A composition having high density and low toxicity suitable for use as a shotgun pellet, a bullet or armor piercing projectile and a method for manufacturing such composition is described. This material and product are developed to economically address the toxicity problems inherent in lead shot and bullets. This composition, in its present embodiment, is also suitable for use in any product requiring high-density and low toxicity. One present embodiment maintains the magnetic properties of the projectile if desired.
Load Carbon (Mix with Binder in some embodiments)

Add FeW

Mix Carbon/Binder and FeW

Pelletize (Pour into Mold in some embodiments)

Mix with SiC (may include W)

Heat to drive out Binder – if Binder Present

Heat to Sinter (may include in some embodiments) add Tungsten Powder prior to sintering steps

Add Custom Material (typically with heat treating)
METHOD FOR MAKING A NON-TOXIC DENSE MATERIAL

BACKGROUND OF INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to methods and compositions for making material useful as shot, bullets and the like. More specifically, this invention relates to methods and compositions, for making non-toxic dense material for use in shot, bullets, milling media, wear media, blasting media, hard tools and the like.

[0003] 2. Description of Related Art

[0004] A variety of materials and methods have been proposed or are in use as shotgun shot and rifle or pistol bullets, hereinafter referred cumulatively as “shot”. Because of its toxic nature, lead has been banned or criticized for use as shot. Lead has been banned in the United States and Canada for use in shotgun shells for hunting waterfowl. Lead has also been banned on all U.S. Federal Refuges where hunting game animals or training dogs. Generally, the reasons for the bans and criticism are that when waterfowl ingest pellets, the lead is retained and ground up in the bird’s gizzard and poisons the bird. The principle substitute for lead is steel, but the density of steel is only about 7.9 grams/cc, as compared to 11.4 grams/cc for lead or 11 grams/cc for commonly used lead alloys. Because of the lower density the effectiveness of steel is greatly diminished when compared to lead. One advantage of steel is that it is ferromagnetic, making it easily detectable by law enforcement with a simple hand held magnet. Several manufacturers have announced that they are working on finding a substitute for lead. These include Federal’s Iron-Tungsten or Tungsten, Environmental’s and Remington’s Hevishot, Kent’s Tungsten-Matrix and Bismuth shot, made by The Bismuth Cartridge Company.

[0005] Federal’s Iron-Tungsten or Tungsten claims a density of about 10.4 grams/cc, although it has been measured at closer to 10.2 grams/cc. Iron-Tungsten uses a powder metallurgy method of making a pellet from tungsten, iron and/or ferro-tungsten powders. The process is described in U.S. Pat. Nos. 5,831,188, 5,527,376, 5,905,936, 5,713,981 and 6,270,549. The process involves pressing each individual pellet in a press with a binder of some sort to hold the pellet together in the “green” state. The pressing operation leaves a band on the pellet that must be removed. After a presintering operation, the pellet is then typically ground or rolled to make it truer (more round) and to eliminate or minimize the band. Firing the pellet at about 1500 degrees C. in hydrogen gas then follows to densify and strengthen the pellet. Further treatment may well include additional grinding and/or the application of a rust inhibitor. This method tends to be expensive due to the high firing temperature, the individual pressing of pellets and the followed rounding steps. This individual pressing of pellets further limits the pellets to larger sizes.

[0006] Environmental and Remington claim that Hevishot has a density of about 12 grams/cc. The process of making Hevishot is generally described in U.S. Pat. No. 6,270,549. Hevishot uses a process of making shot from molten metal similar to the method used historically to make lead shot by dropping molten lead through a screen inside a tower, as the lead falls it becomes round and is quenched in water. Because Hevishot is generally made of an iron, tungsten, nickel and sometimes a manganese alloy it melts at a much higher temperature, about 1637 degrees C., than lead which melts at about 327 degrees C. Therefore, the process is modified to accommodate the much higher temperatures. The process modifications include dropping the molten metal through a ceramic sieve and, in place of the shot tower, into a high velocity stream of air or gas which helps break up the molten droplets of metal alloy and allows the surface tension to form round or rounded droplets that are then quenched in water. Unfortunately, Hevishot does not tend to be very round and frequently has two or more spheres attached to each other of different sizes or can be hollowed out and tend not to be of uniform size.

[0007] Kent’s Tungsten-Matrix is claimed to have a density of 10.8 grams/cc, but depending on the shot size measured between 10.3 and 10.7 grams/cc. This shot, described in U.S. Pat. No. 6,216,598, uses tungsten powder held together by a polymer. Tungsten powder is much more expensive than FeW (ferro-tungsten) powder. Because of the polymer, the resulting shot is comparatively weak and can deform during the shooting process. Also, the process typically requires that the pellets be formed individually be pressing from a polymer sheet, filled with tungsten powder, with opposing rolls.

[0008] Bismuth has also been proposed. However, with a density of 9.8 grams/cc Bismuth, although relatively easy to manufacture, can be excessively brittle, unless alloyed with tin (Sn) in small amounts. Sn has a density of 7.3 g/cc, so any addition of Sn lowers the density of the alloy.

[0009] A number of other shot materials and processes have been proposed. Generally, however, these prior techniques have not made use of carbon to increase the density of the shot and to reduce the firing temperature required, and the associated energy and production costs.

[0010] Although these references may not actually qualify as “prior art,” the reader is referred to the following U.S. patent documents for general background material. Each of these patents is hereby incorporated by reference in its entirety for the material contained therein.

[0011] U.S. Pat. No. 1,847,617 describes hard alloys that include the addition of chromium and cobalt.

[0012] U.S. Pat. No. 2,119,876 describes shot used primarily in shot shells designed for target shooting and game hunting and in air rifles.


[0016] U.S. Pat. No. 3,952,657 describes a cartridge that includes a projectile, which is inserted in a plastic shell receiving a propellant charge, and the cartridge is expelled out of a barrel by propellant gases.


[0018] U.S. Pat. No. 4,027,594 describes shot pellets that are formed from finely divided powder adhered together in pellet form by a thermoplastic polymeric material decomposable in the acid environment of the digestive tract of waterfowl.


[0020] U.S. Pat. Nos. 4,200,456 and 4,297,133 describe a method and member for adding a treating agent for molten metal.
U.S. Pat. No. 4,292,877 describes an ammunition loader with hoppers for shot and/or powder and a slideable bar for measuring.

U.S. Pat. No. 4,316,414 describes a fuse apparatus that arms itself in flight and is especially adapted for use in training shells.

U.S. Pat. No. 4,714,023 describes a non-toxic wildlife shot pellet for shotgun shells and the like that comprises a lead shot pellet with a coating of nickel-phosphorous alloys.

U.S. Pat. No. 4,754,684 describes a method and device for cutting a shotgun shell for shooting in a shotgun.

U.S. Pat. No. 4,784,690 describes a low-density tungsten alloy article and the method for producing the article.

U.S. Pat. No. 4,841,866 describes a tracer shotgun shell that includes an improved tracer element and a single integral wad member.

U.S. Pat. No. 4,854,240 describes a two-stage, shaped charge projectile having a rear principal charge and a front secondary smaller charge with an initiator-fuse assembly.

U.S. Pat. No. 4,856,408 describes a modification or replacement for shot and powder loading systems having wad jammer tubes with telescopic loading funnels.

U.S. Pat. No. 4,949,644 describes non-toxic wildlife shot pellets for shotgun shells that are formed from bismuth or bismuth alloy.

U.S. Pat. No. 4,960,563 describes a process for the production of a heavy tungsten-nickel-iron alloy.

U.S. Pat. No. 5,279,787 describes a high-density projectile and the method of making the same from a mixture of low density and high-density metal powders.

U.S. Pat. No. 5,335,578 describes a retrofitting shell feeding attachment for shotgun shell reloading machines.

U.S. Pat. No. 5,399,187 describes a composite lead-free bullet, comprising a heavy constituent selected from the group of tungsten, tungsten carbide, carb-alloy and ferrotungsten and a second binder constituent consisting of either a metal alloy or a plastic blend.

