June 20, 1972 D. F. NORTH, JR., ET AL 3,671,224

METHODS OF PRODUCING LEADED STEEL

Filed Aug. 17, 1970 3 Sheets-Sheet 1

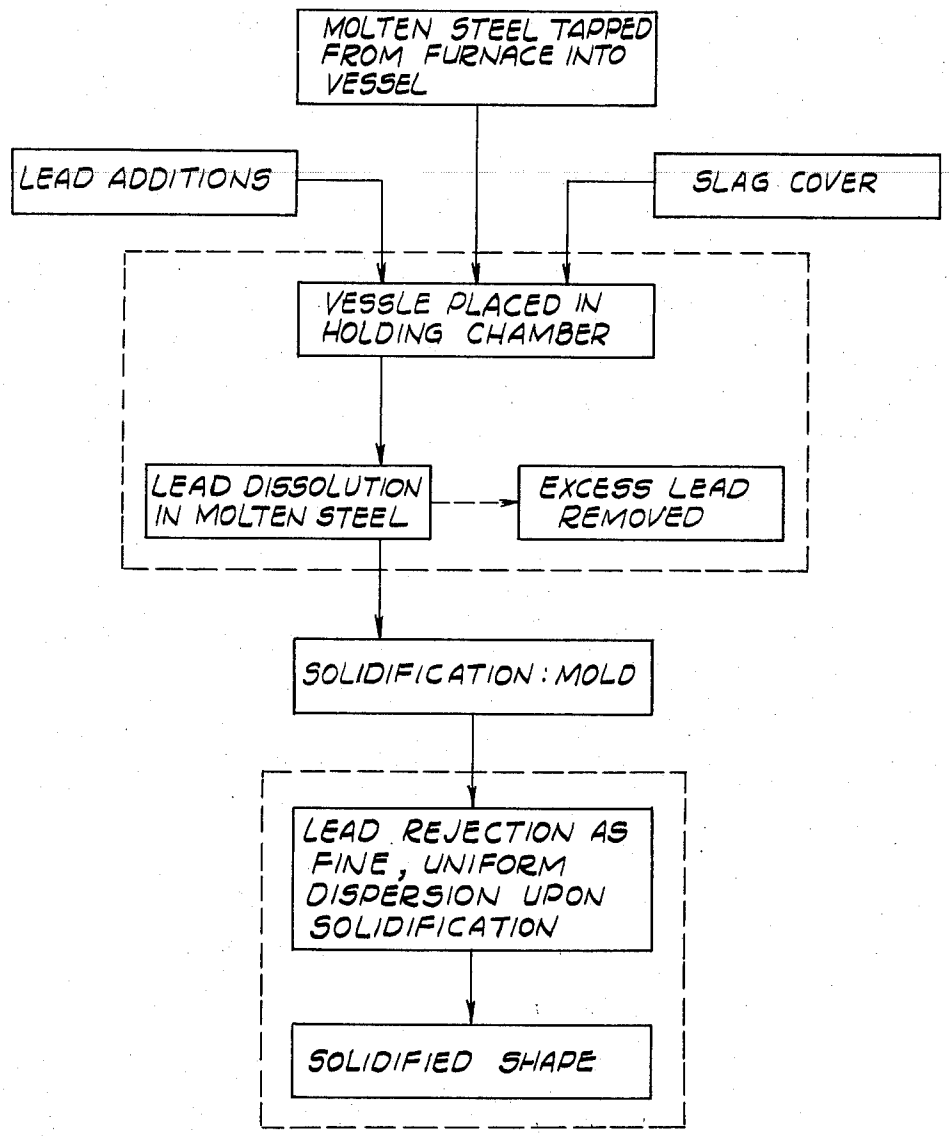


Fig. 1

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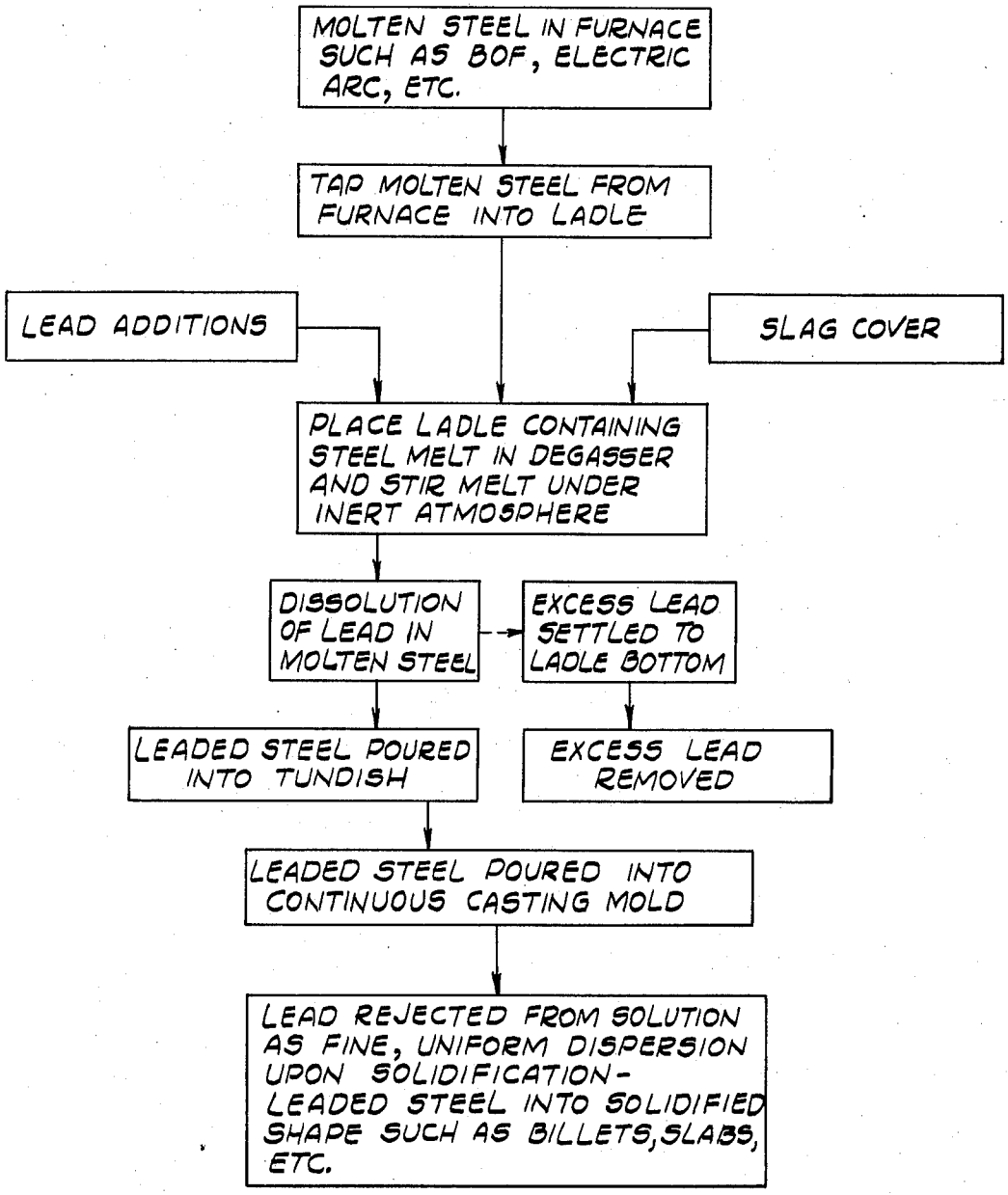


