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(72) Inventors:
• **Molinari, Alberto**
38016 Mezzocorona (prov.of Trento) (IT)
• **Anguillesi, Dimitri**
56016 S.Giovanni Alla Vena Di Vicopisano (IT)

(30) Priority: **26.07.2002 IT MI20021670**

(74) Representative: **Modiano, Guido, Dr.-Ing. et al**
Modiano & Associati,
Via Meravigli, 16
20123 Milano (IT)

(71) Applicant: **Erre-Vis S.p.A.**
56030 Calcinaia, (Prov. of Pisa) (IT)

(54) **Spheroidal cast iron particulary for piston rings and method for its production**

(57) A spheroidal cast iron, particularly for piston rings for pistons of engines, with a particular alloyed chemical composition and subjected to a heat treatment known as austempering, which comprises an austenitization treatment followed by an isothermal hardening treatment, has mechanical characteristics that are com-

parable with those of the steel currently used to produce piston rings, while maintaining the best tribological and self-lubrification characteristics of spheroidal cast irons, and a process suitable to obtain said spheroidal cast iron.

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Description

[0001] The present invention relates to a spheroidal cast iron that can be used for example to produce piston rings for pistons that work inside the cylinders of engines, and to a method for obtaining said spheroidal cast iron.

[0002] It is known that spheroidal cast iron is used in many fields, such as rails for trains, machine beds, sliding guides, engine cylinders, gears, et cetera.

[0003] In these fields, the general requirements of the cast iron are mostly to have a high hardness and therefore a high tensile strength, good resistance to wear and a low thermal expansion coefficient.

[0004] For example, an austempered spheroidal cast iron is known from European patent application 0144907 which is used to produce mechanical parts and is suitable for producing thin parts as well as details that have a thick wall cross-section; this patent also describes that when producing this type of spheroidal cast iron there are inevitable impurities or porosities in the cast iron.

[0005] For this reason, this type of cast iron cannot be able to deal with the elasticity and strength problems that characterize use for example in the field of piston rings for pistons, since it is not produced according to a melting process that allows its use for piston rings. Piston rings are in fact provided from thin castings and accordingly a cast iron that has porosities, despite having even excellent mechanical qualities, cannot meet the necessary conditions of elasticity, deformability, mechanical strength and fatigue strength that are required for the use and reliability of the piston rings.

[0006] A use of spheroidal cast iron that is specifically suitable for the field of piston rings is already known from patent GB 840490; this patent introduced the possibility to provide piston rings for engines made of spheroidal cast iron having a fully bainitic matrix. This patent in fact describes the capability to perform spheroidal cast iron castings for piston rings that are subsequently heat-treated until a fully bainitic metallurgical matrix is provided; it must be known that metallurgical structures such as bainite and martensite, despite having high ultimate tensile strength characteristics, have low toughness and therefore low impact strength.

[0007] It must be known that piston rings of internal-combustion engines are currently divided into two types: cast-iron piston rings and steel piston rings.

[0008] Cast-iron piston rings, which in turn can be made of lamellar graphite cast iron or spheroidal cast iron, are obtained from castings that are subsequently worked on machine tools. The particular workability of cast iron in fact allows to obtain piston rings that have complex geometric shapes that can adapt in an optimum manner to the internal shape of the cylinder and to the shape of the piston, achieving excellent oil-tightness, limiting blow-by in four-stroke engines, facilitating slide and therefore allowing to achieve very high sliding speeds and limited wear, all this in relation to the particular thermal expansions of the cylinder, which work in contrast with the piston, and to the reduced penetrations of the piston ring in the transfer ports of two-stroke engines.

[0009] Another substantial characteristic of cast iron piston rings is that the graphite structure of cast iron allows to have excellent tribological characteristics and high thermal conductivity, such as to allow an excellent self-lubricating capability, thus providing a better slide, a low friction coefficient and accordingly less wear in operation than achievable with steel piston rings.

[0010] One must consider that spheroidal cast iron piston rings, like all components made of spheroidal cast irons, have mechanical and strength characteristics that are in any case better than those of piston rings made of lamellar graphite cast irons, since in lamellar graphite the vertices of the lamellas produce a series of local stress intensification effects which tension and weaken said structure.

[0011] Steel piston rings have a far greater ultimate tensile strength, yield strength, impact strength and toughness than cast iron piston rings, and accordingly can be used without problems even in conditions of very intense physical and mechanical stress, which cannot be withstood by piston rings made of the spheroidal cast irons currently used in this sector. On the other hand, steel piston rings are not easy to work and in view of their microstructure do not have self-lubricating characteristics: for this reason they require the use of antifriction surface coatings in order to be used without problems inside engines.

[0012] The aim of the present invention is to provide a spheroidal cast iron that can be used particularly for example in the production of piston rings and is capable of eliminating or substantially reducing the drawbacks of the known art.

[0013] Within the scope of this aim, an object of the invention is to provide a spheroidal cast iron that can be used in particular for example to provide piston rings and is capable of eliminating or substantially reducing the differences with respect to the steels currently used in the specific sector in terms of mechanical strength while maintaining the above cited typical advantages of spheroidal cast iron with respect to steel.

