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(54) ACTIVATOR MIXTURE FOR INCREASING THE STRENGTH OF IRON ALLOYS.

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Description

The invention relates to an additive composition consisting of a plurality of components which improves the metallurgic quality of iron-based alloy systems and considerably increases the strength thereof when used in the course of steel production and also improves the strength of a weld formed using a powder-cored welding wire in which the core is made of the composition.

The usefulness of a steel depends on its metallurgic quality, e.g. yield strength at permanent deformation, brittleness, stress limit of fatigue, weldability and resistance to wear.

One of the most important properties of a steel is the stress it can withstand without permanent deformation (0% yield strength). The value of 0% yield strength determines the load that can be placed on structures or structural elements made of the steel.

Another important property of a steel is its ductility. In general with steels, an increase in strength is accompanied by a decrease in ductility. The development of presently used steels has concentrated on processing technology. However, the use of alloying additives in iron-based metals in order to increase the load-bearing ability of the metal and thus reduce the quantity of metal necessary to bear a given load has not been properly emphasized in industrial application.

Presently used steels - with the exception of some functional properties required by special technologies - do not meet the requirements of modern technology.

Different methods are known for improving a single property of a steel for a particular final use by alloying of suitable elements or by heat treatment, in accordance with the intended final use. For example boron may be added to increase hardness (see WO 83/00167) in a composition that also contains rare earth elements and titanium and optionally silicon, calcium, manganese and zirconium; the balance of the composition is made up of iron.

With industrially produced steels, as a result of lattice faults and as a result of dislocations resulting from the different form, size and orientation of individual crystals (grains) in the steel, permanent deformation can be induced by a stress that is 1000-times lower than the theoretical lattice strength of the metal. Any means that hinders dislocations between the grains in steel increases the strength of the steels; such means are, for example, elements located in the metal lattice by substitution or interstitially, dislocations, grain boundaries, twin crystals, alien phases, separations, all being independent strengthening mechanisms. Practice has confirmed the fact that presently used methods for increasing steel strength, which activate only one or two strengthening mechanisms and mainly by thermal treatment, can improve ductility but can only increase strength to a limited extent.

The object of the present invention is to provide an additive composition for strengthening steels while simultaneously maintaining the ductility of the steel at an acceptable level whereby the strength of a steel more closely approaches the strength of the metal lattice, thus increasing the load-bearing properties of the steel.

Accordingly, the present invention provides a composition for use in a quantity of 5 to 17 kg/t in the course of steel production or as a powder core of a welding wire electrode; the composition is as follows:

Ca and/or Na	16 to 30 %
Si	13 to 30 %
V and/or Mo	2 to 28 %
Nb and/or Ta	2 to 25 %
Zr and/or Ce	2 to 15 %
Ti	2 to 14 %
Al and/or Ba	1 to 15 %
B and/or Be	0.3 to 3.0 %
C	1 to 5 %
Fe	5 to 20 %
N	1 to 10 %.

The proportion and quantity of the alloying components in accordance with the invention, as well as the method of alloying using such a composition ensure good physico-chemical and metallo-physical conditions in the course of steel production and in the course of welding when used as the powder core of a welding electrode. It thus improves the metallurgical quality and simultaneously considerably increases the strength of industrial iron-based alloy systems and also maintains ductility properties at an acceptable level while, at the same time increasing the proportion of the theoretical lattice force that can be utilized for load bearing.

In the course of steel production the composition may be added with a maximum particle size of 8 mm during discharge of liquid steel into the ladle and the composition will be well-dispersed utilizing the agitating effect of the liquid steel discharge flow; alternatively the composition may be added by means of the widely used method of blowing the composition into the liquid steel after discharge. When producing
 5 filler wire with a powder core, the composition is charged in the prescribed fraction and well mixed.

The properties of the individual alloying components and a properly chosen composition thereof in the alloy systems result in local physico-chemical, nuclear and kinetic conditions in the course of alloying, strengthening, heating and hot working, as well as re-crystallization, which considerably increase the quantity of the elements that can be utilized for increasing the strength of a steel.

10 Some of the components in the additive composition of the present invention, when used in an expedient proportion, form complex compounds with a high melting point in the steel and form partly crystallized nuclei of active size early in the melt thus promoting crystallization of the steel melt and thereby shortening the time of solidification; partly by this effect, the primary grain size and the possibility of grain enrichment are reduced and the conditions of re-crystallization are considerably improved.