U.S. Pat. No. 5,442,989 describes a method of making the casing for fragile armor piercing incendiary projectiles.

U.S. Pat. No. 5,512,080 describes a Fe-based alloy powder adapted for sintering, a Fe-based sintered alloy, and a process for producing the Fe-based sintered alloy.

U.S. Pat. No. 5,527,376 describes a shot pellet or small arms projectile that comprises 40-60% by weight of tungsten and 60-40% by weight of iron formed by sintering tungsten containing powders.

U.S. Pat. No. 5,623,118 describes a shot shell wad that may comprise a powder cup and a shot cup connected by first and second shot cup support members.

U.S. Pat. No. 5,666,634 describes alloy steel powders for sintered bodies.

U.S. Pat. No. 5,713,981 describes a high specific gravity, lead free shot shell pellets that are produced by preparing an iron-tungsten alloy, melting the alloy, pouring the alloy and allowing the alloy to fall by gravity through a gaseous medium to form drops.

U.S. Pat. No. 5,714,573 describes a melt-processable lactide polymer composition, process for manufacturing these compositions and articles made from these compositions.

U.S. Pat. No. 5,719,352 describes a low toxicity shot or pellets for shotgun cartridges or the like that comprises finely divided molybdenum and tungsten particles in a polymer matrix.

U.S. Pat. No. 5,728,349 describes a material primarily for sport shooting ammunition, both pellet ammunition and ball ammunition, including at least the materials zinc and bismuth.

U.S. Pat. No. 5,760,331 describes a projectile made by combining two different metals in proportions calculated to achieve a desired density, without using lead.

U.S. Pat. No. 5,814,759 describes a composite lead-free bullet that comprises a heavy constituent selected from the group of tungsten, tungsten carbide, carb-alloy and ferrotungsten and a second binder constituent consisting of either a metal alloy or a plastic blend.

U.S. Pat. No. 5,831,188 describes methods of making high specific gravity shotgun shot and small arms projectiles from melts containing primarily tungsten and iron.

U.S. Pat. No. 5,861,572 describes a universal shotgun shell wad that may be used to assemble a variety of shotgun shells with a wide variety of shot and powder loadings.

U.S. Pat. No. 5,870,989 describes an abrasion resistant valve seat made of sintered alloy for internal combustion engines.

U.S. Pat. No. 5,874,689 describes a one piece shot cup designed especially for use in protecting the bore of a shotgun barrel.

U.S. Pat. No. 5,905,936 describes generally rough sphere-shaped work pieces made of fragile material that are ground into more uniform spheres.

U.S. Pat. No. 5,913,256 describes a non-lead environmentally safe projectile and explosive container.

U.S. Pat. No. 5,922,832 describes melt-processable lactide polymer compositions.

U.S. Pat. No. 5,932,828 describes a loader with snap-in tools.

U.S. Pat. No. 5,963,776 describes a projectile, such as a bullet, made by combining two different metals in proportions calculated to achieve a desired density, without using lead.

U.S. Pat. No. 5,970,878 describes a combination of shot sleeve and a shot cup base form a universal shot wad that precisely fixes an adjustable volume.

U.S. Pat. No. 5,997,805 describes a manufacturing method for the production of high density, high carbon, and sintered powder metal steels.

U.S. Pat. No. 6,048,379 describes a high-density composite material that may act as a replacement for lead in applications where the high density of lead is important, but where the toxicity of lead is undesirable.

U.S. Pat. No. 6,092,467 describes a flare apparatus that includes a shell base.

U.S. Pat. No. 6,102,820 describes an auto-tensioner that inhibits the generation of heat in an insert bearing made of a synthetic resin.

U.S. Pat. No. 6,112,669 describes a lead-free projectile made from a composition containing about 52.5% by weight of tungsten and more than about 97% by weight tungsten plus iron.

U.S. Pat. No. 6,128,846 describes an improved shotgun choke tube.
SUMMARY OF INVENTION

[0082] It is desirable to provide a method for producing non-toxic materials, which can be used for shot and/or bullets, which are more dense than steel, bismuth or lead. It is particularly desirable to provide an economical method for producing such non-toxic materials.

[0083] Accordingly, it is an object of one embodiment of this invention to provide a method for the manufacture of a dense material that is non-toxic.

[0084] It is another object of one embodiment of this invention to provide a method for the manufacture of non-toxic material having a density of 9 to 11.8 g/cc and in some embodiments even higher, up to and including densities of as much as 15 g/cc.

[0085] Another object of one embodiment of this invention is to provide a method for the manufacture of a more dense than lead material that is economically produced.

[0086] A still further object of one embodiment of this invention is to provide a method for the manufacture of a more dense than lead material that has a relatively low sintering temperature.

[0087] It is a further object of one embodiment of this invention to provide a method for the manufacture of a more dense than lead material that uses relatively less expensive materials.

[0088] It is a still further object of one embodiment of this invention to provide a method for the manufacture of a more dense than lead material that is compatible with a wide range of pellet sizes.

[0089] Another object of one embodiment of this invention is to provide a method for the manufacture of a more dense than lead material that does not necessarily require grinding or shaping, although grinding and shaping may be useful, but not necessary, in some applications.

[0090] A further object of one embodiment of this invention is to provide a method for the manufacture of a dense non-toxic material, which in some embodiments is provided with an uneven dimpled surface.

[0091] A still further object of one embodiment of this invention is to provide a method for the manufacture of a dense non-toxic material that includes sintering a different density material such as tungsten powder to prevent sticking of the material itself.

[0092] Another object of one embodiment of this invention is to provide a method for the manufacture of a dense non-toxic material that uses carbon as a sintering aid.

[0093] It is an object of one embodiment of this invention to provide a method for the manufacturing of a dense non-toxic material that, in some embodiments, employs sintering in SiC, tungsten, ferro niobium and/or tungsten-carbide powder of a large mesh size to prevent sticking of the pellets together during sintering.

[0094] It is another object of one embodiment of this invention to provide a method for the manufacturing of a dense non-toxic material that, in some embodiments, employs sintering in SiC, tungsten, ferro niobium and/or tungsten-carbide powder of a large mesh size to prevent sticking of the pellets together during sintering.

[0095] It is a further object of one embodiment of this invention to provide a method for the manufacturing of a dense non-toxic material that, in some embodiments, includes Boron Nitride (BN) powder or spray to prevent sticking.
It is a still further object of one embodiment of this invention to provide a method for the manufacturing of a dense non-toxic material that, in some embodiments, includes non-wetted, high melting point material to prevent or reduce sticking of the resulting pellets.

Another object of one embodiment of this invention is to provide a method for the manufacturing of dense non-toxic material that, in some embodiments, lowers the sintering temperature of FeW by the addition of a much higher melting temperature material.

A further object of one embodiment of this invention is to provide a method for the manufacturing of dense non-toxic material that, in some embodiments, provides for the varying of the strength and fragility of the resulting material by varying the time and temperature of the sintering stage as well as the composition.

A still further object of one embodiment of this invention is to provide a method for the manufacturing of dense non-toxic material that, in some embodiments, provides the proper strength and fragility to milling media made from these compositions.

Another object of one embodiment of this invention is to provide a method for the manufacture of a dense non-toxic material that does not require compression or pressure to form into a generally round shape.

It is another object of one embodiment of this invention to provide a method for the manufacture of a dense non-toxic material that is useful in the manufacture of hard tools.

It is a further object of some embodiments of this invention to provide a method for the manufacture of dense non-toxic material that retains magnetic properties.

A still further object of some embodiments of this invention is to provide a method for the manufacture of shot of varying sizes with "tailored" densities to enhance the trajectory control of the shot pellets.

Additional objects, advantages and other novel features of this invention will be set forth in part in the description that follows and in part will be apparent to those skilled in the art upon examination of the following or may be learned with the practice of the invention. The objects and advantages of this invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims. Still other objects of the present invention will become readily apparent to those skilled in the art from the following description wherein there is shown and described present preferred embodiments of the invention, simply by way of illustration of the best modes currently known to carry out this invention. As it will be realized, this invention is capable of other different embodiments, and its several steps, details, and specific components, dimensions and materials, are capable of modification in various aspects without departing from the invention. Accordingly, the drawings and descriptions should be regarded as illustrative in nature and not as restrictive.

