressure to about 40 psi above ambient and having a CO₂ concentration ranging from about 50% to about 95% (e.g., from about 60% to about 95%, from about 70% to about 95%, from about 80% to about 95%, from about 90% to about 95%, from about 50% to about 90%, from about 50% to about 80%, from about 50% to about 70%, from about 50% to about 60%).

In yet another aspect, the invention generally relates to an article prepared by a process according to the invention. Such articles includes, for example, hollow core slabs, solid slabs, aerated structures, railroad ties, wall panels, floor panels, roof panels, bridges, frames, pathways, Jersey barriers, linings, foundations, blocks, beams, pipes, culverts utility vaults, septic tanks, and storm drains. The article can be manufactured to any suitable sizes, dimensions and weights.

In yet another aspect, the invention generally relates to an article of manufacture having a body prepared from a composite material. The body is embedded with one or more reinforcement metal wires, cables or bars. Each of the one or more reinforcement metal wires, cables or bars is coated with an anticorrosive coating. The composite material includes: a plurality of bonding elements, wherein each bonding element comprises: a core comprising primarily calcium silicate, a silica-rich first or inner layer, and a calcium carbonate-rich second or outer layer, and filler particles comprising coarse filler particles and/or fine filler particles, wherein the plurality of bonding elements and the plurality of filler particles together form one or more bonding matrices and the bonding elements and the filler particles are substantially evenly dispersed therein and bonded together.

In certain preferred embodiments, the metal surface is a surface of a metal selected from iron and steel. In certain preferred embodiments, the object is selected from bars, wires, cables, shanks, filaments, tubings, pipes, containers, vessels and equipment.

The anticorrosive coating exhibits strong bonding to both the metal (e.g., iron or steel) reinforcement components and to the cured composite material they are embedded in.

In certain preferred embodiments, the anticorrosive coating has a thickness in the range from about 1 μm to about 50 μm (e.g., from about 1 μm to about 40 μm, from about 1 μm to about 30 μm, from about 1 μm to about 20 μm, from about 1 μm to about 10 μm, from about 5 μm to about 50 μm, from about 10 μm to about 50 μm, from about 20 μm to about 50 μm, from about 30 μm to about 50 μm, from about 5 μm to about 40 μm, from about 10 μm to about 40 μm, from about 10 μm to about 30 μm, from about 20 μm to about 30 μm). In certain embodiments, the anticorrosive coating has a surface coverage of about 90% or greater (e.g., about 95% or greater, about 97% or greater, about 98% or greater, about 99% or greater). In certain embodiments, the anticorrosive coating has a porosity of about 2.5x10⁻² or less (e.g., about 2.0x10⁻² or less, about 1.5x10⁻² or less, about 1.0x10⁻² or less, or about 5.0x10⁻⁴ or less).

The plurality of bonding elements may have any suitable median particle size and size distribution dependent on the desired composite material. In certain embodiments, the plurality of bonding elements have a median particle size in the range of about 500 nm to about 100 μm (e.g., about 500 nm to about 80 μm, about 500 nm to about 60 μm, about 500 nm to about 50 μm, about 500 nm to about 40 μm, about 500 nm to about 30 μm, about 500 nm to about 20 μm, about 500 nm to about 10 μm, about 1 μm to about 90 μm, about 1 μm to about 80 μm, about 1 μm to about 70 μm, about 1 μm to about 60 μm, about 5 μm to about 90 μm, about 5 μm to about 80 μm, about 5 μm to about 70 μm, about 5 μm to about 60 μm, about 5 μm to about 50 μm, about 5 μm to about 40 μm, about 10 μm to about 80 μm, about 10 μm to about 70 μm, about 10 μm to about 60 μm, about 10 μm to about 50 μm, about 10 μm to about 40 μm, about 10 μm to about 30 μm, about 10 μm to about 20 μm).

In certain preferred embodiments, the plurality of bonding elements are chemically transformed from ground calcium silicate and the filler particles are lime particles. In certain preferred embodiments, the plurality of bonding elements are chemically transformed from a precursor calcium silicate comprising one or more of aluminum, magnesium and iron. In certain preferred embodiments, wherein the plurality of bonding elements are chemically transformed from a precursor calcium silicate other than ground calcium silicate (e.g., ground Wollastonite).

In certain preferred embodiments, the plurality of bonding elements are prepared by chemical transformation from ground calcium silicate by reacting it with CO₂ via a controlled hydrothermal liquid phase sintering (HILPS) process. In certain preferred embodiments, the plurality of bonding elements are prepared by chemical transformation from the precursor calcium silicate other than ground calcium silicate (e.g., ground Wollastonite) by reacting it with CO₂ via a controlled HILPS process.

In yet another aspect, the invention generally relates to an article of manufacture comprising a metal surface coated with an anticorrosive coating comprising metal carbonate.

In yet another aspect, the invention generally relates to an article of manufacture having a body prepared from Portland cement, the body being embedded with one or more reinforcement metal wires, cables or bars, wherein each of the one or more reinforcement metal wires, cables or bars is coated with an anticorrosive coating comprising metal carbonate.
In certain preferred embodiments, the metal is iron or steel and the anticorrosive coating consists essentially of iron carbonate. The article may be any object, e.g., selected from metal bars, wires, shards, filaments, tubings, pipes, containers, vessels and equipment.

Chemical admixtures may include plasticizers, retarders, accelerators, dispersants and other rheology-modifying agents. Certain commercially available chemical admixtures such as Glenium™ 7500 by BASF® Chemicals and Acumer™ by Dow Chemical Company may also be included.

In certain embodiments, one or more pigments may be evenly dispersed or substantially unevenly dispersed in the bonding matrices, depending on the desired composite material. The pigment may be any suitable pigment including, for example, oxides of various metals (e.g., black iron oxide, cobalt oxide and chromium oxide). The pigment may be of any color or colors, for example, selected from black, white, blue, gray, pink, green, red, yellow and brown. The pigment may be present in any suitable amount depending on the desired composite material, for example in an amount ranging from about 0.0% to about 10% by weight (e.g., about 0.0% to about 8%, about 0.0% to about 6%, about 0.0% to about 5%, about 0.0% to about 4%, about 0.0% to about 3%, about 0.0% to about 2%, about 0.0% to about 1%, about 0.0% to about 0.5%, about 0.0% to about 0.3%, about 0.0% to about 0.2%, about 0.0% to about 0.1%).

The relative humidity environment of the curing process may be adjusted to fit the desired outcome, for example, ranging from about 10% to about 98% (e.g., from about 20% to about 98%, from about 30% to about 98%, from about 50% to about 98%, from about 80% to about 98%, from about 90% to about 98%, from about 10% to about 90%, from about 10% to about 70%, from about 10% to about 50%, from about 10% to about 40%, from about 10% to about 30%, from about 10% to about 20%) and with a CO₂ pressure ranging from about ambient atmospheric pressure to about 100 psig above ambient atmospheric pressure (e.g., from about ambient atmospheric pressure to about 90 psig above ambient, from about ambient atmospheric pressure to about 80 psig above ambient, from about ambient atmospheric pressure to about 70 psig above ambient, from about ambient atmospheric pressure to about 60 psig above ambient, from about 20 psig above ambient to about 100 psig above ambient, from about 30 psig above ambient to about 100 psig above ambient), and having a CO₂ concentration ranging from about 10% to about 90% and above (e.g., from about 20% to about 90%, from about 30% to about 90%, from about 40% to about 90%, from about 10% to about 70%, from about 10% to about 50%) to produce a composite material exhibiting a uniform, homogeneous, and porous structure.