15 Furthermore, the additive composition in accordance with the invention establishes conditions in the course of solidification and re-crystallization that considerably increase the ability of the steel to dissolve interstitial elements in the metal lattice thereby increasing the solubility of such elements and so increasing the number of stressed lattice sites caused by interstitial atoms and also increasing the extent of the stress they induce. Stressing of the lattice by interstitial atoms markedly increases the number of dislocations that
 20 promote and determine the formation of segregated phases for hindering displacement of the metal crystals (grains).

Some components of the composition of the present invention form complex metallic phases of high shear-strength, which both increase and stabilize the internal stress of the lattice of the base steel when built-in into lattice faults. Lattice faults produced metallurgically promote formation of these metallic phases
 25 and determine the location and density of the phases, thereby considerably increasing the efficiency of anchoring performed by the phases in preventing dislocation of the metal crystals under the influence of applied loads.

Some of the components of the composition, when deposited at the grain boundaries, decrease the rate of diffusion of the metal atoms in their vicinity thus delaying the formation there of non-coherent phases. In
 30 such a manner an increase in undesired phases along the grain boundaries is hindered and the segregation of alloying elements will be prevented. In such a manner, the strength of homogeneous grain boundaries will be considerably increased and cracking occurring as a result of stress can be delayed; elongation and contraction at creep break increases, as does the ductility of the alloy system, its cold and hot malleability and ductility, its fatigue limit and its strength for supporting loads.

35 Some of the components of the composition produce inclusions of low specific weight, which rise easily up into the slag, thus considerably reducing the content of harmful inclusions in the steel. In addition, complex spherical inclusions can also be formed that not only remain in the steel and keep their original shape even in the course of plastic deformation, but also they bind sulfur atoms on their surface, forming a sulfide coating, thus considerably reducing the formation of iron sulfide; in this way more advantageous
 40 plasticity and anisotropic properties can be assured for the steel.

Accordingly, the composition according to the invention provides improved metallurgical quality of given steels, promotes strengthening mechanisms without thermal treatment and provides several strengthening mechanisms whose effects are additive, thereby simultaneously increasing the utilizable strength of steels.

The effect of the composition according to the invention will be illustrated by means of the following
 45 examples. Table 1 shows three base steel compositions (B-1, B-2 and B-3) to which the additive composition of the present invention has not been added and the corresponding three steel compositions (A-1, A-2 and A-3) to which a composition of the present invention has been added. The compositions that were added to steels A-1, A-2 and A-3 are shown in Fig. 2.

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Table 1

	A ₁	B ₁	A ₂	B ₂	A ₃	B ₃
C	0,15	0,14	0,23	0,27	0,07	0,07
Mn	1,54	1,65	1,88	1,77	0,60	0,68
Si	0,52	0,42	0,72	0,45	0,47	0,64
P	0,013	0,021	0,009	0,019	0,009	0,008
S	0,006	0,013	0,009	0,021	0,018	0,021
Cr	0,32	0,27	0,50	0,23	11,32	11,43
Ni	0,10	0,07	0,21	0,07	0,08	0,07
Cu	0,09	0,23	0,12	0,21	0,13	0,07
Mo	0,10	0,08	0,16	0,06	0,07	0,02
Nb	0,09	0,04	0,11	-	0,043	-
V	0,14	0,16	0,10	-	0,02	0,04
Zr	0,01	-	0,02	-	0,03	-
Ti	0,02	0,03	0,02	0,01	0,03	0,64
Al	0,04	0,12	0,062	0,072	0,032	0,053
N	0,026	0,007	0,010	0,009	0,029	0,007
B	0,0024	-	0,0017	-	0,0020	-
Ce	0,030	-	0,024	-	0,012	-
Ca	0,0012	-	0,0006	-	0,00009	-
Fe	Balance					

Charges were prepared using UHP + AOD steel-manufacturing equipment with a volume of 50 tons.

Table 2

	A ₁	A ₂	A ₃
Ca	21,14	12,96	19,29
Na	-	-	-
Si	20,50	17,34	27,57
V	10,69	7,51	1,67
Mo	7,63	12,01	5,86
Nb	6,87	8,26	3,60
Ta	-	-	-
Zr	3,05	4,50	7,53
Ce	2,29	1,80	1,00
Ti	3,05	3,00	5,02
Al	6,11	7,51	5,86
Ba	-	-	-
C	1,29	0,75	1,67
Fe	17,1	15,41	10,94
N	3,94	1,88	5,02
B	0,18	0,13	0,17
Be	-	-	-
kg/t	13,10	13,32	11,95

After production, sheets in a thickness of 12.5 mm were formed using traditional hot metalworking.