Fig. 2

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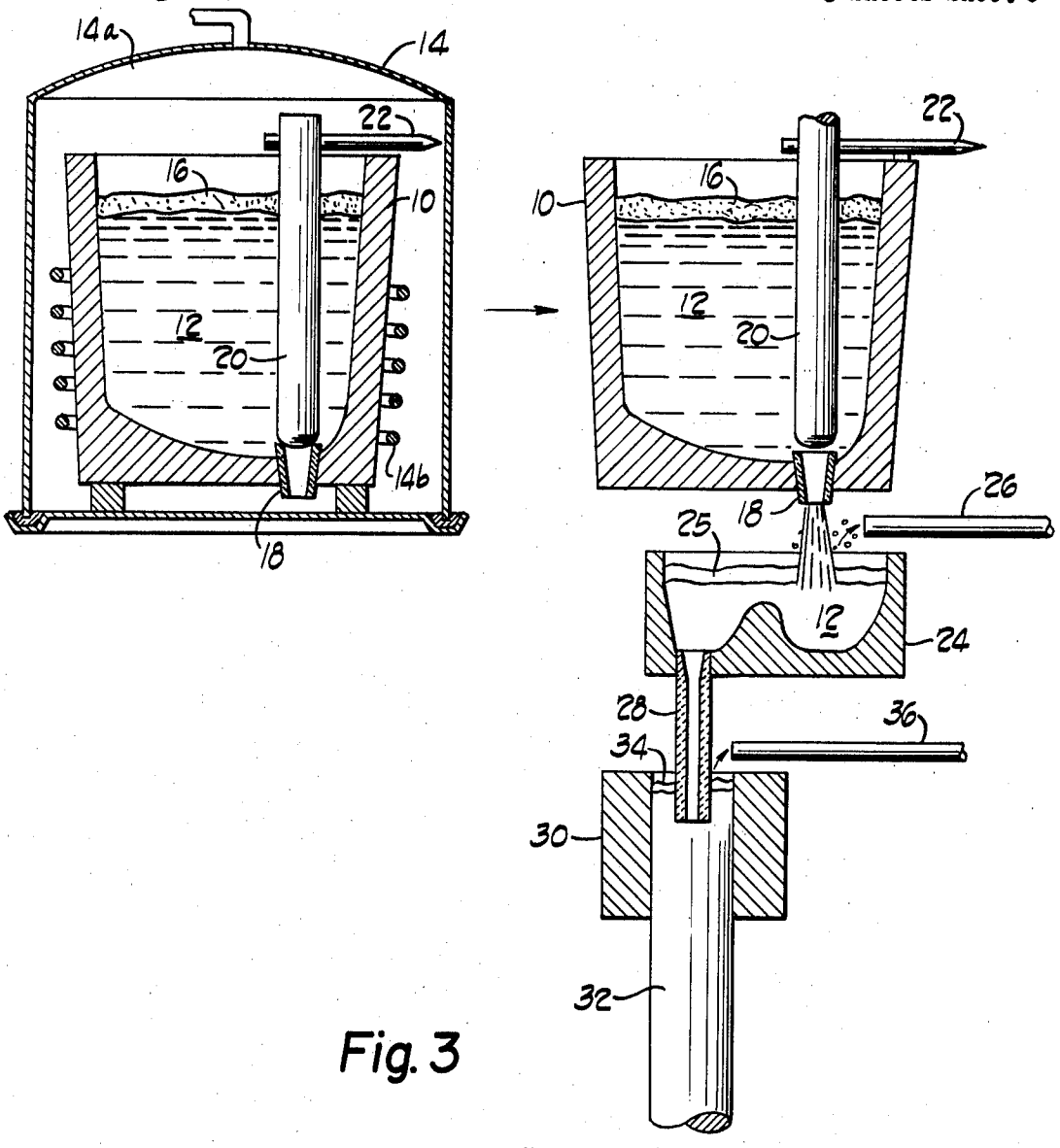


Fig. 3

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3,671,224

METHODS OF PRODUCING LEADED STEEL

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U.S. Cl. 75—129 11 Claims

ABSTRACT OF THE DISCLOSURE

Lead additions to steel are made and an improved leaded steel product is obtained by effectively utilizing the significant solubility of lead in steel at temperatures above the liquidus temperature of the steel. This is accomplished by control of process conditions, including adding the lead to the steel in a vessel separate from the casting mold, allowing a minimum time between the addition of the lead and the pouring and casting of the leaded steel, the use of specific amounts of lead based upon a target percentage of lead to be obtained in the cast steel, which target percentage does not exceed the solubility level of lead in the steel, and the addition of the lead when the temperature of the steel is above the liquidus temperature by at least a minimum amount. The lead content in steel cast continuously or into ingots in accordance with this proces is uniformly and finely dispersed and the steel is characterized by an absence of macrosegregation of lead.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to leaded steel and processes for producing leaded steel.

Prior art

Current practices of leading steel to obtain free machining properties apparently originated in the late 1930's and early 1940's as evidenced by U.S. Pats. Nos. 2,182,759; 2,197,259; 2,215,734, 2,236,479; 2,259,342 and 3,141,767. These patents basically relate to the addition of lead to different steels, certain means of making the lead addition and the forms of the lead additive. As disclosed therein, lead is added to steel in finely divided form either in a vessel, a mold or in the pour stream as the steel is poured into a mold. A further approach, in which a stream of molten steel is fed into a bath of molten lead and allowed to overflow is disclosed in the somewhat later United Kingdom Patent No. 894,019. Notwithstanding a stated desideratum in the prior art of obtaining a highly uniform submicroscopic dispersion of lead in steel, the fact is that leaded steels have suffered from substantial, undesirable, macroscopic, lead segregation. This results in non-uniform distribution of the lead content in cast ingots or billets, both transversely and longitudinally, and disruption of the ingot or billet surface by large particles of lead. Such ingots require bottom discard practice and such steel produces inferior surface quality in machined products.