In exemplary productions as in some embodiments of the invention, the materials used are ground calcium silicate.

The ground calcium silicate may have a median particle size from about 1 μm to about 100 μm (e.g., about 1 μm to about 80 μm, about 1 μm to about 60 μm, about 1 μm to about 50 μm, about 1 μm to about 40 μm, about 1 μm to about 30 μm, about 1 μm to about 20 μm, about 1 μm to about 10 μm, about 5 μm to about 90 μm, about 5 μm to about 80 μm, about 5 μm to about 70 μm, about 5 μm to about 60 μm, about 5 μm to about 50 μm, about 5 μm to about 40 μm, about 10 μm to about 80 μm, about 10 μm to about 70 μm, about 10 μm to about 60 μm, about 10 μm to about 50 μm, about 10 μm to about 40 μm, about 10 μm to about 30 μm, about 10 μm to about 20 μm, about 15 μm, 20 μm, 25 μm, 30 μm, 40 μm, 50 μm, 60 μm, 70 μm, 80 μm, 90 μm, 100 μm), a bulk density from about 0.5 g/ml to about 3.5 g/ml (loose, e.g., 0.5 g/ml, 1.0 g/ml, 1.5 g/ml, 2.0 g/ml, 2.5 g/ml, 2.8 g/ml, 3.0 g/ml, 3.5 g/ml) and about 1.0 g/ml (tapped), a surface area from about 1.5 m²/g to about 3.5 m²/g (e.g., 1.5 m²/g, 2.0 m²/g, 2.3 m²/g, 2.5 m²/g, 2.8 m²/g, 3.0 m²/g, 3.2 m²/g, 3.5 m²/g).

In certain preferred embodiments, the particulate composition comprises about 10 wt. % to about 95 wt. % of ground calcium silicate materials (e.g., about 20 wt. % to about 95 wt. %, about 30 wt. % to about 95 wt. %, about 50 wt. % to about 95 wt. %, about 60 wt. % to about 95 wt. %, about 70 wt. % to about 95 wt. %, about 80 wt. % to about 95 wt. %, about 90 wt. %, about 20 wt. % to about 90 wt. %, about 30 wt. % to about 90 wt. %, about 50 wt. % to about 90 wt. %, about 60 wt. % to about 90 wt. %, about 70 wt. %, about 80 wt. %, about 90 wt. %, about 100 wt. %). In a second exemplary embodiment, water is present in the precursor material (e.g., as residual water from prior mixing step) and CO₂ gas is delivered to an article that has been pre-dried in a drying oven and the curing process is conducted at about 90°C and about 20 psig (i.e., 20 psi above ambient pressure) for about 48 hours. In a third exemplary embodiment, water is present in the precursor material and the curing process is performed at about 60°C and 0 psig (at ambient atmospheric pressure) for about 19 hours. In a fourth exemplary embodiment, water is delivered to an article in a vapor form along with CO₂ and the curing process is performed at about 90°C and 20 psig (20 psi above ambient atmospheric pressure) for about 19 hours.

It is noted that the properties, production time and scale of the article can be fine tuned based on the disclosures herein, for example, by adjusting curing techniques (e.g., CO₂ delivery, system pressure and temperature) as well as mixture proportions and constituents.

Bonding Elements, Bonding Matrices and Composite Materials

Chemical Discussion

This invention provides apparatus and methods used to manufacture novel composite materials that are cured predominantly by a CO₂ consumption reaction. The materials exhibit useful properties and can be readily produced from widely available, low cost precursor materials by a process suitable for large-scale production with minimal environmental impact. The precursor materials include inexpensive and abundant calcium silicate rich compositions, fine particles and coarse particles.

The fine and coarse particles may be comprised of ground limestone or other calcium carbonate based materials, ground quartz or other SiO₂ based materials, sand and crushed rock. The fine and coarse particles may also be comprised of crushed minerals such as granite, mica and feldspar. Other process components include water and CO₂. Various additives can be used to modify and fine-tune the physical appearance and/or mechanical properties of the resulting composite material, such as additives selected from one or more of pigments (e.g., black iron oxide, cobalt oxide and...
chromium oxide), colored glass and/or colored quartz. Additives regarding water usage reduction and changes in rheology can also be used.

[0086] Any suitable calcium silicate composition may be used as a precursor for the bonding elements. As used herein, the term “calcium silicate composition” generally refers to naturally-occurring minerals or synthetic materials that are comprised of one or more of a group of calcium silicate phases including CS (wollastonite or pseudowollastonite), and sometimes formulated CaSiO₃ or CaO·SiO₂, C₃S₂ (rakinite, and sometimes formulated as Ca₃Si₂O₆ or 3CaO·2SiO₂, C₂S (belite, β-Ca₃SiO₅ or ferrite, β-Ca₃SiO₅ or bredigite, α-C₃S·SiO₂ or γ-C₃S·SiO₂ and sometimes formulated as Ca₃SiO₅ or 2CaO·SiO₂), a calcium-silicate based amorphous phase, each of which material may include one or more other metal ions and oxides (e.g., aluminum, magnesium, iron or manganese oxides), or blends thereof, or may include an amount of magnesium silicate in naturally-occurring or synthetic form(s) ranging from trace amount (1%) to about 50% or more by weight.

[0087] Calcium silicate compositions may contain amorphous (non-crystalline) calcium silicate phases in addition to the crystalline phases described above. The amorphous phase may additionally incorporate Al, Fe and Mg ions and other impurity ions present in the raw materials. The calcium silicate compositions may also include small quantities of residual CaO (lime) and SiO₂ (silica). The calcium silicate composition may also include small quantities of C₃S (alite, Ca₃SiO₅).

[0088] The calcium silicate compositions may also include quantities of inert phases such as mullite type minerals (mullite or gehlenite or akermanite) with the general formula (CaₓNaᵧ)(Mg₁₋ₓFeₓ₋₄+₋₄₋ₓAlₓSiₓ₋₄₋ₓOₓ₋₄₋ₓ) and ferrite type minerals (ferrite or brownmillerite or C₄AF) with the general formula Ca₄(Al₁₋ₓFeₓ₋₄₋ₓO₅₋ₓ). In certain embodiments, the calcium silicate composition is comprised only of amorphous phases. In certain embodiments, the calcium silicate comprises only of crystalline phases. In certain embodiments, some of the calcium silicate composition exists in an amorphous phase and some exists in a crystalline phase.

[0089] It is noted that preferably the calcium silicate compositions of the invention do not hydrate. However, minor amounts of hydratable calcium silicate phases (e.g., C₂S, C₃S and CaO) may be present. C₂S exhibits slow kinetics of hydration when exposed to water and is quickly converted to CaCO₃ during curing processes. C₃S and CaO hydrate quickly upon exposure to water and thus should be limited to <5% by mass.

[0090] In certain preferred embodiments, the molar ratio of elemental Ca to elemental Si of the calcium silicate composition is from about 0.80 to about 1.20. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.85 to about 1.15. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.90 to about 1.10. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.95 to about 1.05. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.98 to about 1.02. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.99 to about 1.01.

[0091] The metal oxides of Al, Fe and Mg contained within the calcium silicate composition are generally controlled to be less than about 30%. In certain preferred embodiments, the composition has about 20% or less of metal oxides of Al, Fe and Mg by total oxide mass. In certain preferred embodiments, the composition has about 15% or less of metal oxides of Al, Fe and Mg by total oxide mass. In certain preferred embodiments, the composition has about 10% or less of metal oxides of Al, Fe and Mg by total oxide mass. In certain preferred embodiments, the composition has about 5% or less of metal oxides of Al, Fe and Mg by total oxide mass.