BRIEF DESCRIPTION OF DRAWINGS

The accompanying drawings incorporated in and forming a part of the specification, illustrate embodiments of the present invention. Some, although not all, alternative embodiments are described in the following description.

In the drawings:

FIG. 1 is a flow chart of the present steps of the method of this invention.

Reference will now be made in detail to the present preferred embodiments of the invention, examples of which are illustrated in the accompanying drawings.
presently preferably the processing of the method of this invention is performed in a Hydrogen, Argon or otherwise protective atmosphere.

[0111] Carbide compositions in this invention can be produced from ferroalloys by attrition, the result then blended with carbon and fired at temperatures lower than those necessary for forming carbides of the primary metal. Examples of such carbide compositions include, but are not necessarily limited to, FeW, FeTi, FeCr and other ferroalloys that are suitable for alloying with steel and other alloys that contain iron and carbon. Cutting tools that contain carbides, such as those made by cementing carbides together with cobalt, nickel or iron can also benefit from the addition of carbided or carburized ferroalloys. The carbidizing or carburizing of the master ferroalloy, before the addition of other alloys or cemented carbide tools, can provide an accurate method of controlling the ratios of carbon and of the alloy additive. This control can be helpful in maintaining the desired properties of the final product.

[0112] During the development of this invention the inventor determined that a very dense compact can be made by sintering Nickel (Ni) and Manganese (Mn) with Tungsten powder (W) at temperatures below 1200°C. In some instances and embodiments densities greater than 14 g/cc have been achieved. Using a combination of Ni, Mn, W and FeW densities in excess of 12.5 g/cc have been achieved. NiMn alloys have particular advantages in this process for making dense non-toxic material, including: Ni and Mn together form a low melting eutectic, at about 1050°C to 1040°C, with about 40-60% Ni in the NiMn alloy. Ni melts at about 1453°C and Mn at about 1244°C, so either element alone does not sinter at the low temperature of the eutectic. By varying the quantities of Ni and Mn the hardness of the alloy is also varied, from too soft to measure to a value in the 80’s on the Rockwell A scale. In other words, the ratio between the amounts of Ni and Mn in the alloy can affect the hardness from softer than many steels to as hard as some softer carbides. The range of density achieved in the composition can also be adjusted by selecting the amounts of Ni and Mn used. Using the NiMn sintering agent permits parts to be formed mechanically or machined to a final shape or dimension with standard metal working techniques, i.e., pressing, rolling, cutting and the like. FeW—C parts when used as an alternative, typically require grinding and other processes necessary for hard and brittle materials. Since NiMn acts to hold the other materials in the composition, hardness, toughness, formability and even the magnetic properties can be regulated by the way in which the powders are assembled and sintered. For example, the FeW—C composition is non-magnetic and the FeW, W and NiMn composites are also non-magnetic if the particle sizes in the powders are kept small. However, when larger FeW particles are used the magnetic properties of the large particles is retained, so long as the particles are merely held together and are not allowed to react with the other constituents. Therefore, a non-magnetic or a magnetic product can be produced from either the NiMn, FeW, W, or FeW—C composition. The NiMn—W composition will not yield a magnetic product.

[0113] For some applications it is desirable to have magnetic properties in the product of the process of this invention. One of these applications is the use of the product as shot in shotshells for hunting waterfowl. It is probable that the components of the material of the various present embodiments of this invention are sufficiently non-toxic to be used as shot in shotshells as non-toxic shot. One of the common qualities of non-toxic shot is that it may be easily determined in the field, by non-destructive and non-invasive techniques, that the shot is non-toxic. A simple means that has been developed to make this determination is the use of a magnet. Steel, a common non-toxic shot and some other non-toxic shot have been demonstrated to be magnetic. Naturally, the magnetic properties of nearly any product can be altered by such means as coating the product with a magnetic coating, such as BiMn, A5CuMn, which is both magnetic and non-toxic.

[0114] An alternative method of providing magnetic properties to the product is in the method of manufacture. For example, Tungsten (W); Manganese (Mn); Carbon (C); Nickel-Manganese (NiMn); and Iron-Tungsten-Carbide (FeWC) are all non-magnetic, while Iron-Tungsten (FeW) and Iron (Fe) and Nickel (Ni) are all magnetic. When FeW is reacted with C, the FeW ceases to be magnetic. Similarly, when Ni reacts with Mn it is no longer magnetic above 30 to 40% Mn. If an alloy of Ni and Mn is used where the Ni is about 60% or more the alloy will be magnetic and this magnetism will be retained in the final product. Any of the products of this present invention can be made magnetic by not reacting the magnetic component, that is, by using particles of FeW or Ni that are large enough so that although they are part of the composition, then do not completely react and therefore retain their magnetic qualities. By carefully choosing the desired particle size of the FeW and/or Ni, a degree of magnetism can be retained in or can be removed from the final product. The density of FeW is high so there is generally no sacrifice of overall product density when FeW is used as the chosen material for magnetism, and in fact the use of FeW can enhance or increase the overall density of the resulting product. While coatings may decrease to some degree the overall density of the product, the use of FeW or other similar material that is at least as dense, as the desired final product, does not tend to reduce the final product’s density. Other large particle magnetic materials, that do not tend to be changed by the sintering steps, such as Fe, Ni and the like, can also be used to provide magnetism.

[0115] The following is a brief summary of various elements and compounds that the inventor has determined can be used in various ways and with a variety of results in the process and product of this invention. This list is not intended to be exhaustive but rather only to be exemplary of the wide variety of materials that may be employed in this invention.

[0116] Nickel (Ni) can be applied by electrolysis and is commonly known and used in this manner, although electrolysis may not necessarily be the best way to apply Ni to shot to magnetize the shot. Another alternative and probably better way of applying Ni is to place the shot in a rotating mill with soft Ni powder such as Ni 123 and rotate the mill until the Ni powder covers and adheres to the surface of the shot. This method of applying Ni works equally well for applying Ni to any rough or cylindrical surface for which applying Ni to the surface is desirable. The present product will accept Ni coating in this way and thus provide the desired magnetic qualities required for detection of non-toxic shot in the field with a simple magnet. Ni may also be coated on the shot by applying a slurry of Ni powder and then drying and sintering at a temperature below the point where the Ni would combine with the substrate to lose its magnetic property, but simply sintering to the surface thereby retaining the magnetic qualities.
Bismuth-Manganese (BiMn) can be used as both a coating and as an inherent material. As a coating, the Bi is typically added with a low temperature dip after the product is finished. Although Bi is not magnetic itself, it will tend to combine with the Mn in the product for the requisite alloy. Testing has been performed and has determined that BiMn alloys in the range of 1 part Bi and 3 parts Mn to 3 parts Bi and 1 part Mn produces a magnetic part, therefore close control of the composition is not generally necessary to assure that the product retains magnetic qualities. Bi has a low melting point of about 271°C, which facilitates the application of the Bi to the product. Simply dipping the product in melted Bi and/or reheating can be done relatively easily. Bi also provides some corrosion protection, even though the product itself is generally quite corrosion resistant. Surface coatings of BiMn can be applied in much the same manner as Ni powder if the BiMn is made into a powder first, then rolled and used as is or sintered onto the surface at lower temperatures than are normally required in processing. BiMn can also be used inherent to the product composition to sinter or "glue" the denser materials, such as FeW, W and the like, together. This use of BiMn also facilitates the magnetic quality of the product. A present drawback to the extensive use of Bi is its high cost. However, if the cost of Bi decreases and availability increases, this could be an attractive ingredient for the product composition. Since the alloy, BiMn, would typically be about 80% by weight Bi the cost of the Bi could be driving factor in the determination of its use. The Mn content makes the sintering to good strength more feasible than with just Bi alone and the Bi is not magnetic, while the alloy BiMn is. BiMn also appears to wet to almost anything it contacts and therefore can be a problem as a sintering agent, since it will tend to stick to nearly everything.