SUMMARY OF THE INVENTION

The present invention overcomes certain shortcomings of the known processes for adding lead to steel and assures the production of steel in which the lead content in cast billets or ingots is essentially uniformly dispersed and finely divided. The process comprises a combination of steps that make effective use of the solubility of lead in steel at temperature above the liquidus. Upon solidification of the steel, the dissolved lead is rejected, resulting in the formation of a uniform, fine, dispersion of lead in the steel. By assuring that essentially the entire lead content

in the molten steel is in solution, large particles and macrosegregation of lead are avoided. As a result, bottom discard practice (elimination of lower portions of ingots that contain excess lead) is avoided, ingot loss from gross segregation and large lead particles is eliminated, and the resulting leaded steel product meets critical surface requirements.

In accordance with the present invention, steel containing lead in amounts up to the solubility limit, uniformly and finely dispersed without macrosegregation, is obtained by (a) adding lead to the steel in a vessel from which leaded steel containing essentially only dissolved lead is subsequently removed while molten to a casting mold, (b) establishing a minimum temperature of the molten steel at the time the lead is added that is a specified level above the liquidus temperature of the unleaded steel, and (c) assuring a minimum time period between the addition of lead to the steel and casting of the steel.

In addition, a number of advantageous features of the present process enhance the solubility of the lead, reduce lead loss and/or assure that the lead added appears in the cast steel only as finely divided and uniformly dispersed particles. These features include (a) establishing a target amount of lead to be obtained in the cast steel that is within the solubility limit of lead in the steel, taking into account the particular dissolution kinetics and other conditions of the specific process involved, and adding an actual amount of lead to the steel that exceeds the target amount by an amount of lead that will be actually lost, i.e., volatilized or dissolved in slag or refractory materials, during the process, (b) increasing the temperature of the steel to an optimum level significantly above the minimum acceptable level above the liquidus, (c) adding the lead in finely divided form, as in the form of shot or lead-iron pellets, (d) stirring the molten steel though induction or other means prior to, during, and for at least a short period of time after, the addition of lead, and (e) covering the steel with slag prior to or immediately the addition of lead to restrict loss of lead by volatilization, and (f) etablishing a reasonably fast rate of solidification of the steel after casing.

It is a principal object of this invention to provide a method for producing cast steel containing lead, in which the solubility of lead in steel at temperatures above the liquidus is effectively utilized and the presence of undissolved lead is avoided, to assure a uniform dispersement of finely divided lead particles in the cast steel. It is an advantage of the process that it can be utilized in both continuous casting techniques as well as in the more conventional casting of individual ingots, billets and the like. Processes embodying the present invention are especially compatible with continuous casting techniques because the relatively rapid chilling and solidification utilized with continuous casting assures the formation of a fine, uniform, dispersion of lead in solidified steel.

It is a further object of this invention to produce a leaded steel in which the lead content is uniformly and finely dispersed, with a complete absence of macrosegregation of lead and in which there are no surface or subsurface streaks or blobs of lead.

Various further objects and advantages of the invention will become apparent from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram illustrating a general method ofr adding lead to steel in accordance with the present invention;

FIG. 2 is a flow diagram illustrating a process utilizing the present invention for the continuous casting of steel; and

FIG. 3 is a diagrammatic illustration showing apparatus used in the process of FIG. 2.

DETAILED DESCRIPTION

In a preferred method embodying the present invention lead is added to molten steel in finely divided form while the steel is contained in a vessel, such as a ladle, prior to casting. Preferably, the steel in the ladle is stirred, both before and during the addition of lead and for a short time thereafter. A layer of slag on the molten steel within the ladle reduces fuming and loss of lead during and/or after the lead addition. The amount of lead added, the temperature of the steel at the time of the lead addition, and the time interval between the addition of lead and the pouring of the steel are all controlled to obtain optimum results. Each of these aspects of the preferred method are considered in detail below.

In connection with a preferred embodiment and specific examples of the present invention, it will be appreciated that the composition of the steel will affect the solubility of lead and, hence, the ultimate amount of lead to be added in obtaining a uniform dispersion of finely divided lead in the finished product. Although the actual amount of lead that is obtainable in steel in accordance with this process may thus vary, the present process assures that essentially all of the lead in the finished product was in solution prior to solidification of the steel and in the preferred practice, only that amount of lead will be added that is equal to the sum of the amount that will actually dissolve plus the amount that will actually be lost through volatilization and dissolution into slag and refractory materials.

Amount of lead added

The present process relies upon and utilizes the solubility of lead in molten steel and the insolubility of lead in solidified steel to obtain a uniform dispersion of fine particles of lead in cast, i.e., solidified, steel. In the preferred practice of this process, a target or aimed lead content in the steel is selected consistent with the solubility of lead in the steel at the temperature when added to assure that all lead contained within the molten steel at the time of casting and solidification can be in solution and will be precipitated in a uniformly distributed fine dispersion upon solidification. The actual amount of lead added to the steel is selected to assure that the target amount is obtained at the time of casting. Thus, the actual amount comprises the target amount plus a prescribed excess, based on anticipated lead losses during and after lead addition and prior to casting, due essentially to volatilization and dissolution of lead in the refractory container and the covering slag. The maximum target amount permissible depends upon process variables, especially the temperature of the steel and the dissolution kinetics of the lead in the molten steel, but in accordance with this process an upper target limit of .43% lead in low carbon (less than .10% carbon) steel is established, based on published experimental determination of lead solubility, [1] with a target amount of .15% lead by weight being readily obtainable under practical conditions applicable to commercial proccesses of leading steel for production purposes.

It has been found that if the target amount of lead is to be obtained in the cast steel, the actual lead added during the process must be greater than the target amount by a factor of at least 10%, but not more than 100%. The excess lead over the target amount added to the steel melt takes into account lead losses in the molten steel bath which occur during handling and casting. The lead losses result in four ways: (1) mainly lead volatilization, (2) lead oxidation forming volatile lead oxides, (3) lead taken into the refractories, and (4) lead taken into the slag that covers the melt. The percentage excess lead required to be added is generally constant throughout the range of target lead amounts at various temperatures, the variation or range specified for the excess being due primarily to variations in the effect of the above enumerated factors and the dissolution kentics, the latter of which are influenced primarily by lead particle size and stirring rate. It will be apparent that additional excess lead can be added if it is purposefully allowed to escape, is removed or settles (sometimes accomplished through stirring of the melt) prior to casting, but this amounts to an intentionally incorporated inefficiency and any such additional amounts do not constitute a required excess.

[1] A. E. Lord and N.A. Parlee, "The Solubility of Lead in Liquid Iron," Trans. AIME, 218 (1960), 644–646.