[0092] Each of these calcium silicate phases is suitable for carbonation with CO₂. Hereafter, the discrete calcium silicate phases that are suitable for carbonation will be referred to as reactive phases.

[0093] The various reactive phases may account for any suitable portions of the overall reactive phases. In certain preferred embodiments, the reactive phases ofCS are present at about 10 to about 60 wt % (e.g., about 15 wt % to about 60 wt %, about 20 wt % to about 60 wt %, about 25 wt % to about 60 wt %, about 30 wt % to about 60 wt %, about 35 wt % to about 60 wt %, about 40 wt % to about 60 wt %, about 10 wt % to about 60 wt %, about 5 wt % to about 60 wt %, about 10 wt % to about 60 wt %, about 15 wt % to about 60 wt %, about 20 wt % to about 60 wt %, about 25 wt % to about 60 wt %, about 30 wt % to about 60 wt %, about 35 wt % to about 60 wt %, about 40 wt % to about 60 wt %, about 45 wt % to about 60 wt %, about 50 wt % to about 60 wt %, about 55 wt % to about 60 wt %, about 60 wt % to about 60 wt %, about 65 wt % to about 60 wt %, about 70 wt % to about 60 wt %, about 75 wt % to about 60 wt %, about 80 wt % to about 60 wt %, about 85 wt % to about 60 wt %). C₃S₂ in about 5 to 50 wt % (e.g., about 10 wt % to about 50 wt %, about 15 wt % to about 50 wt %, about 20 wt % to about 50 wt %, about 25 wt % to about 50 wt %, about 30 wt % to about 50 wt %, about 35 wt % to about 50 wt %, about 40 wt % to about 50 wt %, about 45 wt % to about 50 wt %, about 50 wt % to about 50 wt %, about 55 wt % to about 50 wt %, about 60 wt % to about 50 wt %, about 65 wt % to about 50 wt %, about 70 wt % to about 50 wt %, about 75 wt % to about 50 wt %, about 80 wt % to about 50 wt %, about 85 wt % to about 50 wt %), and C₃S in about 5 to 60 wt % (e.g., about 10 wt % to about 60 wt %, about 20 wt % to about 60 wt %, about 30 wt % to about 60 wt %, about 40 wt % to about 60 wt %, about 50 wt % to about 60 wt %, about 55 wt % to about 60 wt %, about 60 wt % to about 60 wt %, about 65 wt % to about 60 wt %, about 70 wt % to about 60 wt %, about 75 wt % to about 60 wt %, about 80 wt % to about 60 wt %, about 85 wt % to about 60 wt %, about 90 wt % to about 60 wt %, about 95 wt % to about 60 wt %, about 100 wt % to about 60 wt %).
Precursor calcium silicate compositions are typically used in powder form having a mean particle size (d50) of about 8 µm to about 25 µm, with 10% of particles (d10) sized below about 0.1 µm to about 3 µm, and 90% of particles (d90) sized above about 35 µm to about 100 µm.

In certain embodiments, the ratio of d90 : d10 is selected to allow improved powder flow or decreased water demand for casting. In certain embodiments, the ratio of d50 : d10 is selected to allow improved reactivity, improved packing, or decreased water demand for casting. In certain embodiments, the ratio of d90 : d50 is selected to allow improved reactivity, improved packing, or decreased water demand for casting.

Any suitable filler particles may be used, for example, calcium oxide-containing or silica-containing materials. Exemplary filler particles include lime, quartz (including sand), wollastonite, xonotlite, burned oil shale, fly- or volcanic-ash, stack dust from kilns, ground clay, pumice dust. Materials such as industrial waste materials (e.g., fly ash, slag, silica fume) may also be used as fillers. In certain preferred embodiments, lightweight aggregates such as perlite or vermiculite may also be used as fillers. In certain preferred embodiments, filler particles are made from a calcium oxide-rich material such as ground limestone.

The filler particles comprise calcium oxide or silica and have a particle size (d50) in the range from about 0.25 µm to about 200 µm (e.g., from about 0.25 µm to about 150 µm, from about 0.25 µm to about 100 µm, from about 0.25 µm to about 50 µm, from about 0.25 µm to about 20 µm, from about 0.25 µm to about 10 µm, from about 0.5 µm to about 200 µm, from about 1 µm to about 200 µm, from about 5 µm to about 200 µm, from about 10 µm to about 200 µm, from about 20 µm to about 200 µm, from about 300 µm to about 200 µm).

In certain embodiments, the filler particles are selected from fly ash, bottom ash, slag having particle sizes ranging from about 0.5 µm to about 300 µm (e.g., from about 1 µm to about 300 µm, from about 5 µm to about 300 µm, from about 10 µm to about 300 µm, from about 50 µm to about 300 µm, from about 100 µm to about 300 µm, from about 0.5 µm to about 200 µm, from about 0.5 µm to about 100 µm, from about 0.5 µm to about 50 µm, from about 0.5 µm to about 20 µm, from about 0.5 µm to about 10 µm, from about 0.5 µm to about 5 µm).

In certain embodiments, the filler particles are selected from limestone, miro-silica, and quartz having particle sizes ranging from about 1 µm to about 500 µm (e.g., from about 1 µm to about 400 µm, from about 1 µm to about 300 µm, from about 1 µm to about 200 µm, from about 1 µm to about 100 µm, from about 1 µm to about 50 µm, from about 1 µm to about 30 µm, from about 2 µm to about 500 µm, from about 0.5 µm to about 200 µm, from about 2 µm to about 100 µm, from about 2 µm to about 50 µm, from about 0.5 µm to about 30 µm, from about 0.5 µm to about 10 µm, from about 0.5 µm to about 5 µm).

In certain embodiments, the filler particles are selected from lightweight aggregates having particle sizes ranging from about 20 µm to about 500 µm (e.g., from about 20 µm to about 400 µm, from about 20 µm to about 300 µm, from about 20 µm to about 200 µm, from about 20 µm to about 100 µm, from about 20 µm to about 50 µm, from about 10 µm to about 500 µm, from about 10 µm to about 300 µm, from about 10 µm to about 200 µm, from about 5 µm to about 300 µm, from about 5 µm to about 100 µm).

In certain embodiments, the set-controlling admixture is selected from a gluconate and sucrose. In certain embodiments, the dispersing/viscosity-modifying agent is a polycarboxilate based material.

In exemplary embodiments, the ground calcium silicate is ground wollastonite, the filler particles comprises ground limestone, and silica, the activating-agent is ground lime, the set-controlling admixture is a gluconate, the viscosity-modifying agent is a polycarboxilate based material, and the aerating agent is aluminum paste.

It should be understood that, calcium silicate compositions, phases and methods disclosed herein can be adopted to use magnesite silicate phases in place of or in addition to calcium silicate phases. As used herein, the term “magnesite silicate” refers to naturally-occurring minerals or synthetic materials that are comprised of one or more of a groups of magnesium-silicon-containing compounds including, for example, Mg2SiO4 (also known as “fosterite”) and Mg2SiO4(OH)2 (also known as “talc”), which material may include one or more other metal ions and oxides (e.g., calcium, aluminum, iron or manganese oxides), or blends thereof, or may include an amount of calcium silicate in naturally-occuring or synthetic form(s) ranging from trace amount (1%) to about 50% or more by weight.