Aluminum-Copper-Manganese (AlCuMn) is also a low melting point alloy and can be applied to the product by dipping, spraying or other similar means to provide a coating on the product. This alloy further has the advantage that Mn is already likely to be present in the base material, so the Co and Al can be the coating. Cu and Mn make a good combination for sintering and can be altered with a small amount of Al to provide the desired magnetic properties. AlCuMn can also be applied in much the same manner as described in relation to Ni powder if made into a powder first, then rolled and used as is or sintered onto the surface at lower temperatures than is typically required in standard processing. The CuMn alloy does not provide as high a density as NiMn, but is sufficient for most applications, such as shot, projectiles, fishing weights and the like.

Iron (Fe) and Chromium (Cr) can also be applied as a powder to the surface, either with adhesive or sintered on to the product to provide the desired magnetic properties. The amount of Fe and Cr that should be used depends on the desired magnetism and the resulting density. Fe, steel, Ni, Cr and other magnetic materials can also be applied as coatings, although for some with difficulty. Fe and steel are not corrosion resistant unless they are in turn coated, as some steel shot presently is. Ni has been coated onto the final product as a powder with separate steps, following the primary sintering, of coating with a Ni powder, which has some kind of binder, such as sugar water, to attach the powder to the sintered article, followed by another sintering step to sinter the Ni metallurgically. This second sintering step can be eliminated if the binder is sufficiently strong to keep the Ni or other magnetic material in place.

Copper-Manganese (CuMn), Manganese-Nickel (MnNi) and Copper-Nickel-Manganese (CuNiMn) all have melting points below or well below 1200°C, thus making processes using these alloys into a relatively less expensive and more economical realm for manufacturing. Other factors, such as the sintering-aid effect previously described as part of the FeW—C mix can also be important in the effectiveness of this process. Mn has been found to provide this sintering-aid effect when it is included in the composition, such as in CuMn, MnNi and CuMnNi alloys. Mn is also beneficial for not only lowering the melting point of the composition but also for assisting the sintering step and densification, whenever Mn is present and if the proportions of Mn is higher the effect is magnified. Cu appears to have the opposite effect and when Cu is increased, the composition sintering-aid effect is reduced, to the point where Cu is the only component, sintering is minimal or almost nonexistent even though the melting point of Cu is well below the processing temperatures. No sintering-aid effect has been found for Ni, since the melting point of Ni is well above the typical processing temperatures. Mn alone, among the studied elements, melts well above the processing temperatures but aids sintering and densification, so that the full benefit of Mn is made available at the process temperatures when Mn is alloyed with other elements that lower the melting temperatures below 1200°C, and typically much below 1200°C. Other elements that Mn alloys well with are Tin (Sn) and Zinc (Zn).

Tin-Zinc (SnZn) and Manganese-Tin-Zinc (Mn-SnZn) are alloys that have very low melting points and are not easy to make into powders. Although powders may not always be necessary at the low temperatures if wetting is good or excellent. SnZn does not wet as well without the Mn, so small amounts of Mn are preferably added to the alloy for wetting and sintering. 4% Mn added to the composition helps wetting at 1200°C, but does not typically increase the density values significantly because there was very little increase in sintering. Greater amounts of Mn are desirable for increasing the sintering and has been demonstrated with 10% Sn and 80% Mn compositions. Larger amounts of Mn can reduce the retained magnetism unless sintering temperatures, and sometimes densities, are lowered or particle size of the magnetic materials are increased.

The following are some examples of compositions, processing temperatures and atmospheres and resulting products of this invention. These examples are not intended to be exhaustive but rather only present examples of various embodiments of the composition of this invention. These examples are presented by showing the approximate quantity of each major constituent, the firing (sintering) temperature, the atmosphere preferred, the sintering time, the resulting hardness in Rockwell Hardness Units (RHA), scale A, the product density, and whether the product is magnetic. For the approximate quantity of the constituent the values provided have been rounded to the nearest percentage. These percentages are not intended to imply that no other constituent elements, alloys, compounds or compositions are included, rather they describe the relative quantities of the major constituents pertinent to the objective of a non-toxic dense material. Other various components may and generally are included in the final product as trace elements or contaminants. Mesh sizes are provided where pertinent using standard US sieve mesh sizes. With this tabular description additional comments and notes are provided to give other specific information related to the particular embodiment.
Example 1
An Example of the Use of Tin

<table>
<thead>
<tr>
<th>Ex#</th>
<th>Sn</th>
<th>Mn</th>
<th>W</th>
<th>FeW</th>
<th>Atmos</th>
<th>Time</th>
<th>Density</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-8.3</td>
<td>-16.6</td>
<td>-41.7</td>
<td>-33.2</td>
<td>Ar</td>
<td>1 hr</td>
<td>11.5</td>
<td>slightly</td>
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</table>

Example 2
FeW Powder is Mixed with Fine Carbon Powder (Graphite)

<table>
<thead>
<tr>
<th>Ex#</th>
<th>FeW</th>
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<th>Atmos</th>
<th>Time</th>
<th>Hardness</th>
<th>Density</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
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<td>2</td>
<td>-98.6</td>
<td>-1.4</td>
<td>H</td>
<td>15 m</td>
<td>67</td>
<td>11.7</td>
<td>no</td>
</tr>
</tbody>
</table>

[0125] High hardness is provided because of the carbides formed at the temperatures where the sintering takes place, some WC can be formed in the reaction sintering as the bond between the Fe and W is broken by C.

Examples 3-6
Ni, Mn and ~100 to +400 Mesh, in a Ratio of about 1/2/4 with W Powder Added as Noted in Each

<table>
<thead>
<tr>
<th>Ex#</th>
<th>Ni</th>
<th>Mn</th>
<th>FeW</th>
<th>W</th>
<th>Atmos</th>
<th>Time</th>
<th>Hardness</th>
<th>Density</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>~10</td>
<td>~20</td>
<td>~40</td>
<td>~30</td>
<td>Ar</td>
<td>15 m</td>
<td>27 ± 10</td>
<td>10.0</td>
<td>no</td>
</tr>
<tr>
<td>4</td>
<td>-8.3</td>
<td>-16.6</td>
<td>-33.2</td>
<td>-41.7</td>
<td>Ar</td>
<td>15 m</td>
<td>41 ± 18</td>
<td>10.9</td>
<td>no</td>
</tr>
<tr>
<td>5</td>
<td>-7.1</td>
<td>-14.2</td>
<td>-28.4</td>
<td>-50</td>
<td>Ar</td>
<td>15 m</td>
<td>31 ± 7</td>
<td>11.6</td>
<td>no</td>
</tr>
<tr>
<td>6</td>
<td>-6.3</td>
<td>-12.6</td>
<td>-25.2</td>
<td>-56.3</td>
<td>Ar</td>
<td>15 m</td>
<td>45 ± 5</td>
<td>11.9</td>
<td>no</td>
</tr>
</tbody>
</table>

[0127] These hardness ranges go from well below that which is accepted hardness for steel shot and other "hard shot to about the same as is found in such steel shot.

[0128] The relatively large variation in hardness in these examples shows the variation possible with a multiple phase product.

Examples 7-10
Ni, Mn and ~200 Mesh FeW Powder, in a Ratio of About 1/2/4, with W Powder Added as Noted in Each Example

<table>
<thead>
<tr>
<th>Ex#</th>
<th>Ni</th>
<th>Mn</th>
<th>FeW</th>
<th>W</th>
<th>Atmos</th>
<th>Time</th>
<th>Hardness</th>
<th>Density</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>~10</td>
<td>-20</td>
<td>~40</td>
<td>~30</td>
<td>Ar</td>
<td>15 m</td>
<td>46 ± 6</td>
<td>10.6</td>
<td>no</td>
</tr>
<tr>
<td>8</td>
<td>-8.3</td>
<td>-16.6</td>
<td>-33.2</td>
<td>-41.7</td>
<td>Ar</td>
<td>15 m</td>
<td>46 ± 9</td>
<td>11.1</td>
<td>no</td>
</tr>
<tr>
<td>9</td>
<td>-7.1</td>
<td>-14.2</td>
<td>-28.4</td>
<td>-50</td>
<td>Ar</td>
<td>15 m</td>
<td>47 ± 3</td>
<td>11.7</td>
<td>no</td>
</tr>
<tr>
<td>10</td>
<td>-6.3</td>
<td>-12.6</td>
<td>-25.2</td>
<td>-56.3</td>
<td>Ar</td>
<td>15 m</td>
<td>47 ± 0</td>
<td>12.0</td>
<td>no</td>
</tr>
</tbody>
</table>

[0130] These examples are somewhat softer than that typically used in the market for "hard" shot.
Example 11
Ni, Mn and W Powders Used to Make a Dense Sintered Product

[0131] The powders are mixed and fired.