[0014] Within the scope of this aim, an object of the invention is to provide a spheroidal cast iron that allows to produce piston rings for pistons whose mechanical characteristics are substantially equal to those of piston rings made of steel and possibly have reduced resisting cross-sections with respect to those of current cast iron piston rings, and has a thermal expansion coefficient that is comparable to the coefficient of steel ($\lambda = 12 \times 10^{-6} / ^\circ\text{C}$).

[0015] An object of the invention is in fact to provide a spheroidal cast iron that can be used to manufacture elastic

elements that can be obtained by virtue of specific castings for cast parts that are small and have a narrow cross-section, shaped like a closed ring, by means of a single cluster casting or centrifugal casting, for example in order to provide piston rings for pistons that work within the cylinders of engines.

[0016] Another object of the invention is to provide a spheroidal cast iron that allows to achieve a high normal modulus of elasticity.

[0017] Another object of the invention is to provide a spheroidal cast iron that allows to produce elements that have a uniform and homogeneous hardness along the entire peripheral extension of the casting.

[0018] Another object of the invention is to provide a cast iron that must have a high ultimate tensile strength; the piston ring, for example, is in fact subjected to intense high-frequency dynamic stresses, and therefore in order to be able to work without breaking, the cast iron must have a high tensile strength and yield strength. In particular, the spheroidal cast iron according to the invention is suitable for manufacturing piston rings for modern internal-combustion engines with a very high performance and low pollution, and therefore the austempering treatment has determined precise values of austenite and bainite that are suitable for this kind of use, with UTS values of 1300 N/mm² and Rp_{0.2} of 1100 N/mm².

[0019] Another object of the invention is to provide a cast iron that is capable of withstanding use at high temperature without tempering.

[0020] Another object of the invention is to provide a cast iron that is capable of high resistance to wear.

[0021] Another object of the invention is to provide a cast iron that has a high fatigue strength.

[0022] Another object of the invention is to provide a cast iron that has high impact strength.

[0023] Another object of the invention is to provide a particular melting process that allows excellent microstructural uniformity in all castings and allows to eliminate porosities and entrainments of inclusions along the entire peripheral region of the casting ring.

[0024] This aim and these and other objects that will become better apparent hereinafter are achieved by an austempered spheroidal cast iron, which comprises, in addition to Fe, the following elements: C, Si, P, S, Mn, Cu, Mo, and is characterized in that it furthermore comprises Cr, Ni, RE, Co, and at least one of the following elements: Ti, V, Nb.

Advantageously, said austempered spheroidal cast iron comprises the elements cited above in the following percentages by weight, while the remaining percentage is constituted by Fe: 3.20 - 4.20% C, 2.00 - 4.00% Si, up to 0.10% P, up to 0.10% S, up to 0.20% Mn, up to 1.30% Cu, up to 0.50% Cr, 1.7% to 5.00% Ni+RE, 0.10 - 2.00% Mo, 0.1% to 2.0% of at least one among Ti, V and Nb, up to 0.20% Co.

[0025] This aim and these and other objects are also achieved by an austempered spheroidal cast iron obtained by means of a process that is characterized by the following steps: a step for preparing the basic cast iron with a controlled chemical composition; a second step for melting the basic cast iron with verification of the preset chemical composition; a subsequent step for adding the intended alloying chemical elements; a step constituted by two successive inoculations of spheroidizing agents; a final step for solidification of the molten material.

[0026] Advantageously, said spheroidizing agents used in the inoculation step of the method for obtaining the cast iron according to the invention are constituted by a base of silicon and other elements such as Mg, Ca, Ce, Ta, Sr, Al and RE.

[0027] Further characteristics and advantages of the invention will become better apparent from the description of a preferred but not exclusive embodiment of the cast iron according to the invention, illustrated by way of non-limitative example hereinafter.

[0028] The spheroidal cast iron according to the invention has the following chemical composition, in which the individual elements are expressed as a percentage by weight, while the remaining percentage is constituted by iron Fe: 3.20 - 4.20% C, 2.00 - 4.00% Si, up to 0.10% P, up to 0.10% S, up to 0.20% Mn, up to 1.30% Cu, up to 0.50% Cr, 1.7% to 5.00% Ni+RE, up to 2.00% Mo, 0.1% to 2.0% Ti+V+Nb, up to 0.20% Co. Optionally, the composition of the cast iron according to the invention can also comprise B, Ca and other elements up to an overall maximum of 1.00%.

[0029] The spheroidal cast iron particularly for producing piston rings according to the invention has a bainitic austenitic matrix, high impact strength, high normal modulus of elasticity, high mechanical strength, and very precise values of measurement of the graphite spheroids and low values of roundness and roughness of spheroids and a thermal expansion coefficient that can be compared with that of steel.

[0030] In order to allow use of a given type of cast iron for example to produce piston rings for motors, said cast iron must in fact have a series of required fundamental characteristics, on penalty of nonfunctionality of said piston rings.

[0031] The present invention therefore relates to a spheroidal cast iron, which is particularly optimized for the production of mechanical elements that must have characteristics of elasticity, good resistance to fatigue and wear, as required for example for piston rings of internal-combustion engines, and furthermore has important properties of impact strength and toughness: spheroidal cast irons with a non-ferrite matrix, even not specifically for piston rings, that achieve appreciable impact strength values are in fact not currently known.