Depending on end user requirements, various other additives such as dispersing, rheology modifying admixtures (to improve mixture consistency), coloring pigments, retarders, and accelerators. Additive materials can include natural or recycled materials, and calcium carbonate-rich and magnesium carbonate-rich materials, as well as additives to the fluid component, such as a water-soluble dispersant.

The composite materials can be produced, as disclosed herein, using the energy-efficient Hydrothermal Liquid Phase Sintering (HLPS) process to create bonding elements which hold together the various components of the composite material. The composite materials can be manufactured at low cost and with favorable environmental impact. For example in preferred embodiments of the invention, CO2 is used as a reactive species resulting in sequestration of CO2 and the creation of bonding elements in the produced composite materials with in a carbon footprint unmatched by any existing production technology. The HLPS process is thermodynamically driven by the free energy of the chemical reaction(s) and reduction of surface energy (area) caused by crystal growth. The kinetics of the HLPS process proceed at a reasonable rate at low temperature because a solution (aqueous or nonaqueous) is used to transport reactive species instead of using a high melting point fluid or high temperature solid-state medium.

In certain embodiments, the composite material is characterized by water absorption of less than about 10% (e.g., less than about 8%, 5%, 4%, 3%, 2%, or 1%).

The composite material may display one or more of desired textures, patterns and physical properties, in particular those that are characteristic of natural stone. In certain preferred embodiments, the composite material exhibits a visual pattern similar to natural stone. Other characteristics include colors (e.g., black, white, blue, pink, grey (pale to dark), green, red, yellow, brown, cyan (bluish-green) or purple) and textures.

Equipment and Processing Discussion

CO₂ Control

In the embodiments described, industrial grade CO₂ at about 99% purity is used, which is provided by a variety of different industrial gas companies, such as Praxair, Inc., Linde AG, Air Liquide, and others. This supply can be held in large pressurized holding tanks in the form of liquid carbon dioxide regulated at a temperature such that it maintains a vapor pressure of approximately 300 psig. This gas is then piped to a CO₂ curing enclosure or chamber. In the simplest system, CO₂ is flowed through the enclosure at a rate sufficient to displace the ambient air in the enclosure. In general, the purge time will depend on the size of the enclosure and the rate that CO₂ gas is provided. In many systems, this process of purging the enclosure of air can be performed in times measured in minutes to get the CO₂ concentration up to a reasonable level so that curing can be performed thereafter. In simple systems, CO₂ gas is then fed into the system at a predefined rate so as to maintain a concentration of CO₂ sufficient to drive the curing reaction.

As an example, we now describe a method for sustaining carbon dioxide concentrations during the reaction that is well suited for keeping a highly consistent concentration, although it is a “closed loop” process which tends to be the most expensive technique. This method uses the measurement of CO₂ concentration in the system directly, and employs a controller such as a PLC to control the CO₂ concentration at a set point with an electronic/automated control valve. A measurement technique to measure CO₂ directly such as NDIR should preferably be employed. In the NDIR measurement method, a gas sample stream is pulled from the system via a low flow pump. A chiller is used to drop moisture out of the gas stream before it is sampled by the NDIR instrument. Therefore the measurement provided by the analyzer is missing the water vapor component of the gas stream and needs to be adjusted to account for the humidity that has been removed from the test sample. A measurement of the humidity in the system gas flow can be performed using a dry bulb-wet bulb psychrometric technique, using a dry bulb-wet bulb humidity measurement device or using a different type of moisture sensor. The true CO₂ concentration can be calculated using the computer control system or PLC. Once the true CO₂ concentration is known, the actuated proportioning control valve can add dry CO₂ into the system when it has been consumed and has gone below the set point that is desired at that time. In various embodiments, the set point can vary with time, if necessary, based on experience in curing specific compositions, shape and sizes of composite material specimens.
Humidity Control

[0119] FIG. 9 is a schematic diagram of a CO₂ composite material curing chamber that provides humidification according to principles of the invention. In FIG. 9, a water supply is provided and water vapor is added to the atmosphere that is circulating within the curing chamber. The water can be any convenient source of potable water. In some embodiments, ordinary tap water is used. In some embodiments, the water can be converted to vapor by flowing through a misting nozzle or an atomizing spray nozzle, an electric vapor generator, a gas fired vapor generator, or by being heated above the gas temperature in the chamber so as to cause evaporation from a liquid water supply an example being a drum reactor with an immersion heater. In yet another embodiment, the CO₂ supply can be flowed into the systems after having been bubbled through a heated water supply in order to increase relative humidity of the incoming gas stream an example being a drum reactor configured for “flow through” or “open loop” processing.

[0120] Relative humidity is an important parameter in both traditional concrete curing as well as CO₂ composite material curing. In a traditional curing chamber a moist air atmosphere exists that is comprised of mostly nitrogen, oxygen, and water vapor. In these systems relative humidity is most often measured by a standard capacitive sensor technology. However, CO₂ curing chambers have a gas atmosphere comprised predominately of carbon dioxide that is incompatible with some types of these sensors. Sensing technology such as dry-bulb wet-bulb techniques that utilize the psychrometric ratios for carbon dioxide and water vapor or dipole polarization water vapor measurement instruments or chilled mirror hygrometers or capacitive humidity sensors can be used in the CO₂ composite material curing systems described herein.

[0121] Depending on the type and geometry of the product being cured, the design of the chamber, and the parking efficiency of product in the chamber the humidity may need to be either decreased or increased and regulated to a specified set point. Set points may range anywhere from 1% to 99% relative humidity. Three different methods for humidity control may exist in CO₂ composite material curing processes that could be combined into a single system. One method for humidification in one embodiment of a CO₂ curing system is represented in FIG. 9. Another method allows one to remove moisture from the system to cure the composite material products with CO₂. A simple method of reducing the relative humidity is by displacing the humid gas in the system with a dry gas, such as carbon dioxide. In still another embodiment, one can increase relative humidity and therefore remove water vapor from the gas by a non-purging method, which in one preferred embodiment is a chilled heat exchanger that performs water extraction.

Temperature Control

[0123] In some embodiments, temperature is measured utilizing a sensor such as a thermocouple or an RTD. The measurement signal is directed back to a controller or computer that is able to regulate energy into the heat exchanger and thereby adjust the temperature of the entire system over time. The blower is an important component of the heating system as it is able to help transfer the heat energy to the gas which transfers to the products and the chamber itself which is an important part of controlled moisture of the samples. The method of heating can be electric or gas fired. Jacket heaters may be utilized to control the temperature of the CO₂ that flows through a chamber in contact with the heating jacket, any convenient source of heat can be used. The means of external heating may include but are not limited to electric heating, hot water heating, or hot oil heating. For CO₂ curing chambers indirect gas fired systems have been utilized thus far and direct fired gas burners have been avoided because they will pull air and products of combustion into the system, thereby diluting the CO₂ and making control of the CO₂ concentration problematic. Some smaller scale systems such as the Drum Reactors utilize electric jacket heaters to heat the entire surface of the chamber rather than a heating element within the chamber.