<table>
<thead>
<tr>
<th>Ex#</th>
<th>Ni</th>
<th>Mn</th>
<th>W</th>
<th>Firing Temp</th>
<th>Atmos</th>
<th>Time</th>
<th>Hrd</th>
<th>Dnsy</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>-6.6</td>
<td>-15.4</td>
<td>-80.0</td>
<td>1200° C.</td>
<td>Ar</td>
<td>15 m</td>
<td>53 ± 2</td>
<td>14 no</td>
<td></td>
</tr>
</tbody>
</table>

[0132] The density of this example is very high compared to related product compositions. The density can be varied by the addition of more or less of the lower density Ni and Mn, in other manufacturing processes these types of higher densities typically require expensive, hot pressing and/or high temperature manufacturing techniques (above 1200° C.). The particle sizes of the W powder can also be modified to control the hardness and density, where the larger the W particle size, leads to lower hardness and increased density. The larger particle W powder also tends to lower the porosity both open and closed for the resulting product.

Examples 12-15

[0133] Examples of the effect of the particle size of W on hardness, the finer the W particles, the harder the resulting product. In this table the tungsten size is average particle size in µm.

<table>
<thead>
<tr>
<th>Ex#</th>
<th>Ni</th>
<th>Mn</th>
<th>FeW</th>
<th>W/size</th>
<th>Firing Temp</th>
<th>Atmos</th>
<th>Time</th>
<th>Hrd</th>
<th>Dnsy</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>-5.5</td>
<td>-12.6</td>
<td>-25.2</td>
<td>-56.7/40</td>
<td>1200° C.</td>
<td>Ar</td>
<td>15 m</td>
<td>41 ± 3</td>
<td>12.3 no</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>-5.5</td>
<td>-12.6</td>
<td>-25.2</td>
<td>-56.7/20</td>
<td>1200° C.</td>
<td>Ar</td>
<td>15 m</td>
<td>42 ± 7</td>
<td>12.2 no</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>-5.5</td>
<td>-12.6</td>
<td>-25.2</td>
<td>-56.7/12</td>
<td>1200° C.</td>
<td>Ar</td>
<td>15 m</td>
<td>48 ± 8</td>
<td>12.4 no</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>-5.5</td>
<td>-12.6</td>
<td>-25.2</td>
<td>-56.7/6</td>
<td>1200° C.</td>
<td>Ar</td>
<td>15 m</td>
<td>60 ± 4</td>
<td>12.4 no</td>
<td></td>
</tr>
</tbody>
</table>

[0134] As can be seen in these examples (Examples 12-15) there is not much effect on the hardness until the particle size approaches 12 µm and finer, with a profound effect at 6 µm average particle size. Showing that hardness can be controlled, within a range, by the particle size of W.

Examples 16-24

Magnetic Enhanced Products

[0135] It is possible, in various embodiments of this invention, to enhance or reduce magnetic qualities of the resulting product by the use of careful selection of particle sizes and the metals chosen as the sintering medium. Metals such as Mn and Ni or C in FeW—C composition, react with the FeW to cause the FeW to lose the ferromagnetic property that is naturally possesses. Other metals, such as Cu, Zn and Sn can be used in sintering with a reduced effect on the magnetic properties of the FeW or other magnetic additions because of the reduced reaction with magnetic materials. For this reason Ni and Mn can be used to sinter and obtain high densities with no magnetism if such is desired and can be mixed with Cu, Sn and/or Zn to achieve the same results, although Cu appears to reduce the sintering/densification and the resultant densities to some degree. However, if Cu, Sn and Zn and their alloys are used the magnetic properties of the resulting product are largely unaffected and their magnetism is retained. Since the NiMn alloy composition provides higher densities, it can also be desirable to use NiMn as the sintering medium, and to thereby retain the magnetic properties of the product. Hence, the magnetic properties of the FeW or other magnetic material in the product mix can be retained even if the sintering medium reacts with the magnetic material by using a particle size that does not react completely but is still sintered densely. Among the several advantages of using a larger particle size FeW are: (1) Since FeW is quite hard and not very friable it is much easier to obtain a larger particle size and therefore is therefore generally less costly to grind to a large size. (2) The density of FeW is about 13.9 g/cc and, if it is used in a larger size, contributes to the overall density by the reduction of porosity or potential porosity. (3) Larger particle sizes tend

<table>
<thead>
<tr>
<th>Ex#</th>
<th>Ni</th>
<th>Mn</th>
<th>FeW</th>
<th>W</th>
<th>Firing Temp</th>
<th>Atmos</th>
<th>Time</th>
<th>Dnsy</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>-7.7</td>
<td>-20.5</td>
<td>-41.0</td>
<td>-30.8</td>
<td>1200° C.</td>
<td>Ar</td>
<td>15 m</td>
<td>10.8 yes</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>-6.4</td>
<td>-17.0</td>
<td>-34.0</td>
<td>-42.6</td>
<td>1200° C.</td>
<td>Ar</td>
<td>15 m</td>
<td>11.4 yes</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>-4.8</td>
<td>-12.7</td>
<td>-25.4</td>
<td>-57.1</td>
<td>1200° C.</td>
<td>Ar</td>
<td>15 m</td>
<td>12.1 yes</td>
<td></td>
</tr>
</tbody>
</table>
In Examples 23-24 are shown other examples for retaining magnetism to a higher degree with larger ferromagnetic particles. The FeW particle sizes are from +100 mesh to -20 mesh.

Each of these examples (23 and 24) were highly ferromagnetic and would be easily detected by a magnet in nondestructive field testing of a shotshell for magnetic shot. Other tests with still larger FeW particle sizes, showed that the retained magnetism increases with the particle size until the particles were too large and allowed open porosity. The presently known optimal size for the FeW particles is found to be between greater than 200 mesh and less than 10 mesh, although mixtures of large mesh size particles can still provide low porosity and high density. Where magnetism is desired with a porous structure, this can be readily obtained with a large mesh sizes, even up to and exceeding 10 mesh.

Examples 25-32 demonstrate the use of CuMn. Cu was previously considered to be eliminated from use because of known toxicity. More recent tests have shown that the toxicity to waterfowl of Copper is dependent on the residence time in the gizzard and the otherwise in the bird. Government approval has been granted to use Cu containing shot so tests have been conducted using CuMn, because of the low melting point of such alloys and the ability of Mn to act as a sintering aid.

Examples 33-36 shows examples CuSn as a sintering aid.
With no shrinkage this composition can be used to fire near net shape of the mold used. This composition has application where no shrinkage is important and little or no density increase from the formed part upon firing.

Example 37 is an example of Sn10Zn sintering. This example is sintered at 1200°C for 1 hour in Ar. Zinc is known to be especially toxic to waterfowl, so this example composition may have application only in non-hunting uses, although the dwell time in the digestion system for ingested shot may be short enough to make this a viable application, especially with low levels of Zn in the alloy. This alloy has a very low melting point at 198.5°C and there are no intermetallics formed, which may harden the alloy more than the initial introduction of Zn. This alloy did not wet the W and FeW component powders so no sintering took place and the alloy is assumed to have limited effectiveness, unless a wetting flux such as flux is applied. Fluxes are available for no lead solders, which this alloy is similar to, and may work with the alloy. A Sn10Zn4Mn alloy was also used to see if the Mn additive can solve the wetting problem in the Sn10Zn alloy described above. The result was that the wetting did occur but that no significant sintering occurred. The result for this composition was similar to that of CuSn, in that it can be used for making a solid low strength piece at a near net forming shape.

