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METHOD OF IMPROVING THE PROPERTIES OF ALLOY STEEL CASTINGS

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ABSTRACT OF THE DISCLOSURE

A process for making semi-finished or finished products having improved properties by a hot-forming treatment of cast ingots or parts thereof, which consist of high-alloy steels containing nickel and chromium in a total amount of at least 20%. These steels are transformed into a state in which they consist substantially of austenite and ferrite by being heated to a temperature within the range of 1150° C. and the solidus temperature of the steel. In an initial step of the process a starting material, which is suitable for remelting, is made. This starting material is then continuously fused in a known manner to form a melt; the melt is converted into cast ingots in a water-cooled mold by zone casting. The resulting ingot is annealed at a temperature between 1150° C. and the solidus temperature of the steel in question until the degree of segregation, as determined by electron beam microanalysis of a carbide-free structure, falls below 1.05. Thereafter, the ingot is subjected to a hot-forming treatment to eliminate the coarse grains formed during annealing and to produce the desired semi-finished or finished product.

The present invention relates to the manufacture of semi-finished or finished products from high-alloy steels, which contain chromium and nickel amounting to at least 20% and which can be transformed into a state in which they consist substantially of austenite and ferrite by being heated to a temperature between 1150° C. and the solidus temperature. In addition to iron and inevitable accompanying elements, these alloys may contain other alloying elements, such as carbon, silicon, manganese, tungsten, molybdenum, vanadium, columbium, cobalt, copper, titanium, zirconium, aluminium, and nitrogen in a total not exceeding 10%. The amount of these additional alloying elements is mainly limited by the requirement that the steel must consist substantially of austenite and ferrite at a temperature above 1150° C. The additional presence of carbides in this state does not affect the usefulness of these steels for the purposes of the invention.

Examples of steels to which the process according to the invention is applicable will be listed hereinafter:

(1) Up to 0.02%, C, 0.4% Si, 1.7% Mn, 21.5% Cr, 11% Ni
(2) Up to 0.02% C, 0.45% Si, 1.55% Mn, 23.5% Cr, 13% Ni, up to 0.2% Mo, 0.7% Nb
(3) Up to 0.02% C, 0.45% Si, 1.55% Mn, 24.5% Cr, 12.5% Ni
(4) 0.2% C, 1.05% Si, 0.85% Mn, 24% Cr, 13.5% Ni, 3% W
(5) Up to 0.8% C, 0.5% Si, 0.85 Mn, 23% Cr, 12.5% Ni
(6) 0.12% C, 0.8% Si, 1.6% Mn, 29% Cr, 9% Ni
(7) 0.2% C, 1.1% Si, 0.8% Mn, 25% Cr, 4% Ni, 0.16%

(8) 0.07% C, 0.5% Si, 0.5% Mn, 16.5% Cr, 6.7% Ni, 1% Al
(9) 0.08% C, 0.5% Si, 0.8% Mn, 18% Cr, 13% Ni, 3% Mo, 0.5% Ti
(10) 0.08% C, 0.6% Si, 0.8% Mn, 18% Cr, 13% Ni, 3% Mo, 0.8% Nb
(11) 0.08% C, 0.6% Si, 0.8% Mn, 18% Cr, 11% Ni, 2% Mo, 0.5% Ti
(12) 0.08% C, 0.6% Si, 0.8% Mn, 18% Cr, 11% Ni, 2% Mo, 0.8% Nb

Above 1150° C., steels 1–8 consist of austenite and ferrite and steels 9–12 contain small amounts of carbides in addition to austenite and ferrite.

It is an object of the invention to improve the production of ingots from these and other steels. In this production, numerous flaws occur, which render the further processing more difficult and more expensive, reduce the output and adversely affect the service properties. Such flaws include, e.g., pores, voids, blowholes, loose places, non-metallic inclusions due to the deoxidation or to the contact of the molten steel with ceramic materials.

Segregation is of special significance for the service properties and, with steels having low carbon and high chromium contents, also for the behavior during hot-forming. A distinction must be made between ingot segregation and crystal segregation. Ingot segregation is defined as a variation in the concentration of accompanying or alloying elements in steel between the skin and the center of the ingot or between the top and the bottom of the ingot. These variations can be detected by taking specimens in the usual manner for a chemical analysis from different points of the ingots and subjecting these samples to conventional chemical investigations. Whereas the degree of ingot segregation is generally low compared to the degree of crystal segregation, ingot segregation may result in the presence of excessive amounts of ferrites in an undesirable distribution, particularly in the interior of the ingot, and these ferrites may give rise to considerable difficulties in hot-forming. The detrimental influences of the other flaws which have been mentioned must not be overlooked, too.