Gas Flow Control

[0124] Another control parameter is gas velocity across the material that is to be cured in the system. The gas velocity can be very dependent on process equipment variables including but not limited to chamber design, baffle design, fan size, fan speed/power, number of fans, temperature gradient within the system, rack design within the system, and sample geometry within the system. The simplest method to control the gas velocity within the chamber is by adjusting the blower speed (RPM’s), typically done by utilization of a variable frequency drive to allow for control of the blower motor speed. The blower can be used to circulate gas at a desired velocity in the curing chamber. Gas velocity in the system is measured in the system via a variety of different techniques including but not limited to pitot tubes measurement and laser Doppler detection systems. The measurement signal for gas velocity can be sent back to a computer system or programmable logic controller and be utilized as a control parameter in the curing profile.

Process of Preparing a Composite Material

[0125] We describe a process for preparing a composite material. The process includes: mixing a particulate composition and a liquid composition to create a slurry mixture; forming the slurry mixture into a desired shape, either by casting the slurry into a mold, pressing the slurry in a mold, pressing the slurry in a vibrating mold, extruding the slurry, slip forming the slurry, or using any other shape-forming method common in concrete production, and curing the formed slurry mixture at a temperature in the range from about 20° C to about 150° C for about 1 hour to about 80 hours under a vapor comprising water and CO₂ and having a pressure in the range from about ambient atmospheric pressure to about 50 psi above ambient atmospheric pressure and
having a CO₂ concentration ranging from about 10% to about 90% to produce a composite material exhibiting a texture and/or a pattern and the desired physical properties related to compressive strength, flexural strength, density, resistance to degradation, and so forth.

[0126] The particulate composition includes a ground calcium silicate composition having a mean particle size in the range from about 1 μm to about 100 μm. In addition the particulate composition may include a ground calcium carbonate or a SiO₂ bearing material having a mean particle size in the range from about 3 μm to about 25 μm. The liquid composition includes water and may include a water-soluble dispersant.

[0127] The process can further include, before curing the mixed paste, the step of drying the mixed paste. The particulate composition further comprises a pigment or a colorant as discussed herein.

[0128] In certain embodiments, curing the formed slurry mixture is performed at a temperature in the range from about 30°C to about 120°C for about 1 hour to about 70 hours under a vapor comprising water and CO₂ and having a pressure in the range from about ambient atmospheric pressure to about 0.3 MPa above ambient atmospheric pressure.

[0129] In certain embodiments, curing the formed slurry mixture is performed at a temperature in the range from about 60°C to about 110°C for about 1 hour to about 70 hours under a vapor comprising water and CO₂ and having a pressure in the range from about ambient atmospheric pressure to about 30 psi above ambient atmospheric pressure.

[0130] In certain embodiments, curing the formed slurry mixture is performed at a temperature in the range from about 80°C to about 100°C for about 1 hour to about 60 hours under a vapor comprising water and CO₂ and having a pressure in the range from about ambient atmospheric pressure to about 30 psi above ambient atmospheric pressure.

[0131] In certain embodiments, curing the formed slurry mixture is performed at a temperature equal to or lower than about 60°C for about 1 hour to about 50 hours under a vapor comprising water and CO₂ and having an ambient atmospheric pressure.

[0132] For example, in some embodiments, the ground calcium silicate composition has a mean particle size range from about 1 μm to about 100 μm (e.g., about 1 μm, 10 μm, 15 μm, 20 μm, 25 μm, 30 μm, 40 μm, 50 μm, 60 μm, 70 μm, 80 μm, 90 μm, 100 μm), a bulk density from about 0.5 g/mL to about 3.5 g/mL (loose, e.g., 0.5 g/mL, 1.0 g/mL, 1.5 g/mL, 2.0 g/mL, 2.5 g/mL, 2.8 g/mL, 3.0 g/mL, 3.5 g/mL) and about 1.0 g/mL to about 1.2 g/mL (tapped), a Blaine surface area from about 150 m²/kg to about 700 m²/kg (e.g., 150 m²/kg, 200 m²/kg, 250 m²/kg, 300 m²/kg, 350 m²/kg, 400 m²/kg, 450 m²/kg, 500 m²/kg, 550 m²/kg, 600 m²/kg, 650 m²/kg, 700 m²/kg).

[0133] In certain preferred embodiments, the liquid composition includes water and a water-soluble dispersant comprising a polymer salt (e.g., an acrylic homopolymer salt) having a concentration from about 0.1% to about 2% w/w of the liquid composition.

[0134] Composite materials prepared according to a process disclosed herein can exhibit a compressive strength from about 3.0 MPa to about 30.0 MPa (e.g., about 3 MPa, 5 MPa, 10 MPa, 15 MPa, 20 MPa, 25 MPa, 30 MPa) and a flexural strength from about 0.3 MPa to about 4.0 MPa (e.g., about 0.3 MPa, 0.5 MPa, 1.0 MPa, 1.5 MPa, 2.0 MPa, 2.5 MPa, 3.0 MPa, 3.5 MPa, 4.0 MPa).

[0135] We also describe one or more articles of manufacture made from a composite material.

[0136] Any suitable precursor materials may be employed including, for example, calcium silicate composition particles formed from CS (wollastonite or pseudowollastonite, and sometimes formulated Ca₂SiO₄ or CaO.SiO₂), C₃S (Rankinite, and sometimes formulated as Ca₃Si₃O₁₀ or 3CaO·2SiO₂), C₂S (belle, β-Ca₂SiO₄ or limestone, β-Ca₂SiO₄ or “bredigite, α-Ca₂SiO₄ or γ-Ca₂SiO₄, and sometimes formulated as Ca₂SiO₄ or 2CaO·SiO₂), and calcium silicate rich amorphous phase. It is believed that calcium cations are leached from the calcium silicate composition particles and transform the peripheral portion of the calcium silicate composition particle into calcium-deficient phase. As the calcium cations continue to be leached from the peripheral portion of the particle, the structure of the peripheral portion eventually become unstable and breaks down, thereby transforming the calcium-deficient peripheral portion of the particle into a predominantly silica-rich first layer. Meanwhile, a predominantly calcium carbonate second layer precipitates from the water.

[0137] More specifically, the first layer and second layer may be formed from the precursor particle according the following reactions (1-3) which can use water as a reaction medium, and not as a reagent (that is, the water is not consumed):

\[ Ca₃Si₃O₁₀ + CO₂(g) \rightarrow CaCO₃(s) + 3SiO₂(g) \]  

\[ Ca₂SiO₄ + 3CO₂(g) \rightarrow 2CaCO₃(s) + 2SiO₂(g) \]  

\[ Ca₃Si₃O₁₀ + 2CO₂(g) \rightarrow 2CaCO₃(s) + 3SiO₂(g) \]  

[0138] For example, in a silicate mineral carbonation reaction such as with calcium silicate compositions, CO₂ is introduced as a gas phase that dissolves into an infiltration fluid, such as water. The dissolution of CO₂ forms acidic carbonate species (such as carbonic acid, H₂CO₃) that results in a decrease of pH in solution. The weakly acidic solution incongruently dissolves calcium species from the calcium silicate phases. Calcium may be leached from calcium containing amorphous phases through a similar mechanism. The released calcium cations and the dissociated carbonate species lead to the precipitation of insoluble carbonates. Silica-rich layers are thought to remain on the mineral particles as calcium depleted layers.

[0139] Thus, according to a preferred embodiment of the invention, CO₂ preferentially reacts with the calcium cations of the calcium silicate composition precursor core, thereby transforming the peripheral portion of the precursor core into a silica-rich first layer and a calcium carbonate-rich second layer. Also, the presence of the first and second layers on the core act as a barrier to further reaction between calcium silicate and carbon dioxide, resulting in the bonding element having the core, first layer and second layer.