Examples 38-43 are of the use of the alloy MnSn, which has a low melting point, as does MnSnCu and MnZn.

<table>
<thead>
<tr>
<th>Ex#</th>
<th>Cu</th>
<th>Mn</th>
<th>W</th>
<th>Temp</th>
<th>Atm</th>
<th>Time</th>
<th>Dnsity</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>-8.3</td>
<td>-16.6</td>
<td>0</td>
<td>-33.3</td>
<td>-16.7</td>
<td>1200°C</td>
<td>Ar 1 hr</td>
<td>some</td>
</tr>
<tr>
<td>39</td>
<td>-4.7</td>
<td>-16.6</td>
<td>0</td>
<td>-33.3</td>
<td>-16.7</td>
<td>1200°C</td>
<td>Ar 1 hr</td>
<td>yes</td>
</tr>
<tr>
<td>40</td>
<td>-4.3</td>
<td>-17.4</td>
<td>0</td>
<td>-34.8</td>
<td>-60.9</td>
<td>1200°C</td>
<td>Ar 1 hr</td>
<td>some</td>
</tr>
<tr>
<td>41</td>
<td>-3.7</td>
<td>-14.8</td>
<td>0</td>
<td>-29.6</td>
<td>-51.8</td>
<td>1200°C</td>
<td>Ar 1 hr</td>
<td>yes</td>
</tr>
<tr>
<td>42</td>
<td>0</td>
<td>-17.4</td>
<td>0</td>
<td>-4.3</td>
<td>-34.8</td>
<td>1200°C</td>
<td>Ar 1 hr</td>
<td>porous</td>
</tr>
<tr>
<td>43</td>
<td>0</td>
<td>-16.0</td>
<td>0</td>
<td>-4.0</td>
<td>-80.0</td>
<td>1200°C</td>
<td>Ar 1 hr</td>
<td>porous</td>
</tr>
</tbody>
</table>

The magnetism in the samples with Sn and the additional magnetism in the sample with Cu provides additional compositions of interest. Particular effects of several of these low melting alloys have been observed. Cu, Sn and to a certain degree Zn, none of which have much solubility in or reactivity with Fe or W, appear to inhibit sintering or densification while many compositions containing Mn have densification enhanced and the more Mn in the composition, the more sintering is provided, so long as the melting point of the mixture or alloy is below the sintering temperature of 1200°C, chosen for the economics of production.

Examples 44-59 show the use of additional alloys for sintering dense materials.

<table>
<thead>
<tr>
<th>Ex#</th>
<th>Cu</th>
<th>Mn</th>
<th>W</th>
<th>Temp</th>
<th>Atm</th>
<th>Time</th>
<th>Dnsity</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>-33.3</td>
<td>-16.6</td>
<td>0</td>
<td>-50.0</td>
<td>1200°C</td>
<td>Ar 15 m</td>
<td>9.5</td>
</tr>
<tr>
<td>45</td>
<td>-22.2</td>
<td>-11.1</td>
<td>0</td>
<td>-66.6</td>
<td>1200°C</td>
<td>Ar 15 m</td>
<td>10.9</td>
</tr>
<tr>
<td>46</td>
<td>-16.6</td>
<td>-8.3</td>
<td>0</td>
<td>-75.0</td>
<td>1200°C</td>
<td>Ar 15 m</td>
<td>11.2</td>
</tr>
<tr>
<td>47</td>
<td>-13.3</td>
<td>-6.6</td>
<td>0</td>
<td>-80.0</td>
<td>1200°C</td>
<td>Ar 15 m</td>
<td>11.9</td>
</tr>
</tbody>
</table>

These results are obtained even though Cu is more dense, 8.96 g/cc, than Mg at 7.43 g/cc. The alloys in these examples are less dense than the lighter of the two components when mixed at a 50-50 weight percentage. This shows that when used as a sintering alloy for W and W plus FeW, the higher Mn content, the less dense the resulting metal and the higher the sintered density. This shows the “sintering aid” effect of the Mn, since even thought the CuMn alloy is less dense with higher Mn sintered product with W is denser.

Examples 60-63 show compositions with Mn, Ni and Graphite (C) without W, only FeW.
This demonstrates the present most economical composition that still provides corrosion resistance and a high density.

Example 64 shows a composition with the use of oxides of FeW.

The use of oxides provides similar results to the mixtures without oxides. This is extremely important to the use of starting materials as they can be either FeW as a compound or the burned oxides of FeW. The easiest way to reduce the particle size to a good range for manufacture may be to "burn", or oxidize the FeW in air or oxygen at high temperature and then screen and add the burned material to the process, either as the total component or mixed with metallic FeW in the chosen proportions. The advantages are lower cost materials and ease of production.

Referring now specifically to FIG. 1, which details the present steps of the processing method of this invention. Carbon is loaded 101 for use in the composition. In some present preferred embodiments this step 101 includes mixing the loaded carbon with a binder in approximately equal proportions by weight, alternatively more or less binder may be used to accommodate the manufacturing technique and to improve even carbon distribution. In some alternative embodiments of the invention other materials, including iron, manganese, nickel, and/or chromium, typically in a micro powder form, are also mixed with the carbon and binder, as a part of this step 101. For the purposes of the disclosure, carbon or carbon-like material is defined as a composition useful as a sintering aid with tungsten, including a carbon composition, such as carbon black, graphite, nano tubes and related carbon forms, diamond, charcoal, hydro carbon and the like and other good sintering aid materials such as tin, bismuth, aluminum and the like.

A sintering aid is an element, compound or the like that when added to a powder to be sintered, aids the sintering process such that some desired physical property is attained. Sometimes a sintering aid may become a part of the final product and other times it may vaporize off, or otherwise be eliminated, after it has acted as an aid. In some embodiments the sintering aid may be reduced or eliminated in a pre-sinter or post-sinter step. In some embodiments, the sintering aid is incorporated into the sintered piece. A property commonly attained with a sintering aid is higher density achieved with lower processing (sintering) temperatures, shorter sintering time or both. Another sometimes desirable property is the drawing together of particles and the enhancement of densification in all directions, to reduce or avoid slumping and distortion. This property can be achieved with lithium compounds as a sintering aid. Another sometimes desirable properties are the maintenance of a designed shape of the final product through production, along with densification at lower sintering temperatures and shorter firing times. These properties can be achieved with the addition of carbon as a sintering aid.

Reactive sintering can be employed in this invention. Reactive sintering is a method of sintering whereby some or all of the components chemically react, thereby resulting in a sintered product that has improvements or enhancements. An example of this reactive sintering is the carbon/FeW reaction, in which the carbon reacts with the FeW alloy and becomes a part of the final product during sintering. It is presently believed by the inventor, that this reaction contributes to the densification of the product at lower temperatures and with shorter firing times, that is, the reactive sintering acts also as a sintering aid. When the reaction of carbon with oxides of FeW occurs, there is some reactive sintering along with the chemical reaction that occurs. In one reaction, the carbon reacts with the oxygen that is combined with the FeW and thereby producing a carbon monoxide and/or carbon dioxide gas, while the excess carbon reacts with the FeW that has been left behind. The reactions in this example occur almost simultaneously, thereby likely enhancing both the reaction sintering and sintering aid effects. A combination of these effects is likely to occur in this invention whether the starting material is ferroalloy or oxidized ferroalloy.

The reactive sintering, which can but need not always be used in this invention, is different from melting or liquid phase formation in a sintering step. Often a liquid or mushy phase may be formed during sintering, that may or may not aid the sintering step. Sometimes there is merely slumping that does not necessarily densify, and does not tend to hold the shape of the part being sintered. In most sintering operations it is desirable to hold the shape of the product, although substantial shrinkage often accompanies firing and densification. If the molten phase assists densification like a sintering aid by causing densification in all dimensions equally without slumping or distortion of the original shape, then the molten phase itself can be considered a sintering aid.