[0032] To make said spheroidal cast iron suitable for use, for example, for piston rings, in addition to having a specific chemical composition as cited above, first of all the raw materials must be selected according to very precise specifi-

cations, and said materials be free from impurities or elements that can cause degeneration of the final structure of the casting.

[0033] The structure that must be obtained for use for example in piston rings must in fact have a spheroidal graphite with uniform distribution throughout the cross-section of the casting and with spheroid sizes from 5 to 8 (according to ISO 945 standard "Cast iron: Designation of microstructure of graphite").

[0034] The casting matrix that must be obtained in castings for piston rings must be predominantly pearlitic, with ferrite areas, in order to have an optimum subsequent austempering treatment.

[0035] The mechanical characteristics cited above are achieved by the spheroidal cast iron according to the invention both by controlling its chemical composition and by identifying optimum melting and austempering processes.

[0036] In the production of piston rings, for example, the high normal modulus of elasticity of the is fundamental so that it applies a contact pressure (tangential force) against the walls of the cylinder in which it is installed, said contact pressure being required in order to ensure the gas-tightness of the combustion chamber. Furthermore, a high elastic modulus is required so that the piston ring does not remain permanently (plastically) deformed following the extensive deformations required for insertion in the piston groove. The normal modulus of elasticity E of the cast iron according to the invention can range from 150,000 to 200,000 N/mm².

[0037] In order to obtain this value of the normal modulus of elasticity E, very specific austempering times have been determined which vary from 30 to 150 minutes, since short times would entail high elasticity but also high brittleness, while long times entail high toughness but a low modulus of elasticity.

[0038] In order to obtain the intended mechanical and physical characteristics for the spheroidal cast iron according to the invention, it is fundamentally important to provide a melting process that allows excellent microstructural uniformity on all the castings and the elimination of porosities and entrainments of inclusions on the entire peripheral region of the casting ring. Furthermore, as mentioned, the piston rings produced with the spheroidal cast iron according to the invention must have uniform and homogeneous hardness along the entire peripheral extension of the casting.

[0039] For these reasons, a particular and clearly defined casting process has been identified which allows to have in single-cast rings or in centrifuged castings uniform cooling and microshrinkage over the entire peripheral region of the ring, so as to obtain uniform and even hardness along the entire peripheral distribution of the piston ring even after the austempering treatment, with hardness values comprised between 103 and 115 HRB (250-600 HV_{0.1} on the Vickers scale). A particular casting process has been studied and optimized in order to minimize segregations of carbon, manganese, silicon and molybdenum, so as to avoid the forming of "blocky austenite", whose presence gives brittleness to the structure, since these are macroformations of unstable residual austenite which tend to convert to martensite under stress.

[0040] For this reason, ferrite in an amount exceeding 1% must not be present in the metallographic matrix of the material.

[0041] The high ultimate tensile strength required of the cast iron according to the invention is achieved through control of the chemical composition of the cast iron but also through control of the heat treatment. In particular, it is noted that it is necessary to ensure that an amount of residual austenite greater than 20% and lower than 40% is present inside the matrix of the material.

[0042] The other mechanical characteristics required of the cast iron according to the invention are, as mentioned, high resistance to wear, high fatigue strength, and high impact strength.

[0043] As regards resistance to wear, it is in fact advisable to note that the piston ring must have a high resistance to wear, which is suitable to ensure the durability of the performance and of the reliability of the engine in which it is used; for this reason, a particular chemical composition of the cast iron according to the invention has been identified, with alloy elements such as Ti, V and Nb, which are capable of controlling the submicroscopic size of primary carbides and their uniform distribution in the primary solidification structure.

[0044] The spheroidal cast iron according to the invention is characterized by a specific chemical composition that is optimized in order to provide, in combination with the heat treatment, a submicroscopic precipitation of primary carbides MC, which are uniformly distributed in the primary solidification structure, which compensates for the effect of reducing wear resistance caused by the presence of the austenite within the structure and due to the fact that the wear coefficient of austenite is higher than that of bainite and martensite.

[0045] This requires the presence, in the chemical composition, of particular quantities of specific elements such as Ti, V and Nb, which form these carbides.

[0046] For this reason, a particular distribution of spheroids inside the metallographic matrix has been provided, with a concentration between 6 and 12%, such as to ensure a high self-lubricating capability, and a particular chemical composition has been identified with alloy elements such as Ti, V and Nb and Mo, which allow high resistance to wear even with permanent use at high temperature.

[0047] As regards fatigue strength, it is noted that the piston rings must have a high fatigue strength due to the extremely intense stresses that the high rotation rates (rpm) of engines produce (up to approximately 24,000 rpm on modern two-stroke engines and approximately 18,000 rpm for modern four-stroke engines), so as to ensure the dura-

bility and reliability of the engine in which the piston ring is used.

[0048] For this reason, a particular distribution of spheroids inside the metallographic matrix has been provided in order to increase the fatigue life of piston rings obtained with the spheroidal cast iron according to the invention.