[0140] In some embodiments, silicate materials having metals other than Ca or in addition to Ca, for example fosterite (Mg₂SiO₄), diopside (CaMgSi₂O₆), and talc (Mg₃Si₄O₁₀(OH)₂) can react with carbon dioxide dissolved in water in a manner similar to the reaction of calcium silicate, as described above. It is believed that such silicate materials can be used, alone, in combination, and/or in combination with calcium silicate, as precursors for bonding elements according to principles of the invention.

[0141] Preferably, gas-assisted HLPS processes utilize partially infiltrated pore space so as to enable gaseous diffusion
to rapidly infiltrate the porous preform and saturate thin liquid interfacial solvent films in the pores with dissolved CO₂. CO₂-based species have low solubility in pure water (1.5 g/L at 25°C, 1 atm.) Thus, a substantial quantity of CO₂ must be continuously supplied to and distributed throughout the porous preform to enable significant carbonate conversion. Utilizing gas phase diffusion offers a huge (about 100-fold) increase in diffusion length over that of diffusing soluble CO₂ an equivalent time in a liquid phase. (“Handbook of chemistry and physics”; Editor: D. R. Lide, Chapters 6 and 8, 87th Edition 2006-2007, CRC.) This partially infiltrated state enables the reaction to proceed to a high degree of carbonation in a fixed period of time.

[0142] Liquid water in the pores speeds up the reaction rate because it provides a medium for ionization of both carboxylic acid and calcium species. However, water levels need to be low enough such that CO₂ gas can diffuse into the porous matrix prior to dissolution in the pore-bound water phase. Furthermore, the actively dissolving porous preform serves as a template for expansive reactive crystal growth. Thus, the bonding element and matrices can be formed with minimal distortion and residual stresses. This enables large and complex shapes to result, such as those needed for infrastructure and building materials, in addition to many other applications.

[0143] Thus, various combinations of curing conditions may be devised to achieve the desired production process, including varied reaction temperatures, pressures and lengths of reaction. In a first exemplary embodiment, water is present in the precursor material (e.g., as residual water from prior mixing step) and liquid water is provided to precursor materials (e.g., to maintain water level and/or control the loss of water from evaporating) along with CO₂ and the curing process is conducted at about 90°C and about 20 psig (i.e., 20 psi above ambient pressure) for times ranging from about 2 to 90 hours.

[0144] In a second exemplary embodiment, water is present in the precursor material (e.g., as residual water from prior mixing step) and water vapor is provided to precursor materials (e.g., to maintain water level and/or control the loss of water from evaporating) along with CO₂ and the curing process is conducted at about 90°C and about 20 psig (i.e., 20 psi above ambient pressure) for times ranging from about 2 to 90 hours.

[0145] In a third exemplary embodiment, water is present in the precursor material (e.g., as residual water from prior mixing step) and water vapor is provided to precursor materials (e.g., to maintain water level and/or control the loss of water from evaporating) along with CO₂ and the curing process is performed at about 25 to 90°C and 0 psig (at ambient atmospheric pressure) for about 2 to 72 hours.

[0146] In the above embodiments, the time required for curing of a composite material object is determined by the ability of water vapor and CO₂ gas to diffuse throughout the object. In general, thicker objects take longer to cure than thinner objects. Similarly, objects with high density (and fewer open pore spaces) take longer to cure than objects with low density (and more open pore spaces). The following table provides examples of how the curing times may vary with respect to the smallest thickness (or wall thickness or section thickness) of the three dimensions and the bulk density of an object that is being manufactured.

<table>
<thead>
<tr>
<th>Composite Material Smallest Thickness (mm)</th>
<th>Composite Material Bulk Density (g/cm³)</th>
<th>Approximate Curing Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.6-2.3</td>
<td>8-12</td>
</tr>
<tr>
<td>75</td>
<td>2.1-2.3</td>
<td>16</td>
</tr>
<tr>
<td>100</td>
<td>0.4-0.8</td>
<td>8-12</td>
</tr>
<tr>
<td>200</td>
<td>1.5</td>
<td>72</td>
</tr>
<tr>
<td>200</td>
<td>2.4</td>
<td>72</td>
</tr>
</tbody>
</table>

Discussion of Manufactured Microstructures

[0147] As schematically illustrated in FIGS. 11(a)-11(c), a bonding element includes a core (represented by the black inner portion), a first layer (represented by the white middle portion) and a second or encapsulating layer (represented by the outer portion). The first layer may include only one layer or multiple sub-layers and may completely or partially cover the core. The first layer may exist in a crystalline phase, an amorphous phase or a mixture thereof, and may be in a continuous phase or as discrete particles. The second layer may include only one layer or multiple sub-layers and may also completely or partially cover the first layer. The second layer may include a plurality of particles or may be of a continuous phase, with minimal discrete particles.

[0148] A bonding element may exhibit any size and any regular or irregular, solid or hollow morphology depending on the intended application. Exemplary morphologies include: cubes, cuboids, prisms, discs, pyramids, polyhedrons or multifaceted particles, cylinders, spheres, cones, rings, tubes, crescents, needles, fibers, filaments, flakes, spheres, sub-spheres, beads, grapes, granulars, oblongs, rods, ripples, etc.

[0149] In general, as discussed in greater detail herein, a bonding element is produced from reactive precursor materials (e.g., precursor particles) through a transformation process. The precursor particles may have any size and shape as long as they meet the needs of the intended application. The transformation process generally leads to the corresponding bonding elements having similar sizes and shapes of the precursor particles.

[0150] Within the bonding matrix, the bonding elements may be positioned, relative to each other, in any one of a number of orientations. FIGS. 12(a)-12(f) schematically illustrate an exemplary bonding matrix that includes fiber- or platelet-shaped bonding elements in different orientations possibly diluted by the incorporation of filler material, as represented by the spacing between the bonding elements. FIG. 12(a), for example, illustrates a bonding matrix that includes fiber-shaped bonding elements aligned in a one-direction (“1-D”) orientation (e.g., aligned with respect to the x direction). FIG. 12(b) illustrates a bonding matrix that includes platelet-shaped bonding elements aligned in a two-direction (“2-D”) orientation (e.g., aligned with respect to the x and y directions). FIG. 12(c) illustrates a bonding matrix that includes platelet-shaped bonding elements aligned in a three-direction (“3-D”) orientation (e.g., aligned with respect to the x, y and z directions). FIG. 12(d) illustrates a bonding matrix that includes platelet-shaped bonding elements in a random orientation, wherein the bonding elements are not aligned with respect to any particular direction. FIG. 12(e) illustrates a bonding matrix that includes a relatively high
concentration of platelet-shaped bonding elements that are aligned in a 3-D orientation. FIG. 12(f) illustrates a bonding matrix that includes a relatively low concentration of platelet-shaped bonding elements that are situated in a random orientation (a percolation network). The composite material of FIG. 12(f) achieves the percolation threshold because a large proportion of the bonding elements are touching one another such that a continuous network of contacts are formed from one end of the material to the other end. The percolation threshold is the critical concentration above which bonding elements show long-range connectivity with either an ordered, e.g., FIG. 12(c), or random orientation, e.g., FIG. 12(f), of bonding elements. Examples of connectivity patterns can be found in, for example, Newnhaim, et al., “Connectivity and piezoelectric-pyroelectric composites”, Mat. Res. Bull. Vol. 13, pp. 525-536, 1978).

[0151] The plurality of bonding elements may be chemically transformed from any suitable precursor materials, for example, from any suitable calcium silicate composition precursor. The precursor calcium silicate composition may also include one or more chemical elements of aluminum, magnesium and iron.