The lead additions specified herein are applicable to steel alloys typified by AISI types 1020, 1118, 4118 and 4140, among others. It will be appreciated that the upper limit of lead that can be added in accordance with this process, based on actual solubility, is influenced by differences in the steel composition, because of the affect of certain elements upon the solubility of lead.

The amount of lead that can be added and the uniform dispersion and fine particle size that is obtained, is also influenced by process conditions as set forth below.

Point in process where lead is added

In the casting of steel according to this process, the steel is contained in a ladle prior to teeming. For a number of reasons, it is advantageous to add the lead to the steel in the ladle. One principal reason is that in the event the actual lead losses are less than anticipated and the target amount of lead was near or at the solubility limit, excess undissolved lead will or can be segregated within the ladle and the steel removed from the ladle and cast will contain only dissolved lead. Other reasons are that it facilitates providing the steel at the proper temperature for the lead addition, the steel can be conveniently stirred before, during and after lead addition, and adequate time can be provided for dissolution of the lead in the steel prior to casting. Further, it is relatively easy and convenient to add lead into the ladle, an important consideration due to the high volatility of lead. Addition of lead at this point in the process, i.e., into a ladle prior to casting, also provides flexibility by which the process is readily adapted to a variety of casting techniques, especially continuous casting.

Temperature of steel when lead added

To obtain leaded steel in a fine dispersion and uniformly distributed in accordance with this invention, the steel must be at least ten degrees Fahrenheit above the liquidus temperature of the steel. This limit is arbitrary to the extent that there is no sharp break in the solubility curve at that temperature, but is a realistic and necessary limitation from a practical standpoint in assuring adequate solubility. Optimum conditions for obtaining maximum solubility and maximum lead content require still higher temperatures above the liquidus. In accordance with this invention, optimum lead solubility in low carbon (i.e., less htan .10% carbon) rimmed steel is obtained by adding lead to the steel bath with the steel bath at a temperature of between 75 to 135 degrees Fahrenheit above liquidus. Thus, where the liquidus is 2775 degrees Fahrenheit, the temperature of the melt at the time of lead addition in this instance is 2850 to 2910 degrees Fahrenheit. This may be referred to as the optimum temperature for this steel and is that temperature of the melt necessary to attain the maximum solubility of lead in the molten steel, optimum ingot quality, and/or optimum casting practice. Higher temperatures of the steel melt in the ladle at the time of the lead additions result in higher lead solubility, with the published experimentally determined maximum of 0.43% lead requiring a temperature of 3092 degrees Fahrenheit. However, temperatures at this upper level are not typicaly considered optimum for the present process and the high lead content is not necessary for most purposes.

Experimentally reported solubilities indicate that the solubility of lead in steel at temperatures of 2850 to 2910 degrees Fahrenheit is between about .25 and .40% by weight. Actual experience, as indicated in examples set forth subsequently, under conditions more closely related to production conditions, indicate a lower percentage recovery of lead.

As indicated previously in connection with the amounts of lead to be added, the solublity of the lead in the steel bath is affected by the composition of the steel, but the above-specified levels of solubility are generally typical of the compositions referred to above and in the examples set forth subsequently.

Time for dissolution

The time needed to dissolve lead in steel is relatively short. With induction stirring of the melt, the target content of dissolved lead in the steel can be reached in an average time of one to two minutes. In the absence of stirring, the time is longer. In the present process, the lead will be in contact with molten steel prior to being cast, for a minimum of between five to twenty-five minutes, i.e., from lead addition to the start of casting, thereby providing a minimum time of five to twenty-five minutes for dissolution. During the minimum time, the steel is at a temperature substantially above the liquidus, especially in the process of continuous casting, where the steel temperature when introduced to the ladle is about 50 to 150 degrees Fahrenheit higher than the temperature normally used for ingot casting.

Stirring

By limiting the maximum target amount of lead to the solubility limit of lead in the particular steel at the temperature at which the lead is added, mechanical mixing is not relied upon to provide a dispersion of the lead in the steel. Mechanical mixing, i.e., stirring, is nevertheless advantageously employed in the present process to hasten dissolution of the lead, especially when the target amount approaches the limit of solubility. Furthermore, it has been found that stirring has the effect of cleansing the steel of undissolved lead in instances where some excess of lead may exist above the solubility limit. In such instances the undissolved lead is rapidly settled from the steel within the ladle or other vessel, assuring that with proper pouring or teeming techniques no undissolved lead will be removed with the steel.

In the preferred process, then, the melt is stirred to improve dissolution of the lead and to segregate any excess lead that may fail to dissolve, as where actual lead losses fail to reach the anticipated level allowed for by the quantity of lead added to the steel. Stirring is begun prior to lead addition and continued for a short time after the lead addition. Stirring for one to two minutes for a 200 ton ladle is sufficient to obtain complete mixing and maximum lead solubility, as influenced by the composition and operating conditions.

Form of lead added

This process contemplates the addition of lead in any form, but preferably it is added in the form of lead shot or lead-iron pellets, which increase the degree of inmediate dispersion and decrease the time required for dissolution and dispersion. In general, a small lead particle size enhances the possibility of reaching maximum lead solubility.

No particular mechanism is required to introduce the lead and in a typical process the lead is allowed to merely fall into the bath. Alternatively, the lead additive, especially steel capsules, can be submerged beneath the bath surface, and shot or capsule can be poured through a tube in which the lower end is submerged beneath the bath surface. Lead shot or capsules can also be injected pneumatically or otherwise projected into the bath.

Slag cover

The slag cover typically used over steel is desirable for steel in which lead has been added, because it restricts the loss of lead through volatilization. Any typical slag is satisfactory, for example, vermiculite or bauxite-lime. The slag cover must be present immediately after lead addition, and typically is present initially and pushed aside to expose a portion of the bath surface to which the lead is added. Tests have indicated that lead loss for heats without slag cover averaged .006% per minute. With slag cover, the loss is reduced to an average of .0013% per minute, measured when the bath was under heavy stirring from induction heating. In commercial operations, with a slag cover, the lead content will remain relatively constant throughout a normal teeming operation.

Leaded steel products

The present process is contemplated for use with a composition of steel to which lead can be added and is especially useful in producing free machining steels. In a preferred process, the steel is produced in billet form by continuous casting. Alternatively, the process is also applicable to the casting of ingots or the like.

The product produced is a steel alloy having enhanced machinability over a conventional steel without lead, but which will not have drawbacks, i.e., defects, as in conventionally leaded steel, which defects include surface and subsurface streaks of lead and blobs of lead. The product is characterized by an absence of macrosegregation of lead. A preferred steel alloy suitable for machining and useful as a bearing material, will have a lower lead content, i.e., .09 to .12% or .15% lead by weight, than conventional machining steel. Maximum lead particle size in the solidified product will in general be no greater than about 30 microns and the predominant lead particle size will be below 10 microns.