With regard to sectional density, it is known that typically the sectional density of round objects changes with the diameter of the object as a function of object volume. Round shotshell shot has a sectional density that decreases with decreasing size of the shot. Accordingly, for example, if #2 shot and #6 shot are fired from the same gun at the same initial velocity, the #6 shot will slow down faster than the #2 shot. This difference can be important for accurate firing at long ranges. This invention can make different densities of shot and can therefore be used to maintain consistent density regardless of shot size and can therefore minimize or eliminate the differences in deceleration of different shot sizes. This advantage can have particular importance when loading

<table>
<thead>
<tr>
<th>Ext</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>FeW</th>
<th>Temp</th>
<th>Atm</th>
<th>Time</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>-6.0</td>
<td>-1.9</td>
<td>-1.2</td>
<td>-82.7</td>
<td>1200° C.</td>
<td>H</td>
<td>15 m</td>
<td>10.2</td>
</tr>
<tr>
<td>61</td>
<td>-5.9</td>
<td>-2.0</td>
<td>-1.4</td>
<td>-82.5</td>
<td>1200° C.</td>
<td>H</td>
<td>15 m</td>
<td>10.8</td>
</tr>
<tr>
<td>62</td>
<td>-5.8</td>
<td>-2.1</td>
<td>-1.6</td>
<td>-82.3</td>
<td>1200° C.</td>
<td>H</td>
<td>15 m</td>
<td>11.4</td>
</tr>
<tr>
<td>623</td>
<td>-5.9</td>
<td>2.0</td>
<td>1.8</td>
<td>-82.1</td>
<td>1200° C.</td>
<td>H</td>
<td>15 m</td>
<td>11.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ext#</th>
<th>Oxide</th>
<th>C</th>
<th>FeW</th>
<th>Temp</th>
<th>Atm</th>
<th>Time</th>
<th>sty</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>-17.2</td>
<td>-4.0</td>
<td>-78.7</td>
<td>1200° C.</td>
<td>H</td>
<td>15 m</td>
<td>.5</td>
<td>no</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ext#</th>
<th>Oxide</th>
<th>C</th>
<th>FeW</th>
<th>Temp</th>
<th>Atm</th>
<th>Time</th>
<th>sty</th>
<th>Mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>-17.2</td>
<td>-4.0</td>
<td>-78.7</td>
<td>1200° C.</td>
<td>H</td>
<td>15 m</td>
<td>.5</td>
<td>no</td>
</tr>
</tbody>
</table>
different sizes of shot in the same shotshell, because with this invention, despite the differences in size, all the shot pellets will travel at the same speed and the pattern will tend to stay together. As the pattern stays together, the long range effectiveness is improved. Alternatively, in some commercial loadings, two or more different sizes of shot are used specifically to cause the pattern to “string”, that is, to lengthen out as it travels from the bore with the larger shot leading to the smaller shot. In some dual shot size loads, the larger shot is placed behind the small shot and may cause the larger shot to push through the smaller and disrupt the shot pattern. While pattern disruption or “stringing” of the pattern may be the objective in this type of load, with the density control of this invention this disruption or “stringing” can be minimized or enhanced in a controlled manner according to the shot pattern characteristics desired.

Presently, the preferred form of carbon is in the form of graphite powder, although alternative carbon sources or in some cases tin (Sn) can be substituted for the graphite in the mixture. The present binder is a binding composition such as Acrawax, Polyvinyl Alcohol (PVA), Paraffin or the like, although alternative binders as previously described can be substituted without departing from the concept of this invention. FeW is added 102 to the mixture of carbon and binder, presently in proportions of approximately 97% by weight FeW; 1.5% by weight of carbon and 1.5% by weight of binder. In alternative embodiments the iron in the FeW composition is replaced with one or more of Nickel; Manganese; Cobalt; Copper; Silver; Gold; Gallium; Germanium; Chromium; Vanadium; Nickel; Niobium; Molybdenum and the like, although generally not in sufficient quantities so as to lower the density of the final product. Currently, the FeW is provided in a mesh-200 powder form, or with an average particle size of 10 microns, with about 20% of the particles being substantially larger. Although FeW is typically provided in mesh sizes of 2” by down; 3/8” by down, 1/4” by down or in a range, such as minus 2” plus 1” or minus 3/4” plus 1/4”, the FeW is presently brought down to the desired size through the use of attrition mills, ball mills, jet mills, jaw crushers, hammer mills or any other customary technique for reducing the size of a material. After being reduced in size, a variety of techniques, including screens, gas classifiers and the like, can be used to assure that the corrector optimum size distribution is achieved. Blending can be used as necessary to achieve the desired average particle size. An alternative technique for reducing the size of the FeW, or similar material, is to oxidize the material in an appropriate furnace so that it changes form and is more easily attrited, ball milled, jet milled or otherwise reduced in average particle size. This oxidation process provides partially or completely oxidized FeW, which can then be classified for blending or mixing to the appropriate proportions. Moreover, this oxidized FeW, or other material, can also then be formed into a desired shape or loaded into a mold that will provide the desired shape after having been mixed with an appropriate amount of carbon and then fired in a hydrogen furnace. In such a furnace, the carbon and the hydrogen will then reduce the FeW oxide, and facilitate the sintering to the desired density. Since oxides have a larger volume than the FeW, or other substituted materials, there will be greater composition shrinkage, a characteristic that can be used to reach a desired density. The combination of carbon/binder and FeW is mixed 103 to an approximately uniform mixture. The resulting mixture is pelletized 104, presently using standard pelletization techniques well known in the art. In alternative embodiments, rather than pelletizing, the resulting mixture is poured into a mold to be molded, pressed or compacted into the desired shape and/or is extruded. The pelletizing technique presently used in this invention involves mixing the powders (typically FeW and carbon-like materials) with a binder material, and then processing the mixed material in a machine for rolling, tumbling or the like in order to cause the powders to adhere to each other and to grow into spheres, pellets, rods and the like. This process is also used to homogenize powder mixes. A wide variety of pellet sizes are possible using this pelletizing technique. This preferred pelletizing technique uses no compaction or pressure to form the pellets; rather it is similar to rolling a snowball until it is large enough to make a snowman.

In the molding alternative, the molding is accomplished by mixing the FeW powder and the Carbon-like material (typically graphite) and then pouring the resulting mixture into a mold of the desired shape for firing. The mixture in its mold is then fired. This firing of the mixture can be accomplished with one or more steps as necessary to achieve the desired result. For example, “green” material can be fired at just enough time and temperature to strengthen it sufficiently so that it can be further shaped before final firing, typically without the mold. This final firing stage may be done in the tungsten powder or in SiC grit or in graphite. The designation of SiC is not intended to indicate any particular proportion of the composition, nor is the designation of graphite intended to limit the forms of carbon.

The pressure or compaction alternative technique involves pressing or compacting the mixed powder (typically FeW and graphite, usually with a binder) in a die to form the desired shape, that is a product such as round pellets, bullets, milling media and the like. The green (“unfired”) pressing or compacted product is then typically fired, similar to the molded product, to either a complete or an intermediate stage, where further shaping can be accomplished with a stronger partially fired pellet, bullet or the like.

The extruded technique is another method of forming or making pellets, bullets and bullet cores, rods, milling media and the like. Mixed powders, with or without a binder, are forced through a die, which can be shaped and sized to give the desired cross section, and can be of nearly any desired length. When the desired length is reached the extrusion is sheared off and is processed further to shape the product into the desired shape. Again, the firing steps can include one or more firings as desired to further work or shape the product prior to final firing. The extrusion die can have a single or multiple openings. Extrusion, although not previously used in the manufacture of shotgun pellets or bullets, is well known in the production of products from ceramics to metals, to plastics and to foods. When extrusion is used to make the bullet cores, typically a follow on step of “swaging” is performed to finalize the shape and dimensions of the bullet, and/or to add a jacket to the core. In this invention, the extrusion technique will typically be used on a FeW, graphite and binder mixture. The extruded product may be rolled or shaped after shearing to specific desired lengths to complete the shaping of the pellet to the desired shape.