[0152] The plurality of bonding elements may have any suitable mean particle size and size distribution dependent on the desired composite material. In certain embodiments, the plurality of bonding elements have a mean particle size in the range of about 1 μm to about 100 μm (e.g., about 1 μm to about 80 μm, about 1 μm to about 60 μm, about 1 μm to about 50 μm, about 1 μm to about 40 μm, about 1 μm to about 30 μm, about 1 μm to about 20 μm, about 1 μm to about 10 μm, about 5 μm to about 90 μm, about 5 μm to about 80 μm, about 5 μm to about 70 μm, about 5 μm to about 60 μm, about 5 μm to about 50 μm, about 5 μm to about 40 μm, about 5 μm to about 30 μm, about 10 μm to about 70 μm, about 10 μm to about 60 μm, about 10 μm to about 50 μm, about 10 μm to about 40 μm, about 10 μm to about 30 μm, about 10 μm to about 20 μm).

[0153] In some instances a composite material includes: a plurality of bonding elements and a plurality of filler particles. Each bonding element includes: a core comprising or primarily calcium silicate composition, a silico-rich first or inner layer, and a calcium carbonate-rich second or outer layer. The plurality of bonding elements and the plurality of filler particles together form one or more bonding matrices and the bonding elements and the filler particles are substantially evenly dispersed therein and bonded together, whereby the composite material exhibits one or more textures, patterns and physical properties. In some instances, the bonding elements may have a core of magnesium silicate, and a silico-rich first or inner layer, and a magnesium carbonate-rich second or outer layer. The magnesium silicate can include aluminum, calcium, iron or manganese oxides.

[0154] The plurality of filler particles may have any suitable mean particle size and size distribution. In certain embodiments, the plurality of filler particles has a mean particle size in the range from about 5 μm to about 7 mm (e.g., about 5 μm to about 5 mm, about 5 μm to about 4 mm, about 5 μm to about 3 mm, about 5 μm to about 2 mm, about 5 μm to about 1 mm, about 5 μm to about 0.5 mm, about 5 μm to about 0.05 mm, about 5 μm to about 0.005 mm, about 5 μm to about 0.0005 mm, about 5 μm to about 0.00005 mm, about 5 μm to about 0.000005 mm, about 5 μm to about 0.0000005 mm, about 5 μm to about 0.00000005 mm, about 5 μm to about 0.000000005 mm, about 5 μm to about 0.0000000005 mm, about 5 μm to about 0.00000000005 mm, about 5 μm to about 0.000000000005 mm, about 5 μm to about 0.0000000000005 mm).

[0155] In certain preferred embodiments, the filler particles are made from a calcium carbonate-rich material such as limestone (e.g., ground limestone). In certain materials, the filler particles are made from one or more of SiO₂-based or silicate-based material such as quartz, mica, granite, and feldspar (e.g., ground quartz, ground mica, ground granite, ground feldspar).

[0156] In certain embodiments, filler particles may include natural, synthetic and recycled materials such as glass, recycled glass, coal slag, calcium carbonate-rich material and magnesium carbonate-rich material.

[0157] The weight ratio of (bonding elements : filler particles) may be any suitable ratios dependent on the desired composite material, for example, in the range of about (10 to 50):about (50 to 90).

[0158] In certain embodiments, these composite materials may display various patterns, textures and other characteristics, such as visual patterns of various colors. In addition, the composite materials of the invention exhibit compressive strength, flexural strength and water absorption properties similar to conventional concrete or the corresponding natural materials.

[0159] In certain embodiments, the composite further includes a pigment. The pigment may be evenly dispersed or substantially unevenly dispersed in the bonding matrices, depending on the desired composite material. The pigment may be any suitable pigment including, for example, oxides of various metals (e.g., iron oxide, cobalt oxide, chromium oxide) The pigment may be of any color or colors, for example, selected from black, white, blue, gray, pink, green, red, yellow and brown. The pigment may be present in any suitable amount depending on the desired composite material, for example in an amount ranging from about 0.0% to about 10% by weight (e.g., about 0.0% to about 8%, about 0.0% to about 6%, about 0.0% to about 5%, about 0.0% to about 4%, about 0.0% to about 3%, about 0.0% to about 2%, about 0.0% to about 1%, about 0.0% to about 0.5%, about 0.0% to about 0.3%, about 0.0% to about 2%, about 0.0% to about 1%).

[0160] The processes of the invention may be employed to form anticorrosive coating on reinforcement used with any types of concrete (including Portland cement-based concrete) or to form protective coatings for a variety of different components and equipment.

EXAMPLES

Example 1
Anticorrosive Coating for Steel Rebar

[0161] Anticorrosive coatings were formed and corrosion performance was tested. The raw materials were mixed. The mixture proportions (Solidia Cement) used to cast concrete cylinders are shown in Table 2.
TABLE 2

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Wt. %</th>
<th>Amount (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground calcium silicate</td>
<td>18%</td>
<td>1.701</td>
</tr>
<tr>
<td>Sieved Construction sand</td>
<td>31%</td>
<td>2.929</td>
</tr>
<tr>
<td>½&quot; aggregate</td>
<td>25%</td>
<td>2.344</td>
</tr>
<tr>
<td>⅛&quot; aggregate</td>
<td>26%</td>
<td>2.457</td>
</tr>
<tr>
<td>Total of Solid Components</td>
<td>94.40%</td>
<td>9.431</td>
</tr>
<tr>
<td>Tap water</td>
<td>5.50%</td>
<td>0.556</td>
</tr>
<tr>
<td>Glunium7500</td>
<td></td>
<td>0.013</td>
</tr>
<tr>
<td>Total of Liquid Components</td>
<td>5.60%</td>
<td>0.563</td>
</tr>
<tr>
<td>Total of Solid and Liquid</td>
<td>100%</td>
<td>10.000</td>
</tr>
</tbody>
</table>

Cylinder-shaped objects (4" diameter×8" long as shown in FIG. 13) were casted in a mold with plain carbon steel embedded inside as reinforcing components. The cylindrical objects were demolded after 2 hours of casting.

The two-casted cylinders were placed in a curing chamber and cured at about 60°C for about 60 hours under an atmosphere of water and CO₂ having a pressure at about ambient atmospheric pressure and having a CO₂ concentration about 90%. The specimens were removed from the curing chamber and reinforcement was inspected under Scanning Electron Microscope (SEM).

FIG. 14 shows the micrograph for rebar specimen cured at about 60°C. It shows plain carbon steel, iron carbonate coatings formed and the bulk cured composite material. FIG. 15 shows EDX analysis of the coating formed on carbon steel rebar at 60°C. Similarly, specimens were cast and cured at the same conditions except at about 90°C. The SEM micrographs are shown in FIG. 16. FIG. 17 shows EDX analysis of the coating formed on iron rebar at 90°C. In each case, EDX analyses confirmed that the coating was iron carbonate.

The initial half-cell potential values with reference to copper-copper sulfate half-cell were about −200 mV and remained under −350 mV even after 7 days of exposure to water. This indicates no corrosion activity on rebar. These specimens are exposed to salt solutions, which is similar to environment for certain types of concrete applications such as bridge deck slabs.