Crystal segregation has also a great influence on the behavior during hot-forming, particularly when large amounts of ferrites are present in addition to austenite during hot-forming because the arrangement of the ferrites is closely related to the pattern of crystal segregation. Particularly unfavourable conditions will be obtained if the ferrite encloses the grains of austenite to a large extent. In such cases the yield of hot-forming treatments may be too low from an economic aspect.

It is an object of the present invention to provide a process of making steels which are free of the above-mentioned flaws and have as a distinguishing feature a highly homogeneous state particularly as far as segregation is concerned so that the workability and the service properties are improved.

It is known that the usual zone casting processes, such as vacuum arc melting using a consumable electrode, electron beam melting or electric slag remelting, result in products which distinguish themselves from conventionally made ingots by reduced contents of undesired impurities, lower contents of non-metallic inclusions, a considerable freedom of pores, loose places and blowholes and, as a result of zone melting, by the absence of ingot segregation. In the above-mentioned remelting processes, these flaws are reduced in varying degrees, which depend also on the kind of steel to be made. The appropriate process will be selected in view of the requirements to be met in this respect. In the elastic slag remelting process, best results will be obtained if alter-

nating current rather than direct current is used and the formation of an electric arc is avoided.

In a zone casting process, a starting product made by any desired process, such as continuous casting, is continuously melted. The melt is allowed to drip into a water-cooled mould and is continuously solidified therein. The resulting ingot can be processed much better than ingots cast by conventional processes.

Another flaw which has a considerable influence on the behaviour during hot-forming and the service properties even of such ingots which are free of ingot segregation is crystal segregation.

Crystal segregation can only be investigated by electron beam microanalysis and this investigation is preferably carried out by a recording of concentration profiles. For such recordings, specimens may be mechanically moved across the electron beam transversely to the direction of the axes of the dendrites. The recorder may be arranged to record the changes in concentration of an element which has a characteristic line to which the spectrometer has been adjusted. The record must enable a determination of the amount of segregation, i.e., the highest and lowest concentration of the investigated element, as well as of the distances between the concentration peaks which occur between the dendrites. The ratio of the highest concentration of an element to the lowest one is described as the degree of segregation of said element. With those steels to which the invention can be applied it must be borne in mind, that they consist of austenite and ferrite even when they have been quenched or cooled to room temperature and these two structural constituents contain the alloying elements in different proportions. For this reason, the degree of segregation of an alloying element must be separately determined for each of these two structural constituents. This will now be explained with reference to an example:

An ingot having a composition according to steel **2** was made by electric slag remelting. Records showed chromium contents between 31.5% and 34.5% in the ferritic constituent and between 19.9% and 22.2% in the austenitic constituent. This corresponds to a degree of segregation of chromium amounting to 1.10 in ferrite and 1.12 in austenite. The nickel contents ranged between 7.2% and 8.4% in ferrite and between 16.0% and 18.5% in austenite, corresponding to a degree of segregation of nickel amounting to 1.17 in ferrite and 1.16 in austenite.

An annealing treatment at 1200° C. for 24 hours reduced the degrees of segregation of chromium and nickel in ferrite and austenite below 1.05. As a further result of this treatment, the ferrite previously present in the form of a finely branched structure was transformed into a globular or cardioid form so that it constituted ferrite inclusions in an austenitic matrix. By this annealing treatment, the yield in the production of hot-rolled strips was increased by more than 20%. In torsion tests, in which the hot-forming properties were evaluated by determining the number of turns at which the specimen was fractured at a given temperature, the number of turns was more than doubled by the annealing treatment.

When such annealing treatments are carried out on steels which contain small amounts of carbides in addition to austenite and ferrite at temperatures above 1150°, these carbides will also be present when the steel has been cooled or quenched to room temperature. When concentration profiles of such steels, which may have for example, the composition of steels **9–12**, are recorded, such carbide or such carbide region may be sensed by the electron beam. In these cases, distinct concentration peaks of chromium will be recorded in the recording of chromium profiles and these peaks must not be taken into account in the determination of the degree of segregation of that element. Similarly, the concentration drops of nickel found in the carbide region must not be taken into account in such cases in the recording of nickel profiles.

As the alloying elements have a higher diffusivity in ferrite than in austenite, it will be sufficient in practice to check the effect of the annealing treatment by electron beam microanalysis only for the austenitic constituent. It will also be sufficient to carry out the check in the steels to which the invention is applicable only for one of the two elements chromium and nickel.