A Silicon-Carbide (SiC) composition is mixed 105 into the pelletized product to more evenly distribute the heat that is applied in the following steps. As an alternative, the SiC composition mixing step 105 can be substituted with step of mixing in tungsten powder, ferro-tungsten powder, tungsten-carbide powder or ferro niobium powder during sinter-
ing. Heat of approximately 600°C is applied 106 to the pelletized (or molded) mixture for about fifteen minutes to drive out the binder, if such binder is present. In some alternative embodiments, the choice of binder or the lack of a binder may make this step unnecessary. An application of additional heat of approximately, in one embodiment of 1150°C for approximately fifteen minutes is applied 107 to sinter the entire product into the pelletized form. These heating steps 106, 107, can include, in some embodiments, heating in a protective or reducing atmosphere. In the present embodiment it is desirable the temperature is maintained at or below 1200°C, because such lower temperatures dramatically reduce the production cost. Also, by sintering at a temperature at or below 1200°C, high densities with a smooth finish and little or no porosity may be achieved. The inventor has found that the addition of Mn or Ni with Carbon will enable the lowering of the sintering temperature to below 1200°C, may reduce the tendency of the resulting product to rust, but may also lower the resulting density to about 10.4 g/cc. However, the addition of both Mn and Ni combined with lowering the sintering temperature to about 1100°C, has been shown to retain magnetic properties of the product and to maintain densities in the 11.7 to 12.2 g/cc range. The sintering with carbon, presently in a graphite form, is used instead of melting because the pellet is first made and then is hardened, while melting requires higher processing temperatures and accordingly a high resulting manufacturing cost. In an alternative embodiment, tungsten powder, tungsten carbide, manganese nickel, ferro niobium and/or silicon carbide is added 108 as part of the sintering step 107 and thereafter sintered to reduce the likelihood of the final material to stick to itself. In some embodiments of this invention, this sintering step 107 is enhanced with small quantities of manganese. This sintering in of tungsten or tungsten carbide powder further increases the density of the resulting material and permits the alteration of the surface characteristics of the resulting material, as well as improving the heat distribution during sintering. Relatively large tungsten, tungsten carbide, ferro niobium or silicon carbide particle sizes are preferred for the added 108 powder because of the improved heat distribution characteristics of larger particles. For example, one present embodiment of the produced material is provided with a dimpled surface. In another embodiment of this invention, the sintering step also includes the sintering in of SiC powder in a relatively large mesh size. In alternative embodiments, both the temperatures, compositions and heating times are modified to produce product with different densities, strength, toughness or friability, or when alternative substitute materials are used. For example, if Sn is used instead of carbon, a sintering temperature of about 1050°C to 1200°C is appropriate. In this tin alternative, it is preferred to add tin prior to sintering and again when molten during sintering. Tin (Sn) or tin alloys can also be added after sintering to fill voids and increase density and to provide corrosion protection. After cooling, the resulting product is a pellet composed of a composition of matter consisting essentially of iron-carbide-tungsten (Fe₇₋₉C₆₋₉W₄₋₉), or in alternative embodiments, iron-tungsten-tin (Fe₇₋₉C₆₋₉W₄₋₉Sn₄₋₉) or iron-carbide-tungsten-tin (Fe₇₋₉C₆₋₉W₄₋₉Sn).  

In some alternative embodiments the sintering 107 includes a pre-sinter step followed by some machining (which may include grinding, drilling, rounding etc.) followed by a final sinter step to finalize the formation of the product. Also, in some alternative embodiments, the porosity as well as the density of the resulting product may be controlled through the addition 109, typically after the sintering step 107 with possible heat treating, of an additional material. Materials such as metals, plastics and the like, can be used to increase or decrease the final density of the product. Tin or other corrosion resistant metals, plastics, paints and the like can be added to increase corrosion resistance. Ductile materials, like Teflon, can also be added to cushion or reduce the surface hardness of the final product. In some embodiments of this invention, after sintering 107 color is added to provide a technique of identifying the shot, for example 54 is blue, 46 is red, etc., or color can be used to correspond to a weight, density, shape or size. A variety of surface coatings can also be added to make a slick, sticky or rough surface as desired. In some embodiments, a variety of additional materials, selected from the above may be combined in this 109 step to create a desired combination effect or use where a non-toxic material can be useful or required.  

As noted above, in alternative embodiments, where it is desirable to retain the magnetic properties of the resulting pellet(s) the firing (sintering) temperature is lowered from typically about 1200 degrees C. to about 1100 degrees C. and the firing time can be reduced by about 15 minutes. The lower temperature and/or reduced firing time can provide sintering without a complete reaction of the MnNi (which individually were typically added during the mixing step 103, although alternative could have been added during the mix with SiC step 105) with the FeW. In testing, the resulting pellet product retains its magnetic properties and has a density of between 11.7 and 12.3 g/cc.  

While the invention has been described with respect to certain specific embodiments, compositions and steps, it will be appreciated that many modifications and changes may be made by those skilled in the art without departing from the invention. It is intended, therefore, by the appended claims to cover all such modifications and changes as may come within the true spirit and scope of the invention.  

1. A method for manufacturing high-density materials, comprising:  
   combining nickel with manganese and a tungsten composition to form a mixture;  
   shaping said mixture;  
   sintering said mixture for a time of between about 1 to about 60 minutes at a temperature of from about 1030°C to about 1200°C to produce a high-density low toxicity material.  

2. The method of claim 1, wherein said nickel, said manganese, and said tungsten are in powdered form.  

3. The method of claim 1, further comprising adding a sintering aid to said mixture.  

4. The method of claim 3, further comprising heating said mixture, prior to said sintering.  

5. The method of claim 1, further comprising adding a binder to said mixture.  

6-10. (canceled)  

11. The method of claim 1, wherein said tungsten composition consists of tungsten.  

12. The method of claim 3, wherein said sintering aid is selected from the group consisting of tin, bismuth, aluminum, carbon black, graphite, nano tubes, diamond, charcoal and hydro carbon.  

13. The method of claim 1, wherein said tungsten composition further comprises a material selected from the group
consisting of Iron; Nickel; Manganese; Cobalt; Copper; Silver; Gold; Gallium; Germanium; Chromium; Vanadium; Niobium; Molybdenum.

14. The method of claim 1, wherein said sintering occurs in a protective environment.

15. The method of claim 4, wherein said heating further comprises heating in a protective environment.

16. The method of claim 5, wherein the ratio of nickel to manganese in said mixture ranges from about 40% nickel to 60% manganese to about 60% nickel to about 40% manganese.

17. A method for manufacturing high-density non-toxic materials, comprising:
   combining a carbon-based material, nickel, and manganese with a tungsten composition to form a tungsten-carbon mixture;
   shaping said tungsten-carbon mixture;
   sintering said tungsten-carbon mixture at a temperature in the range of about 1030° C. to about 1200° C. to produce a high-density low toxicity material.

18. The method of claim 17, further comprising adding a sintering aid to said tungsten-carbon mixture.

19. (canceled)

20. The method of claim 17, wherein said sintering is performed in a protective atmosphere.

21. The method of claim 17, wherein said sintering is done at about 1100° C.

22. The method of claim 17, wherein said produced high-density low toxicity material is a generally round pellet.

23. The method of claim 17, wherein said produced high-density low toxicity material is a generally round dimpled pellet.

24. The method of claim 17, wherein said carbon-based material is graphite and said sintering step sinters said graphite to said tungsten composition.

25-46. (canceled)

47. The method of claim 17, further comprising selecting the hardness of said produced high-density low toxicity material by adjusting the temperature of said sintering step.

48-50. (canceled)

51. A method comprising:
   forming a mixture consisting essentially of nickel, manganese and a tungsten composition;
   shaping said mixture;
   sintering said mixture for a time of between about 1 to about 60 minutes at a temperature of from about 1030° C. to about 1200° C. to produce a high-density low toxicity material.

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