[0049] As mentioned, a particular chemical composition has been identified, with alloy elements such as Ni, Ti, V and Nb capable of controlling the submicroscopic size of the primary carbides; moreover, a particular and clearly defined melting and casting process has been identified which is capable of providing graphite spheroids of controlled roundness, expressed in terms of ovalization ($D_{\max}/D_{\min}$), between 1.0 and 1.4, thus ensuring a low coefficient of stress intensification. Another parameter for characterizing graphite spheroids is roughness, expressed as $\text{Roughness} = (\text{Perimeter})^2 / (4 \cdot \pi \cdot \text{Area})$, which in this case must be comprised between 1.0 and 1.3 in order to ensure a low stress intensification coefficient.

[0050] Another object of the invention is to provide a spheroidal cast iron with high impact strength. For a conventional austenitic-bainitic cast iron, values of impact strength higher than 15 joule are generally not observable.

[0051] With the present invention, a new type of cast iron has been sought which would have high impact strength values, so as to be able to produce piston rings such as to withstand the very intense stresses that the high rotation rates (rpm) of engines cause during the passage of said piston ring on the transfer ports in two-stroke engines and to withstand high-frequency vibration inside the piston groove in modern four-stroke engines, so as to ensure the durability and reliability of the engine in which the piston ring is used.

[0052] It has been demonstrated that the cast iron according to the present invention has a Charpy impact strength of 80 to 165 joule.

[0053] To achieve this result, a particular chemical composition has been identified, with alloy elements that are suitable to toughen the structure, and a particular and clearly defined melting and casting process has been identified which is capable of providing cross-sections of the castings without porosities, pinholes or impurities.

[0054] For this reason, embrittling elements such as Mn, Cu, Al, Pb and W have been kept within narrow ranges and at the same time inside the metallographic matrix of the material there must be, in accordance with what was noted earlier, an amount of residual austenite that is higher than 20% and lower than 40%.

[0055] Furthermore, also in order to achieve these impact strength values it is important to keep under control the shape parameters of the graphite spheroids, i.e., the ovalization and roughness mentioned earlier, which must be kept within the cited values in order to ensure a low stress intensification coefficient.

[0056] As mentioned earlier, the cast iron according to the invention must be capable of withstanding use at high temperatures without tempering. The piston ring, for example, is in fact used in internal-combustion engines at high temperatures, and it is clearly necessary for the piston ring not to lose its characteristics of elasticity and mechanical strength during use. One of the weak aspects of austempered cast iron is high sensitivity to tempering, since at a high temperature the austenitic-bainitic structure tends to be converted according to the TTT curve into mixed bainitic-sorbitic structures.

[0057] For this reason, a specific range of austempering temperature and time has been determined in order to avoid tempering said piston ring due to holding at high temperatures (250-400 °C).

[0058] Furthermore, the particular chemical composition that has been identified, which includes alloy elements such as Ni, Mo, Ti, V and Nb, and the particular melting process are very important for this object as well, allowing to achieve a high mechanical strength of the piston rings during use at high temperature, and so is great insensitivity to tempering, combined with high resistance to wear.

[0059] The spheroidal cast iron according to the present invention has been devised with a production process in which the fillers and all those refinements that are indispensable to achieve, after melting, the physical/chemical characteristics described above, have been studied specifically; the mechanical characteristics are instead achieved after a heat treatment, devised exclusively in order to optimize the structures and mechanical characteristics of small-size, small-section castings.

[0060] A preferred but not exclusive embodiment of the process for melting the spheroidal cast iron according to the invention is described hereafter and is illustrated by way of non-limitative example.

[0061] The spheroidal cast iron according to the present invention has been devised by taking into account that the castings to be performed with said cast iron are individual cluster castings or centrifuged castings with cross-sections that vary from 2 mm² to 50 mm², meant to make compression rings for all internal-combustion engines.

[0062] The filler used to obtain these structures has been conceived by taking into account some important considerations regarding the production of spheroidal cast iron, such as: composition of the basic alloy, spheroidizing pre-treatment, percentage of alloy added, inoculation, final chemical composition of the spheroidal cast iron, microstructure, mechanical properties.

[0063] In particular, the chemical analysis has been verified carefully, making sure that in the basic cast iron there were no elements that could damage the spheroidization of the graphite, since a graphite distribution that is not uniform or not perfectly regular in the shape or dimensions of the spheroids would entail a degradation of the mechanical characteristics of the piston ring produced starting from said basic cast iron.

[0064] Furthermore, the entrainment of molding sand or other impurities in the casting, caused for example by inadequate cooling gradients and therefore by vortical or scarcely fluid motions of the liquid metal, would entail on the casting, and therefore on the piston ring, regions of high brittleness at risk of breakage once said piston rings are subjected to external stresses during i use.

[0065] The determination of the basic master alloy for obtaining the spheroidal cast iron is therefore particularly important: some chemical elements are in fact distinctly dangerous in a cast iron for piston rings, and if they exceed a limit value of concentration in the master cast iron they hinder the nodulization of the graphite.