Exemplary process and apparatus in general

The present process is applicable generally for producing leaded steel for casting ingots, billets and the like, and is especially applicable to continuous casting. A flow diagram illustrative of the general process embodying the present invention is shown in FIG. 1 of the drawings. A flow diagram of a more specific process embodying the present invention, applicable to continuous casting of leaded steel, is shown in FIG. 2 of the drawings.

Referring first to the general process as illustrated in the flow diagram of FIG. 1, molten steel, such as low carbon steel, is tapped from a steel making furnace into a vessel. The vessel is transferred to a holding chamber in which lead is added and a slag cover provided to reduce fuming and lead loss after lead addition. The slag may be added prior to the lead or immediately thereafter. The steel in the vessel is at a temperature at least 10 degrees Fahrenheit above the liquidus temperature of the steel at the time the lead is added, and typically at a temperature of between 2850 and 2910 degrees Fahrenheit for best results, considering the type of steel, the solubility of lead, and good casting practice. The lead is added in any convenient form, but preferably is finely divided, i.e., in the form of shot or lead-steel pellets.

The lead is added in excess of the target amount desired in the finished steel product, by at least 10% and not more than 100%. The excess over the target amount represents an anticipated true loss in the system through volatilization, lead oxidation forming volatile lead oxides, lead taken into the refractories, and lead taken into the slag. It will be appreciated that the exact excess amount between 10 and 100% must be based on the particular system, as already indicated. As a safeguard against gross segregation due to undissolved lead content, should some of the lead losses anticipated not be actually experienced, any such excess lead is separated from the steel containing the dissolved lead, in the vessel. This separation can be aided by stirring the melt. The steel and dissolved lead is

then removed from the vessel during casting in a manner that retains the undissolved lead within the vessel, either through the pouring technique or through a particular vessel constuction, as shown in FIG. 3. By careful selection of the excess lead added over the target amount desired, and by adding the lead to the steel in a vessel, where excess can be segregated prior to casting, lead in the finished product is all initially in a dissolved state. If the steel melt is stirred in the vessel, the lead added will be quickly mixed and dissolved and can be poured within one to two minutes after the lead addition. In the absence of stirring, a somewhat longer time is required.

The steel containing the dissolved lead, by now at the target concentration, is then cast and solidified. The lead content, being entirely dissolved at the time of casting, is uniformly dispersed. Upon solidification of the steel, the dissolved lead will be rejected from solution as a fine, uniform, dispersion.

With reference to the process shown diagrammatically in FIG. 3 and the apparatus shown in FIG. 3, relating to the addition of lead to steel in a continuous casting process, molten steel is tapped from a steel making furnace (not shown), such as a BOF, electric arc, or the like furnace, to a ladle **10**. In a commercial process, the ladle may typically hold 100 to 200 tons of steel, indicated at **12**. The temperature of the steel in the ladle is about 75 to 135 degrees Fahrenheit above the liquidus temperature of the steel. The ladle is placed in a degasser **14**, which provides an enclosed chamber **14***a* and induction stirring apparatus **14***b*. The steel melt **12** is stirred by induction in an inert atmosphere. Lead is added and the typical slag cover **16** is provided over the steel in the ladle, which, in addition to preventing oxidation of the steel, inhibits fuming of the lead. Such fuming is not only a safety hazard, but also reduces the lead content in the steel. Preferably, the steel melt is stirred prior to the addition of lead and for a short time thereafter, typically for a period of one to two minutes after lead addition. Within this time, the lead will dissolve within the steel. The lead is added in the form of small shot particles or lead-iron pellets, in an amount from 10% to 100% in excess of the target content of the lead desired in the finished product. An amount of about 50% in excess is perhaps typical for optimum results; i.e., will assure obtaining the target lead content without substantial undissolved excess. The additional lead above the target amount allows for the anticipated consumption of actual loss of lead from the melt during addition and dissolution through lead volatilization, lead oxidation forming volatile lead oxides, lead taken into the refractories, and lead taken into the slag. In accordance with the present process, the target amount of lead is limited to a maximum of .43% by weight, and typically a target of .12 to .15% by weight is more realistic and sufficient for most intended purposes.

The ladle **10** is constructed to prevent any excess lead not dissolved in the steel from being teemed during the continuous casting process. To this end, the nozzle **18** of the ladle projects upward from the bottom of the ladle a short distance so that the bottom of the ladle acts as a reservoir that will retain any excess undissolved lead, which settles from the melt. A rod **20** within the ladle functions as a stopper for the nozzle and is moved vertically to open and close the nozzle by a lever **22**. With this construction, in the event the lead losses are not as great as anticipated or in the event the actual solubility due to the temperature or composition of the melt is somewhat less than anticipated, excess undissolved lead will not be teemed from the ladle to become a part of the cast product. Further, the stirring that forms a part of this process quickly segregates and settles any undissolved lead by the stirring action and, in effect, cleanses the steel melt of undissolved lead.

The steel containing the dissolved lead is teemed from the ladle into a tundish **24**, which provides a uniform flow of steel to the continuous casting mold. The steel in the tundish is covered by a protective layer of slag **25**. A ventilation tube **26** is provided adjacent the top of the tundish to withdraw any volatilized lead. The tundish serves to provide a substantially uniform pressure head and, hence, flow rate of the steel, which flows from the tundish through a fused silica nozzle **28** to a continuous casting mold **30**, where it is solidified and advanced as a continuous formed billet **32**.

The continuous casting mold is typically a water cooled copper mold. A special low fusion point refractory material **34** is utilized over the steel in the continuous casting mold to reduce lead fuming from the molten leaded steel poured into the mold and to lubricate the mold surfaces to avoid sticking of the solidified steel to the mold walls. A ventilation tube **36** is provided at the top of the mold **30** to withdraw any volatilized lead. Upon solidification of the steel containing the dissolved lead, the lead is rejected from solution as a fine, uniform dispersion within the steel.

Results in practice—examples

While the maximum level of lead obtainable in steel, rejected from solution, is approximately 0.43%, based upon the upper solubility limit, the dissolution kinetics of lead in actual processes typically result in a lower level of solubility and hence an upper target limit lower than 0.43%. It has been found that under commercially practical conditions, a lead solubility level of .15% by weight can be readily obtained, but that this represents a realistic upper limit under such conditions. In such a situation, the actual amount of lead added should be based upon a target amount desired that is consistent with the realistic or practical upper limit of lead solubility as influenced by the kinetics and variables of the particular process, so that an excess of lead above that which is soluble plus that which is lost in the process is not introduced, only then to require mechanical segregation.

Some appreciation of the process and readily obtained levels of lead in fine dispersion within steel of typical types to which lead may be advantageously added, may be gained from the following table of steel compositions, obtained through small scale tests, and a brief description of the processes by which the compositions were obtained.