It is surprising that an annealing treatment carried out in the same temperature range as the usual diffusion annealing treatments should make any sense with steels which consist substantially of austenite and ferrite in this temperature range. The improved behaviour during hot-forming and particularly the increase in yield, however, are a sufficient justification of this step. A check of the effect of the annealing treatment by electron beam microanalysis to the extent which has been suggested is essential because inadequate annealing treatments involve only considerable costs without giving the desired result.

Whereas the application of such annealing treatments to ingots made by conventional methods may lead to improvements in many cases, this is not ensured because such ingots inevitably exhibit flaws, such as pores or blowholes, which indicate that there is a considerable enriching of alloying elements and undesired precipitates close to said flaws. These phenomena can only be avoided by zone casting. Similar phenomena are caused by ingot segregation, which can also be avoided only by zone casting.

When it is desired to reduce crystal segregation by annealing, it must be decided in each case whether high temperatures and short holding times or comparatively low temperatures and long holding times are preferable. Long holding times result in an increased formation of scale and may result in excessive grain coarsening. On the other hand, long holding times cannot be avoided if the temperatures which can be used are limited by plant conditions. Annealing temperatures lower than about 1150° C. must be rejected because they are uneconomical in any case.

As annealing treatments at high temperatures result in a grain coarsening, which in the steels to which the invention is applicable occurs mainly in the austenite and reduces the quality of the steel, it is recommended according to the invention to subject the annealed steel to hot-forming, preferably in the temperature range which is suitable for the alloy steel concerned. The hot-forming treatment may be carried out in known manner for the manufacture of semi-finished or finished products by forging, rolling, extruding or drop forging ingots or parts thereof.

Thus, the invention provides a process of making semi-finished or finished products having improved properties by a hot-forming treatment of cast ingots or parts thereof, which consist of high-alloy steels that contain chromium and nickel in a total of at least 20% and which can be transformed into a state in which they consist substantially of austenite and ferrite by being heated to temperatures between 1150° C. and the solidus temperature. The invention resides in that a starting material which is suitable for a continuous remelting process is first made from such steels and is continuously fused in known manner to form a melt, which is caused to solidify in a water-cooled mould by zone casting, the resulting ingot is annealed at temperatures above 1150° C. and below the solidus temperature in a state in which it consists substantially of austenite and ferrite until the degree of segregation of chromium or nickel in the austenitic constituent, as determined by electron beam microanalysis, is less than 1.05, and the annealed ingot or parts thereof is or are subjected to a hot-forming treatment to eliminate the grain coarsening due to the annealing treatment and to produce the desired semi-finished or finished product.

The steps which are recommended by the invention enable an economical production of alloy steels which are partly very difficult to control and considerably im-

prove the service properties of such alloys as to the degree of homogeneity which can be obtained, the corrosion behaviour, the welding behaviour, the behaviour under mechanical stresses and under alternating stresses, particularly because metallurgical notches are avoided to a large extent. By the application of the process according to the invention, the appearance of the sigma phase in steels having a very high chromuim content is either entirely avoided or occurs in such a uniform distribution, owing to the reduction of crystal segregation and the suppression of ingot segregation, that actual damage to the material due to this cause can no longer be found. Previously, the occurrene of the sigma phase has rendered the working of the steels more difficult and has resulted in an embrittlement of the final product.

It will be understood that in carrying out the process according to the invention the usual practice as to the inspection of the products and the requirements regarding the machining of the ingot must be complied with.

Although this invention is illustrated and described with reference to one preferred embodiment thereof, it is to be understood that it is in no way limited to the disclosure of such a preferred embodiment but is capable of numerous modifications in accordance with the appended claims.

What we claim is:

1. A process of manufacturing semi-finished or finished high-alloy steel products having improved properties by a hot-forming treatment of cast ingots or parts thereof, said cast ingots essentially consisting of high alloy steels having a content of nickel and chromium which totals at least 20% and being formed of a starting material suitable for continuous remelting, comprising the steps of

continuously fusing said starting material until it forms a molten mass;

solidifying said molten mass by passing it through a water cooled zone thereby obtaining a cast ingot;

annealing said cast ingot at a temperature between 1150° C. and the solidus temperature thereof, thereby transforming it into a steel consisting principally of austenite and ferrite;

microanalyzing by electron beam the degree of segregation of at least one of a group of elements consisting of chromium and nickel in said cast ingot;

and hot-forming said cast ingot when the degree of segregation of at least one of said group of elements has decreased to less than 1.05 due to being subjected to said annealing step, so as to eliminate the formation of coarse grains formed during said annealing step and to produce a semi-finished or finished product.

2. A process as set forth in claim 1, wherein said starting material is produced by means of a continuous casting process.

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