[0066] The limit values of these elements are considered to be contents of:

Pb <0.1 % Sb <0.1 % Al <0.2 % S <0.2 %
Bi <0.1 % P <0.1 %

For other impurities, their total sum must not exceed 0.2%.

[0067] During the preparation and completion of the melting of the basic cast iron, samples are taken periodically in order to check its composition and therefore its compliance with the preset chemical analysis.

[0068] The intended chemical elements are then added.

[0069] In order to obtain the spheroidal cast iron according to the invention, with the specific microstructural characteristics described earlier, having graphite spheroids with size, shape and roughness clearly defined as described, after the addition of the intended chemical elements in the molten metal two successive inoculations of further elements are performed according to the methods known to the person skilled in the art.

[0070] These elements are constituted, in the specific case, by a combination of a mixture of metals that belong to the lanthanide group, known in metallurgy as "mischmetall", with many other metallic elements in the form of oxides. The combination of this mixture of lanthanides with oxides of other metals forms so-called rare earths (RE).

[0071] In the process for obtaining cast iron according to the present invention, said mixture of rare earths, which is used in metallurgy to produce alloys and superalloys, is used as inoculant, and its particular properties for control and purification of the microimpurities contained in the basic cast iron are used.

[0072] In particular, the melting process has been optimized by providing two successive inoculations that have the compositions specified hereafter merely by way of non-limitative example:

- in the first inoculation, the spheroidizing agents used are constituted by a base of silicon with Mg, Ca, Ce, Ta, and RE;
- in the second inoculation, there is again a base of silicon with Sr, Ca, and Al.

[0073] The percentages by weight of these elements, in the example considered, were by way of indication the following: Mg $\approx$ 3.2%, Ca $\approx$ 0.6%, Ce+Ta+RE $\approx$ 2.0%, Sr $\approx$ 0.8%, Ca<0.5%, Al<0.5%.

[0074] After the two described inoculations, the molten metal is solidified with a solidification time comprises between 50 and 400 seconds, depending on the cast cross-section.

[0075] To conclude the process thus described, the final analysis on the resulting cast iron casting should show the presence of the various elements according to the values described above and summarized in the following table:

Cast iron	C	Si	P	S	Mn	Cu	Cr	Mo	Ni+RE	Ti+V+Nb	Co
Minimum	3.2	2.0	0	0	0	0	0	0.1	1.7	0.1	0
Maximum	4.2	4.0	0.1	0.1	0.2	1.3	0.5	2.0	5.0	2.0	0.2

[0076] It has been found that the spheroidal cast iron having the indicated chemical composition, obtained by virtue of the process described above and subjected to the described heat treatment, achieves the intended aim and objects.

[0077] In particular, with this production process it has been found that an abundant graphitization is obtained on the casting with a uniform distribution and with spheroid sizes 5 to 8 (according to the ISO 945 standard) and a predominantly pearlitic matrix with a regular halo of ferrite around the spheroids.

[0078] The various elements that compose the cast iron according to the invention have been chosen to allow better hardenability of the material and therefore raise the bainitic transformation threshold, and also to obtain mechanical characteristics, such as tensile strength (UTS and R_{p0.2}), percentage elongation (A%), toughness, impact strength and fatigue strength that are better than in spheroidal cast irons for piston rings currently in use.

[0079] The variation ranges of the elements that compose the cast iron according to the invention have been determined by means of tests repeated in order to optimize the mechanical characteristics of the material without exceeding values that might compromise castability, spheroidization, workability and/or brittleness of said cast iron.

[0080] It must be noted that the balancing of the chemical composition among carbide former elements and graphitizing elements of the spheroidal cast iron for piston rings according to the invention is extremely critical and particular; exact dosage must in fact be ensured and performed specifically for each casting, varying the quantities of added elements also according to the chemical composition of the raw material used.

[0081] This particular reason justifies the need to adopt extended ranges of the individual elements in the chemical composition of the invention.

[0082] In particular, the carbon variation range has been determined in order to have an optimum graphite structure, so as to achieve high toughness and strength while ensuring good forming and spheroidal graphite distribution.

[0083] The nickel content has been limited to the values cited above in order to avoid compromising the castability and workability of the cast iron.

[0084] The molybdenum content was limited to the value indicated above in order to avoid compromising the mechanical characteristics of the cast iron due to the forming of complex structures of free cementite and due to segregation.

[0085] The chromium, manganese and tungsten content was limited to the values indicated above in order to avoid the forming of complex carbides, which would considerably reduce workability and would increase brittleness considerably.

[0086] The heat treatment to which the cast iron is subjected in castings according to the invention comprises an austenitization treatment, with holding of the cast iron up to 120 minutes at a temperature of 840-1000 °C and an isothermal hardening (austempering) treatment, with holding of the cast iron for 5 to 100 minutes at a temperature of 250-450 °C.

[0087] Optionally, the heat treatment can be completed by a stress relieving treatment at a temperature that is higher than the isothermal hardening temperature.

[0088] Although austempering is an already-known heat treatment for spheroidal cast irons in general, in the case being considered said treatment has been optimized in order to balance, in the specific case of the production of piston rings for internal-combustion engines, a high mechanical strength (UTS and $R_{p0.2}$) with high fatigue strength and high impact strength and toughness.