TABLE I.—LEADED STEEL HEAT COMPOSITION

Example	Approx. Total weight, pound.	Steel type[1]	C	Mn	Si	P	S	Cr	Mo	Al	Pb
1	250	4118	0.18	0.89	0.30	0.025	0.213	0.59	0.10		0.155
2	250	Free machining	0.04	0.88		0.043	0.33				0.15
3	250	Free machining	0.028	0.76		0.05	0.35				0.135
4	250	4140	0.36	1.3	0.25	0.002	0.030	1.17	0.21		0.15
5	250	1118	0.145	1.10		0.002	0.13				0.135
6	250	1020	0.22	0.59	0.35		0.010			0.027	0.125
7	[2] 150	8620 leaded, 0.40-0.70 Ni	0.18/0.23	0.70/0.90	0.20/0.35	[3] 0.035	[3] 0.040	0.40/0.60	0.15/0.25		0.08
8	[2] 150	Free machining	[3] 0.09	0.75/1.05		0.04/0.90	0.26/0.35				0.08

[1] Numbers indicate AISI designation.
[2] Tons.
[3] Max.

EXAMPLE 1

Steel of a type designated 4118 (AISI designation) in an amount of 250 pounds at a tap temperature of 2900 degrees Fahrenheit was placed in an induction heated refractory vessel. Melt additions of Mn, FeP, Cr, and FeSi were added to the steel in the vessel in amounts to produce the composition identified as Example 1 in Table I. Lead was added to the melt in an amount of 0.25% by weight, in the form of lead shot dropped into the steel melt, and a slag cover was applied over the melt. Prior to and during the lead addition, the melt was induction stirred, and stirring was continued after lead addition for a period of 4½ minutes. Pin tests were taken and the composition of the steel was determined as follows: carbon content by Leco analysis; other elements by spectrographic analysis. The composition was as indicated in Table I. Electron microprobe and sweat tests were used to examine the presence, distribution and size of the lead particles in the solidified ingot specimens. The lead appeared as an exudate and was of substantially uniform size and distribution, finely dispersed throughout the steel, as indicated by the sweat test.

EXAMPLE 2

Example 1 was repeated except that a free machining steel was used and the lead was added after additions of Mn, FeP and FeS. The composition is indicated as Example 2 in Table I.

EXAMPLE 3

Example 2 was repeated with a somewhat different free machining steel composition, as indicated in Table I.

EXAMPLE 4

Example 1 was repeated except that a type 4140 steel was used and the lead was added after additions of FeSi, Mn, Cr and FeS and the temperature of the steel when tapped into the vessel was 2850 degrees Fahrenheit. The composition of the steel is indicated as Example 4 in Table I.

EXAMPLE 5

Example 1 was repeated except that a type 1118 steel was used and the lead was added after additions of Mn and FeS. The composition is indicated as Example 5 in Table I.

EXAMPLE 6

Example 1 was repeated except that a type 1020 steel was used and the lead was added after additions of FeSi, Al, Mn and FeS. The composition is indicated as Example 6 in Table I.

EXAMPLE 7

The composition of this example, specified under Example 7 in Table I, was obtained by the addition of lead to a plant heat in a ladle after the normal ladle additions and at the tapped temperature. The lead was added to the steel in the form of lead shot in an amount of nine pounds per ton (i.e., .45% by weight) while the ladle was in a degasser. The steel was induction stirred in the degasser.

EXAMPLE 8

Example 7 was repeated except that the lead was added in five pound chunks in an amount of four pounds per ton or .20% by weight.

Additional experimental determinations

Additional experimental data has provided further insight to the mechanism of the present process. A series of 30 five-pound induction heats of type 4118 steel were prepared with a base composition that was as follows, in percent by weight: .26 C, .90 Mn, .35 Si, .030 P, .035 S, .50 Cr, .12 Mo. The temperature was held constant at 2825 degrees Fahrenheit and the heats were made in a magnesia crucible with no slag cover. Lead in the form of shot was added under an Argon atmosphere to the molten bath with induction furnace power on after all other additions were completed. In different instances the lead was added by four methods: (1) as free shot (less than 20 mesh), (2) as steel capsules formed of lead encased by a steel wall .001 to .002 inch thick and submerged below the bath surface, (3) poured through a quartz tube submerged below the bath surface, and (4) as 5/16 inch diameter lead-1008 steel composites added directly to the bath surface. Lead additions were in amounts of .15, .25, .35 and 1.00 percent of the bath weight.

Ingots from several heats produced as above were examined in the vertical ingot plane and at various horizontal ingot planes including the ingot bottom. No significant variation in lead content was found and the maximum content was .15% by weight. Lead retention was found to vary with melt temperature, increasing with an increased temperature. Chemical analysis, optical examination and sweat tests indicated a fine and uniform lead dispersion and very little variation in lead within each ingot, with a lead particle size typically varying between one and ten microns, and no larger than fifteen microns. Maximum sized particles were associated with MnS inclusions. A metallographic procedure used for optical examination of the heats comprised polishing a sample with Al_2O_3 and etching with dilute acetic acid sufficient to etch the lead. A standard sweat test was used to check uniformity of lead distribution and occurence of large lead particles, in which ingot sections were fine ground on a wet belt sander, immersed in heavy oil, heated at 1270 degrees Fahrenheit for ten minutes in air, and observed. Both the consistent uniform lead content from heat to heat and the dependence of lead retention on temperature indicate the formation of a lead-steel solution. Simple drilling tests on leaded slabs gave decided improvement in machining when compared with 4118 type steel without lead.

The above experiments further indicated that the lead content did not vary more than ±.01% with the different methods of lead addition as described previously and with the different amounts added, as shown in Table II.

TABLE II.—LEAD ADDITION METHODS, INDUCTION MELTED 4118 UNDER 1 ATM. ARGON, NO SLAG COVER

	Percent Pb in ingot, percent by weight			
Percent Pb added, percent by weight	Free shot	Method of addition lead-steel capsule	Quartz tube	Lead-1008 steel composite
.15		.072	.061	
.25	.09	.083	.086	.100
.35		.092	.084	
1.00			.150	

The smaller increase in the percent of lead in the ingot for the relatively greater increasing amounts added indicates that the dissolution kinetics of the system materially limited the solubility level with respect to the potential level of .43%. Excess lead over that lost through volatilization and to the slag and refractories was not evidenced in the ingots due, it is believed, to mechanical separation by the induction stirring.

As illustrated by Table III, the level of lead is increased by a slag cover over the melt and by an increased bath temperature. Lead in the amount of .25% by weight was added in the form of a lead-1008 steel composite. Measurements of lead content with respect to the time after the lead addition indicates maximum lead content within about 1 to 2 minutes on the average.