Example 2

Anticorrosive Coating for Steel Panel

In another experiment, ductile cast iron specimen (0.71 diameter×2.055 inch long) were put in 1 M Na₂CO₃ solution in 1500 mL jars. The jars were put in oven at 60°C and 90°C for 24 hours. The specimens were then removed and rinsed with tap water before XRD and SEM analysis to characterize the corrosion products formed. FIG. 19 depicts XRD pattern which shows siderite coatings formed on the surface. FIG. 20 shows SEM image for this specimen which confirms the formation of siderite coatings during this reaction.

In this specification and the appended claims, the singular forms "a," "an," and "the" include plural reference, unless the context clearly dictates otherwise.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described. Methods recited herein may be carried out in any order that is logically possible, in addition to a particular order disclosed.

INTEGRATION BY REFERENCE

References and citations to other documents, such as patents, patent applications, patent publications, journals, books, papers, web contents, have been made in this disclosure. All such documents are hereby incorporated herein by reference in their entirety for all purposes. Any material, or portion thereof, that is said to be incorporated by reference herein, but which conflicts with existing definitions, statements, or other disclosure material explicitly set forth herein is only incorporated to the extent that no conflict arises between that incorporated material and the present disclosure material. In the event of a conflict, the conflict is to be resolved in favor of the present disclosure as the preferred disclosure.

EQUIVALENTS

The representative examples disclosed herein are intended to help illustrate the invention, and are not intended to, nor should they be construed to, limit the scope of the invention. Indeed, various modifications of the invention and many further embodiments thereof, in addition to those shown and described herein, will become apparent to those skilled in the art from the full contents of this document, including the examples which follow and the references to the scientific and patent literature cited herein. The following examples contain important additional information, exemplification and guidance that can be adapted to the practice of this invention in its various embodiments and equivalents thereof.

1. A process for forming an anticorrosive coating on a metal surface, comprising contacting the metal surface with an aqueous atmosphere of CO₂ and water vapor at a temperature and for a time period sufficient to form an anticorrosive coating on the metal surface.

2. The process of claim 1, wherein the metal surface is a surface of a metal selected from iron and steel.
3. The process of claim 2, wherein the metal surface is that of an object selected from bars, wires, cables, shards, filaments, tubings, pipes, containers, vessels and equipment.

4. The process of claim 1, wherein the aqueous atmosphere of CO₂ and water vapor is characterized by a pH value between about 3.5 to about 14.

5. The process of claim 1, wherein the anticorrosive coating comprises metal carbonate.

6. The process of claim 5, wherein the anticorrosive coating consists essentially of iron carbonate.

7. The process of claim 1, wherein the anticorrosive coating has a thickness in the range from about 1 μm to about 50 μm.

8. The process of claim 1, wherein the anticorrosive coating has a surface coverage of 90% or greater.

9. The process of claim 1, wherein the anticorrosive coating has a porosity of about 2.5 × 10⁻² or less.

10. A process for passivating iron or steel reinforcement wires or bars for corrosion resistance, comprising contacting the iron or steel reinforcement wires, cables or bars with an aqueous suspension of particulate calcium silicate under an atmosphere of CO₂ and water vapor at a pH from about 3.5 to about 14 to form an anticorrosive coating of iron carbonate covering the surface of iron or steel reinforcement wires, cables or bars, wherein the step of contacting the iron or steel surface with an aqueous suspension of particulate calcium silicate is conducted at a temperature in the range from about 10° C. to about 150° C., for a time period from about 1 hour to about 150 hours, under an atmosphere of water and CO₂ having a pressure in the range from ambient atmospheric pressure to about 150 psi above ambient and having a CO₂ concentration ranging from about 10% to about 99%, and with the particulate calcium silicate having a median particle size in the range from about 1 μm to about 100 μm.

11. The process of claim 10, wherein the pH value is between about 3.5 to about 14.0.

12. The process of claim 10, wherein the temperature is in the range from about 10° C. to about 150° C.

13. The process of claim 10, wherein the atmosphere of water and CO₂ has a pressure in the range from ambient atmospheric pressure to about 40 psi above ambient and having a CO₂ concentration ranging from about 50% to about 95%.

14. The process of claim 10, wherein the anticorrosive coating has a thickness in the range from about 1 μm to about 50 μm.

15. The process of claim 14, wherein the anticorrosive coating has a thickness from about 1 μm to about 30 μm.

16. The process of claim 10, wherein the anticorrosive coating has a surface coverage of 90% or greater.

17. The process of claim 16, wherein the anticorrosive coating has a porosity of about 2.5 × 10⁻² or less.

18. An article prepared by a process according to claim 1.

19. An article of manufacture having a body prepared from a composite material, the body being embedded with one or more reinforcement metal wires, cables or bars, wherein each of the one or more reinforcement metal wires, cables or bars is coated with an anticorrosive coating; and the composite material comprises:

- a plurality of bonding elements, wherein each bonding element comprises: a core comprising primarily calcium silicate, a silica-rich first or inner layer, and a calcium carbonate-rich second or outer layer, and

- filler particles comprising coarse filler particles and/or fine filler particles, wherein the plurality of bonding elements and the plurality of filler particles together form one or more bonding matrices and the bonding elements and the filler particles are substantially evenly dispersed therein and bonded together.

20. The article of claim 19, wherein the anticorrosive coating has a thickness in the range from about 5 to about 50 μm.

21. The article of claim 20, wherein the anticorrosive coating has a thickness in the range from about 10 to about 40 μm.

22. The article of claim 19, wherein the anticorrosive coating has a surface coverage of 90% or greater.

23. The article of claim 19, wherein the anticorrosive coating has a porosity of about 2.5 × 10⁻³ or less.

24. The article of claim 19, wherein the metal is selected from iron and steel.

25. The article of claim 19, wherein the article is selected from hollow core slabs, solid slabs, railroad ties, wall panels, floor panels, roof panels, Jersey barriers, blocks, beams, columns, and aerated structures and members thereof.

26. An article of manufacture comprising a metal surface coated with an anticorrosive coating comprising metal carbonate.

27. The article of claim 26, wherein the anticorrosive coating consists essentially of metal carbonate.

28. The article of claim 26, wherein the article is selected from metal bars, wires, shards, filaments, tubings, pipes, containers, vessels and equipment.

29. The article of claim 26, wherein the metal is selected from iron and steel.

30. The article of claim 26, wherein the anticorrosive coating has a thickness in the range from about 5 to about 50 μm.

31. The article of claim 26, wherein the anticorrosive coating has a surface coverage of 95% or greater.

32. The article of claim 26, wherein the anticorrosive coating has a porosity of about 2.5 × 10⁻³ or less.

33. The article of claim 26, wherein the metal is steel and the metal carbonate is iron carbonate.

34. An article of manufacture having a body prepared from Portland cement, the body being embedded with one or more reinforcement metal wires, cables or bars, wherein each of the one or more reinforcement metal wires, cables or bars is coated with an anticorrosive coating comprising metal carbonate.

35. The article of claim 34, wherein the anticorrosive coating has a thickness in the range from about 5 to about 50 μm.

36. The article of claim 35, wherein the anticorrosive coating has a thickness in the range from about 10 to about 40 μm.

37. The article of claim 34, wherein the anticorrosive coating has a surface coverage of 90% or greater.

38. The article of claim 34, wherein the anticorrosive coating has a porosity of about 2.5 × 10⁻³ or less.

39. The article of claim 34, wherein the metal is selected from iron and steel.

40. The article of claim 34, wherein the article is selected from hollow core slabs, solid slabs, railroad ties, wall panels, floor panels, roof panels, Jersey barriers, blocks, beams, columns, and aerated structures and members thereof.