[0089] Generally, as the residual austenite increases, fatigue strength in fact increases but tensile strength decreases.

[0090] For a piston ring, however, it is necessary to have both high tensile strength and high fatigue strength, in order to ensure good elastomechanical operation for the reliability of the component and therefore of the engine on which the piston rings are fitted.

[0091] The optimum heat treatment for the cast iron according to the invention was determined by conducting repeated experimental tests and comparing the results, in terms of mechanical strength, with those of piston rings made of steel, so as to have clearly defined quantitative goals to achieve.

[0092] In terms of results, the spheroidal cast iron according to the invention is a spheroidal cast iron with a type VI uniform graphite distribution, with size 5 to 8 graphite spheroids (according to the ISO 945 standard "Cast iron: Designation of microstructure of graphite"). The concentration of the graphite spheroids with respect to the matrix is comprised between 6 and 12%, ensuring optimum self-lubrication.

[0093] The roundness of the graphite spheroids, expressed in terms of ovalization (D_{max}/D_{min}), is comprised between 1.0 and 1.4, ensuring a low coefficient of stress intensification.

[0094] The roughness of the graphite spheroids is comprised between 1 and 1.3 and ensures optimum fatigue strength.

[0095] The cast iron according to the invention has a matrix structure of the bainitic-austenitic type, with austenite percentages that can vary between 20 and 40%.

[0096] Furthermore, the cast iron according to the invention has uniform and homogeneous hardness along the entire peripheral distribution of the casting, with hardness values comprised between 103 HRB and 115 HRB (250-600 HV0.1 on the Vickers scale).

[0097] The cast iron cooling gradient, during the heat treatment, is kept as uniform and homogeneous as possible in order to avoid hardness variations, on a same , of more than 4 HRB points, which might compromise significantly the elastic behavior of the piston ring in contact with the cylinder of the engine during operation.

[0098] The cast iron according to the invention has excellent tensile strength ($R_m > 1100 \text{ N/mm}^2$), high strength and toughness [impact strength on unnotched test specimens (Impact Energy) $KC > 80 \text{ Joule}$] and a high percentage elongation ($A\% > 2.5\%$).

[0099] Merely by way of non-limitative indication, the results of tests conducted on two types of cast iron (TYPE 1 cast iron and TYPE 2 cast iron) according to the invention and the results of tests conducted on a steel (X90 CrMoV18) of a known type used to produce piston rings for pistons are listed hereafter.

[0100] The tests were conducted on test specimens of the type shown in the accompanying figures, wherein:

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Figure 1 is a view of a round tension test specimen (according to the ASTM standard E8M);

Figure 2 is a view of a Charpy impact test specimen (according to the ASTM standard E23).

[0101] The chemical composition of the two cast irons according to the invention is listed in Table 1.

Table 1

Cast iron	C	Si	P	S	Mn	Cu	Cr	Ni+RE	Mo	Ti+V+Nb	Co
TYPE 1	3.7	2.9	0.03	0.02	0.08	0.0	0.05	2.1	0.1	0.3	0.05
TYPE 2	3.6	2.4	0.07	0.03	0.07	1.3	0.02	0.5	0.1	0.6	0.2

[0102] The chemical composition of the steel is given in Table 2.

Table 2

Steel type	C	Si	P	S	Mn	Cu	Cr	Ni	Mo	V	W	Co
X90 CrMoV18 (W. Nr 1.14112)	0.92	0.51	0.024	0.022	0.74	-	17.25	-	0.97	0.09	-	-

TYPE 1 cast iron

[0103] Seven different types of heat treatment were performed for this type of cast iron according to the invention, whose chemical composition is given in Table 1.

[0104] In all the tests listed hereafter, round tension test specimens (Figure 1) and Charpy impact test specimens (Figure 2) prepared specifically and subjected to different heat treatments were used in order to evaluate the mechanical characteristics.

[0105] Five round tension test specimens and five Charpy impact test specimens were used for each test; the results listed are the average of the results obtained in the five tests, the average values of which related to each test are given in Table 3.

Table 3

TYPE 1 cast iron	Austenitization	Austempering	UTS [Mpa]	Rp0.2 [Mpa]	ϵ_r %	Impact Energy [J]
Test no. 1	930°C x 30 min	300°C x 60 min	1355	1053	2.42	86.63
Test no. 2	930°C x 30 min	300°C x 120 min	1358	1093	2.32	101.39
Test no. 3	930°C x 30 min	330°C x 60 min	1066	772	4.17	150.73
Test no. 4	930°C x 30 min	330°C x 120 min	1249	978	3.38	108.88
Test no. 5	930°C x 30 min	360°C x 60 min	1035	771	4.62	165.17
Test no. 6	930°C x 30 min	360°C x 90 min	1007	777	4.05	144.94
Test no. 7	930°C x 30 min	360°C x 120 min	1044	786	5.88	122.8

TYPE 2 cast iron

[0106] Seven different types of heat treatment were performed for this type of cast iron according to the invention, whose chemical composition is given in Table 1; in all the tests listed hereafter, round tension test specimens (Figure 1) and Charpy impact test specimens (Figure 2) prepared specifically and subjected to different austempering treatment were used in order to evaluate the mechanical characteristics. Five round tension test specimens and five Charpy impact test specimens were used for each test; the results listed are the average of the results obtained in the five tests, the average values of which related to each test are given in Table 4.