TABLE III.—EFFECT OF SLAG COVER AND BATH TEMPERATURE

Steel type	Slag cover	Bath temp., °F.	Analysis of ingot percent (by wt.) Pb
4118	No	2,825	.115
4118	Yes	2,825	.130
4118	Yes	3,000	.150

Induction stirring was found to produce no systematic variation in ingot lead content, through the production of a series of heats made with furnace power off during lead additions.

The effect of certain chemicals on lead retention is indicated by Table IV. Magananese and sulfur were varied in a series of heats using type 4118 steel, with the lead additions (by the composite pellet method) held constant at .25%. The lead contents of these heats together with lead retention in pure iron and 1080 steel is tabulated. Only where elements were varied was the content of these elements determined by chemical analysis.

TABLE IV.—EFFECT OF STEEL CHEMISTRY ON LEAD RETENTION

Steel Type	Element varied	Analysis of Ingot, percent Mn	S	Pb
Pure Iron		tr.	tr.	.092
		[1].90	[1].035	.100
	Mn	.41	[1].035	.070
4118	Mn	1.35	[1].035	.094
	S	.79	.007	.122
	S and Mn	.01	.33	.076
1080		[1].80	[1].035	.083

[1] Aim chemistry. Ingot not analysed for this element.
NOTE.—Lead addition constant at .25% of bath weight.

In addition to the above, it was determined that the addition of tin and arsenic (content in ingots were greater than .10% by weight) to 4118 steel with a .25% lead addition reduced the recovery of lead by approximately 50% to .05% lead. The recovery of lead, when lead was added as LiPb, in 4118 steel was likewise reduced to a lead content of .051%.

The time required for complete mixing of lead additions through induction stirring was determined by analyzing lead content during the dissolution of lead in 5 pound steel heats. Times have also been determined for commercial size heats by using radioactive tracer techniques in which 56_{Mn} was added to a steel melt and the time determined when the 56_{Mn} was completely, uniformly, mixed. Times varied for complete, uniform mixing, as indicated by the radioactive tracer in the larger scale tests, from 47 to 300 seconds. Optimum times depend on the induction stirring unit capabilities and the power applied. Other tests on 300 pound leaded steel heats in an induction furnace required an average of one to two minutes to reach maximum lead content in the solidified steel (assuming that the dissolved lead content in the molten steel approximately equals the target lead content of the solid steel when the solid steel contains only a fine, uniform dispersion of lead particles with no gross segregation or agglomeration).

The methods described above and the parameters involved are applicable to steel making processes in which it is desired to produce a leaded steel of high quality. It will be apparent to those skilled in the art that variations can and will be made to meet various conditions and specific data has been provided herein to provide a guide for achieving variations that may be desired. It will be appreciated, then, that while preferred embodiments of the invention have been described with particularity, the intention is to cover and secure all modificaions, alternatives and equivalents within the spirit and scope of the invention expressed in the appended claims.

What is claimed is:

1. A process of adding lead to steel to assure a uniform distribution of only finely dispersed lead particles the largest of which are no greater than 30 microns in diameter, including the steps of first adding lead to steel in a vessel and then removing the leaded steel from the vessel to a mold, such as an ingot mold or a continuous casting mold or the like, wherein the temperature of the steel is at least 75 degrees Fahrenheit above the liquidus temperature of the steel when the lead is added, but no higher than 3092 degrees Fahrenheit, the steel is maintained within the vessel for at least one minute after the lead is added, and essentially all of the lead in the steel removed from the vessel is in a dissolved state.

2. A process of adding lead to steel to assure a uniform distribution of finely dispersed lead particles in the steel when solidified, including the steps of containing molten steel to which lead is to be added in a vessel at a temperature at leat 10 degrees Fahrenheit above the liquidus temperature of the steel; providing a cover layer of slag over the steel in the vessel; adding lead to the steel in the vessel in a quantity substantially equal to an amount of lead desired in the solidified steel plus an amount of lead determined to be lost through volatilization and combination with refractory and slag materials in contact with the steel, the first said amount not to exceed the actual solubility level of the lead in the steel under existing process conditions; retaining the steel within said vessel for a time period of at least one minute after said addition of lead prior to removing the steel from the vessel; removing steel containing lead essentially only in the dissolved state from the vessel; and solidifying the steel removed from the vessel.

3. A process of adding lead to steel to assure a uniform distribution of finely dispersed lead particles in the steel when solidified, including the steps of containing molten steel to which lead is to be added in a vessel at a temperature at least 10 degrees Fahrenheit above the liquidus temperature of the steel; providing a cover layer of slag over the steel in the vessel; adding lead to the steel in the in a quantity substantially equal to an amount of lead desired in the solidified steel plus an amount of lead determined to be lost through volatilization and combination with refractory and slag materials in contact with the steel, the first said amount not to exceed the actual solubility level of the lead in the steel under existing process conditions; retaining the steel within said vessel for a time period of at least one minute after said addition of lead prior to removing the steel from the vessel; inductively stirring the steel within the vessel for at least one minute after the lead is added; removing steel containing lead essentially only in the dissolved state from the vessel; and solidifying the steel removed from the vessel.

4. A process of adding lead to steel to assure in the steel, when solidified, a uniform distribution of finely dispersed lead particles the predominant size of which is less than 10 microns in diameter, including the steps of containing molten steel to which lead is to be added in a vessel at a temperature at least 10 degrees Fahrenheit above the liquidus temperature of the steel; adding only enough lead to the steel to obtain a lead content substantially equal to the solubility limit under existing process conditions; retaining the steel within said vessel for a time period of at least one mintue after said addition of lead prior to removing the steel from the vessel; removing steel containing lead essentially only in the dissolved state from the vessel; and solidifying the steel removed from the vessel.

5. A process of adding lead to steel to assure in the steel, when solidified a uniform distribution of finely dispersed lead particles the predominant size of which is less than 10 microns in diameter, including the steps of containing molten steel to which lead is to be added in a vessel at a temperature at least 10 degrees Fahrenheit above the liquidus temperature of the steel; providing a cover layer of slag over the steel in the vessel; adding lead to the steel in the vessel in a quantity substantially equal to an amount of lead desired in the solidified steel plus an amount corresponding to that which will be lost through volatilization and combination with refractory and slag materials in contact with the steel, the first said amount not to exceed 0.43 percent by weight of the steel and the said additional amount not to exceed 100 percent of said first amount; retaining the steel within said vessel for a time period of at least one minute after said addition of lead prior to removing the steel in the vessel; removing steel containing lead essentially only in the dis-

solved state from the vessel; and solidifying the steel removed from the vessel.