Table4

TYPE 2 Cast iron	Austenitization	Austempering	UTS [Mpa]	Rp0.2 [Mpa]	ϵ_r %	Impact Energy [J]
Test no. 1	930°C x 30 min	300°C x 60 min	1359	1118	1.97	68.63

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Table4 (continued)

TYPE 2 Cast iron	Austenitization	Austempering	UTS [Mpa]	Rp0.2 [Mpa]	ϵ_r %	Impact Energy [J]
Test no. 2	930°C x 30 min	300°C x 120 min	1357	1130	1.97	81.09
Test no. 3	930°C x 30 min	330°C x 60 min	1266	1019	2.99	104.32
Test no. 4	930°C x 30 min	330°C x 120 min	1219	978	3.15	105.10
Test no. 5	930°C x 30 min	360°C x 60 min	1231	995	3.51	103.40
Test no. 6	930°C x 30 min	360°C x 90 min	999	785	4.45	105.90
Test no. 7	930°C x 30 min	360°C x 120 min	1071	840	5.84	116.52

X90 CrMoV18 steel (W. Nr. 1.4112)

[0107] For this type of steel, whose chemical composition is listed in Table 2, five tests were conducted; round tension test specimens (Figure 1) and Charpy impact test specimens (Figure 2) prepared specifically and subjected to a different heat treatment were used in all the tests listed hereafter in order to evaluate the mechanical characteristics. The results of these tests are listed in Table 5.

Table 5

Test	Quenching	Tempering	UTS [Mpa]	Rp0.2 [Mpa]	ϵ_r %	Impact Energy [J]
Test no. 1	1050°C and hardening in oil	600°C x 120 min	1354	1191	1.17	68.42
Test no.2	1050°C and hardening in oil	600°C x 120 min	1338	1226	1.08	79.49
Test no. 3	1050°C and hardening in oil	600°C x 120 min	1295	1196	0.97	58.44
Test no. 4	1050°C and hardening in oil	600°C x 120 min	1303	1204	1.00	72.59
Test no.5 5	1050°C and hardening in oil	600°C x 120 min	1295	1181	0.94	74.81

[0108] In practice the spheroidal cast iron according to the invention fully achieves the intended aim and objects, since it allows to produce piston rings with mechanical strength characteristics that are comparable with those of piston rings made of steel while preserving all the advantages that are typical of spheroidal cast iron.

[0109] Although the cast iron according to the invention has been conceived in particular for the production of piston rings of internal-combustion engines, it may be used advantageously also to produce piston rings for compressor units or for the production of rings for hydraulic or pneumatic units or for other uses.

[0110] The spheroidal cast iron thus conceived and the melting process described are susceptible of numerous modifications and variations, all of which are within the scope of the inventive concept.

The disclosures in Italian Patent Application No. MI2002A001670 from which this application claims priority are incorporated herein by reference.

LEGEND OF SYMBOLS:

[0111]

UTS = *Ultimate Tensile Strength (in Newton/mm²)*

R_{p0.2}= *Yield stress: stress of deviation from proportionality of 0.2% (Newton/mm²)*

E = *Elasticity modulus or Young modulus (Newton/mm²) Ratio between normal strength and the corresponding longitudinal deformation as per the Hooke law: $E = \sigma / \epsilon$*

$\varepsilon_r =$ Longitudinal deformation calculated as:

$$\varepsilon_r = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0}$$

with:

L_0 (mm) = Initial length

$\Delta L_0 = L - L_0$ (mm) = Variation in length consequent to application of load

$A\% =$ Ultimate Elongation: longitudinal deformation expressed as percentage of initial length L_0 :

$$A = 100 \cdot \frac{L_u - L_0}{L_0}$$

with:

L_u (mm) = ultimate length value at break

$\lambda =$ coefficient of linear thermal expansion ($^{\circ}\text{C}^{-1}$) expressed as:

$$\lambda = \frac{1}{l} \cdot \frac{dl}{dT}$$

Mpa = Mega Pascal = 10^6 Pascal

$$1 \text{ Mpa} = \frac{1 \text{ Newton}}{\text{mm}^2}$$

Claims

1. Spheroidal cast iron comprising the following elements: Fe, C, Si, Mo and **characterized in that** it furthermore comprises Ni, RE, and at least one element among Ti, V, Nb.
2. The spheroidal cast iron according to claim 1, **characterized in that** the elements of the group formed by Ti, V and Nb are present in percentages by weight that range from 0.1% to 2.00% of the total weight of the cast iron.
3. The spheroidal cast iron according to one or more of the preceding claims, **characterized in that** it comprises said elements in the following percentages by weight: 3.20 - 4.20% C, 2.00 - 4.00% Si, up to 0.10% P, up to 0.10% S, up to 0.20% Mn, up to 1.30% Cu, up to 0.50% Cr, 1.7% to 5.00% Ni+RE, 0.10 - 2.00% Mo, 0.1% to 2.0% of the sum of the percentages of the elements of the group constituted by Ti, V and Nb, and up to 0.20% Co.
4. The spheroidal cast iron according to one or more of the preceding claims, **characterized in that** the remaining percentage by weight in order to reach the value of 100% of the weight is constituted by Fe.
5. The spheroidal cast iron according to one or more of the preceding claims, **characterized in that** it is subjected to a heat treatment, known as austempering, which comprises an austenitization treatment followed by an isothermal hardening treatment.
6. A process suitable to obtain a spheroidal cast iron according to at least one of claims 1 to 5, comprising the steps that consist in:
 - providing a conventional basic cast iron
 - melting the base cast iron

- checking the molten metal during the preparation and completion of the melting of the basic cast iron by taking samples, which undergo chemical analyses in order to check their composition
- adding chemical elements chosen from the class that comprises C, Si, P, S, Mn, Cu, Mo, Cr, Ni, Ti, V, Nb
- inoculating spheroidizing agents in the molten mass, said agents being constituted by a silicon base which comprises RE with the addition of at least one of the elements chosen from the class that comprises Mg, Ca, Ce, Ta, Sr, Al, RE.

7. The process for obtaining a spheroidal cast iron according to one or more of the preceding claims, **characterized in that** it comprises an austenitization treatment with a holding time of up to 120 minutes at a temperature of 840-1000 °C and an isothermal hardening (austempering) treatment with holding of the cast iron for 5 to 100 minutes at a temperature of 250-450 °C.

8. The process for obtaining a spheroidal cast iron according to claim 7, **characterized in that** said austenitization treatment also comprises a thermal strain relieving treatment at a temperature that is higher than the temperature of said isothermal hardening treatment.

9. The spheroidal cast iron according to one or more of the preceding claims, **characterized in that** it has a matrix structure of the bainitic-austenitic type with an austenite percentage substantially comprised between 20 and 40%.

10. A piston ring, particularly for pistons of internal-combustion engines, **characterized in that** it is made of an austempered spheroidal cast iron according to one or more of the preceding claims.

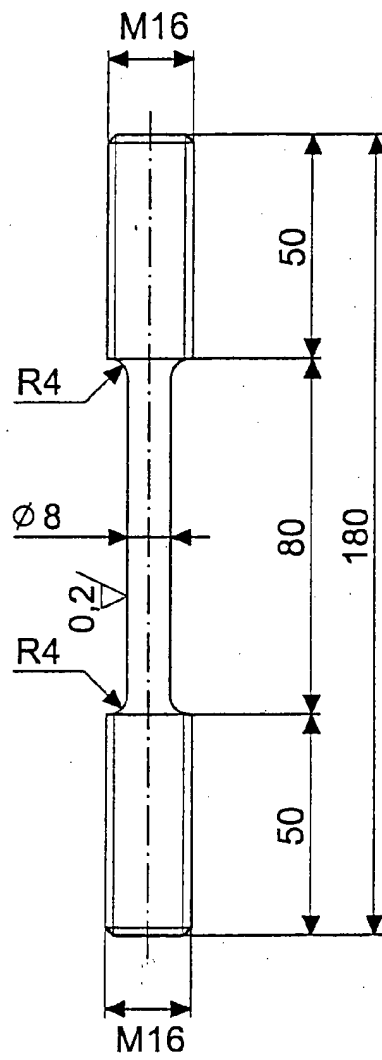


Fig. 1

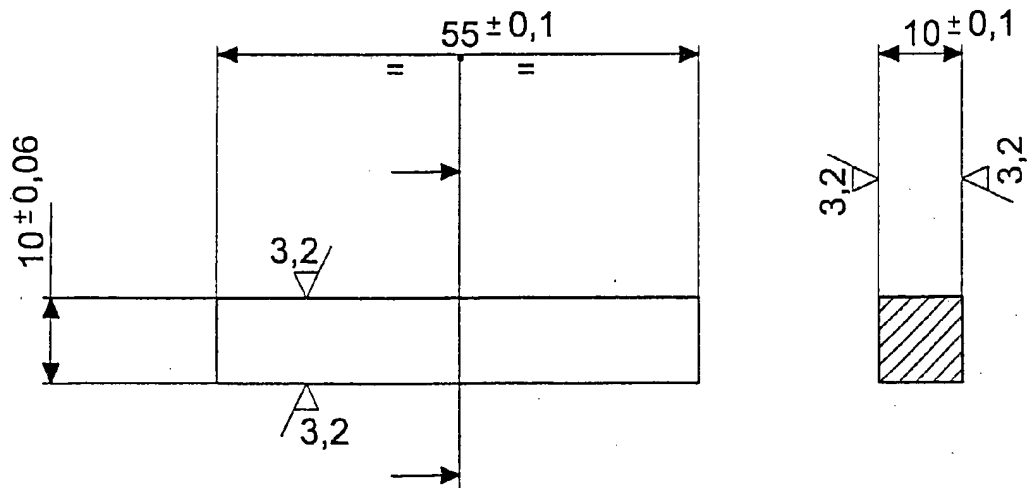


Fig. 2



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 03 01 6555

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EPO FORM 1503 03.82 (P04001)

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