6. A process of adding lead to steel to assure in the steel, when solidified a uniform distribution of finely dispersed lead particles the predominant size of which is less than 10 microns and the largest of which are no greater than 30 microns in diameter, including the steps of containing molten steel to which lead is to be added in a vessel at a temperature at least 10 degrees Fahrenheit above the liquidus temperature of the steel; providing a cover layer of slag over the steel in the vessel; adding lead to the steel in the vessel in a quantity substantially equal to an amount of lead desired in the solidified steel plus an amount corresponding to that which will be lost through volatilization and combination with refractory and slag materials in contact with the steel, the first said amount not to exceed 0.43 percent by weight of the steel and the said additional amount not to exceed 100 percent of said first amount; retaining the steel within said vessel for a time period of at least one minute after said addition of lead prior to removing the steel in the vessel; inductively stirring the steel within the vessel for at least one minute after the lead is added; removing steel containing lead essentially only in the dissolved state from the vessel; and solidifying the steel removed from the vessel.

7. A process of adding lead to steel to assure in the steel, when solidified a uniform distribution of finely dispersed lead particles the predominant size of which is less than 10 microns in diameter, including the steps of containing molten steel to which lead is to be added in a vessel at a temperature at least 75 degrees Fahrenheit above the liquidus temperature of the steel; adding lead to the steel in the vessel in a quantity substantially equal to an amount of lead desired in the solidified steel plus an amount corresponding to that which will be lost through volatilization and combination with refractory and slag materials in contact with the steel, the first said amount not to exceed .15 percent by weight of the steel and the said additional amount not to exceed 100 percent of said first amount; retaining the steel within said vessel for a time period of at least one minute after said addition of lead prior to removing the steel in the vessel; removing steel containing lead essentially only in the dissolved state from the vessel; and solidifying the steel removed from the vessel.

8. A process of continuously casting steel containing a uniform distribution of finely dispersed lead particles the predominant size of which is less than 10 microns in diameter, including the steps of: containing molten steel to which lead is to be added in a vessel at a temperature at least 10 degrees Fahrenheit above the liquidus temperature of the steel, adding lead to the steel in the vessel in a quantity substantially equal to an amount of lead desired in the cast steel plus an amount corresponding to that which will be lost through volatilization and combination with refractory and slag materials in contact with the steel, the first said amount not to exceed the actual solubility level of the lead in the steel under existing process conditions; applying a slag cover to the steel in the vessel; stirring the steel in said vessel for at least one minute after the addition of said lead; removing steel containing lead essentially only in a dissolved state from said vessel and introducing it to a continuous casting mold; and continuously casting a solidified shape of leaded steel.

9. A process of continuously casting steel containing a uniform distribution of finely dispersed lead particles the predominant size of which is less than 10 microns in diameter and the largest of which are no greater than 30 microns in diameter, including the steps of: containing molten steel to which lead is to be added in a vessel at a temperature at least 75 degrees Fahrenheit above the liquidus temperature of the steel, adding lead to the steel in the vessel in a quantity substantially equal to an amount of lead desired in the cast steel plus an amount corresponding to that which will be lost through volatilization and combination with refractory and slag materials in contact with the steel, the first said amount not to exceed the actual solubility level of the lead in the steel under existing process conditions; applying a slag cover to the steel in the vessel; inductively stirring the steel in said vessel and under an inert atmosphere for at least one minute after the addition of said lead; teeming steel containing lead essentially only in a dissolved state from said vessel to a tundish and flowing said steel from the tundish to a continuous casting mold; and continuously casting a solidified shape of leaded steel.

10. A process of continuously casting steel containing a uniform distribution of finely dispersed lead particles the predominant size of which is less than 10 microns in diameter, including the steps of: containing molten steel to which lead is to be added in a vessel at a temperature at least 10 degrees Fahrenheit above the liquidus temperature of the steel; adding lead to the steel in the vessel in a quantity substantially equal to an amount of lead desired in the cast steel plus an additional amount at least equal to that which will be lost through volatilization and combination with refractory and slag materials in contact with the steel, the first said amount not to exceed the actual solubility level of the lead in the steel under existing process conditions; applying a slag cover to the steel in the vessel; stirring the steel in said vessel for at least one minute after the addition of said lead; removing steel containing lead essentially only in a dissolved state from said vessel; and solidifying the steel removed from the vessel.

11. A process of continuously casting steel containing a uniform distribution of finely dispersed lead particles the predominant size of which is less than 10 microns in diameter, including the steps of: containing molten steel to which lead is to be added in a vessel at a temperature at least 10 degrees Fahrenheit above the liquidus temperature of the steel; adding lead to the steel in the vessel in a quantity substantially equal to an amount of lead desired in the cast steel, not exceeding the actual solubility level of the lead in the steel under existing process conditions, plus an additional amount up to an amount corresponding to 100% of said amount desired; applying a slag cover to the steel in the vessel; stirring the steel in said vessel for at least one minute after the addition of said lead; removing steel containing lead essentially only in a dissolved state from said vessel; and solidifying the steel removed from the vessel.

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L. DEWAYNE RUTLEDGE, Primary Examiner

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U.S. Cl. X.R.

75—49, 59, 123 F

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,671,224 Dated June 20, 1972

Inventor(s) Donald F. North, Jr.; Jerry D. Thomas; Gerald W. Worth

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 27, "proces" should be -- process --.
Column 2, line 38, after "immediately" should be -- following --
Column 2, line 41, "casing" should be -- casting --.
Column 2, line 68, "ofr" should be -- of --.
Column 3, line 60, "proccesses" should be -- processes --.
Column 4, line 5, "kentics" should be -- kinetics --.
Column 4, line 58, "htan" should be -- than --.
Table I, column S, line 1, "0.213" should be -- 0.023 --.
Table I, column Pb, line 1, "0.155" should be --0.15 --.
Column 12, line 7, "leat" should be -- least --.
Column 12, line 28, after "steel in the" (second occurrence) should be -- vessel --.

Signed and sealed this 1st day of May 1973

(SEAL)
Attest:

EDWARD M. FLETCHER, JR
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334

UNITED STATES PATENT AND TRADEMARK OFFICE

Certificate

Patent No. 3,671,224 Patented June 20, 1972

Donald F. North, Jr., Jerry D. Thomas, and Gerald W. Worth

Application having been made by Donald F. North, Jr., Jerry D. Thomas and Gerald W. Worth, the inventors named in the patent above identified, and Republic Steel Corporation, Cleveland, Ohio, the assignee, for the issuance of a certificate under the provisions of Title 35, Section 256, of the United States Code, deleting the name of Jerry D. Thomas as a joint inventor, and a showing and proof of facts satisfying the requirements of the said section having been submitted, it is this 1st day of June 1976, certified that the name of the said Jerry D. Thomas is hereby deleted to the said patent as a joint inventor with the said Donald F. North, Jr. and Gerald W. Worth.

FRED W. SHERLING,
Associate Solicitor.