The mechanical properties of the sheets in a hot rolled state and annealed at three different temperatures are contained in Table 3, which also shows the corresponding values for the base steels (B-1, B-2 and B-3).

Table 3.

	R_m N/mm ²	%	$R_p^{0.2}$ N/mm ²	%	$R_p^{0.002}$ N/mm ²	Δ %	A_5 %
hot rolled							
A-1	841	147	720	149	600	259	20,7
B-1	572	100	483	100	231	100	21,0
A-2	1443	173	1130	151	994	258	15,9
B-2	832	100	750	100	384	100	14,6
A-3	1362	250	988	244	810	346	18,0
B-3	545	100	405	100	234	100	16,0
annealed * and air cooled							
A-1	854	158	749	184	758	303	20,1
B-1	540	100	407	100	250	100	21,3
A-2	1175	142	1113	149	1084	302	17,1
B-2	872	100	747	100	359	100	15,0
A-3	1338	257	1131	290	1038	447	20,6
B-3	520	100	390	100	232	100	20,0

R_m = tensile strength

$R_p^{0.2}$ = yield strength at 0.2% elongation

$R_p^{0.002}$ = elastic limit (0.002% elongation)

A_5 = elongation at fracture of a length (l) wherein l = 5x diameter of the specimen

% = percentage difference between elastic limit as compared to the elastic limit of the corresponding base charge ("B" steels)

Annealing conditions:

* = A_1 and B_1 at 400 °C for 90 min
 A_2 and B_2 at 500 °C for 90 min
 A_3 and B_3 at 600 °C for 90 min.

It should be noted that the composition according to the invention may be applied for welding as well.
 The composition can be used in the form of a powder to form the core of a powder-filled band electrode.

Claims

1. A composition for addition to iron-based alloys to improve the strength thereof characterized in that, except for incidental elements and impurities, it consists of Ca and/or Na 16 to 30%; Si 13 to 30%; V and/or Mo 2 to 28%, Nb and/or Ta 2 to 25%; Zr and/or Ce 2 to 15%; Ti 2 to 14%; Al and/or Ba 1 to 15%; B and/or Be 0.1 to 3.0%; C 1 to 5%; Fe 5 to 20% and N 1 to 10%.
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2. A process for producing steel, characterised in that the composition as claimed in claim 1 is added to the liquid steel in a quantity of 5 to 17 kg/t steel in the final phase of the steel production prior to solidification of the steel.
- 10 3. A process as claimed in claim 2, wherein the composition is added to the steel during discharge thereof into a ladle.
4. A process as claimed in claim 2, wherein the composition is blown into the molten steel.
- 15 5. A powder-core welding electrode, wherein the powder core of the electrode comprises a composition as claimed in claim 1.

Patentansprüche

- 20 1. Zusatzgemisch zum Zumischen zu Eisenlegierungen für eine Erhöhung der Festigkeit derselben, dadurch gekennzeichnet, daß das Zusatzgemisch abgesehen von Nebenelemente und Verunreinigungen aus 16 bis 30% Ca und/oder Na; 13 bis 30% Si; 2 bis 28% V und/oder Mo; 2 bis 25% Nb und/oder Ta; 2 bis 15% Zr und/oder Ce; 2 bis 14% Ti; 1 bis 15% Al und/oder Ba; 0,1 bis 3,0% B und/oder Be; 1 bis 5% C; 5 bis 20% Fe und 1 bis 10% N besteht.
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2. Verfahren zum Herstellen von Stahl, dadurch gekennzeichnet, daß das Zusatzgemisch nach Anspruch 1 dem flüssigen Stahl in einer Konzentration von 5 bis 17 kg/t Stahl in der Endphase der Stahlherstellung vor dem Erstarren des Stahls zugemischt wird.
- 30 3. Verfahren nach Anspruch 2, wobei das Zusatzgemisch dem Stahl während dem Einfüllen des Stahls in eine Gießpfanne zugesetzt wird.
4. Verfahren nach Anspruch 2, wobei das Zusatzgemisch in den geschmolzenen Stahl eingeblasen wird.
- 35 5. Schweißelektrode mit Pulverkern, wobei der Pulverkern der Elektrode das Zusatzgemisch nach Anspruch 1 enthält.

Revendications

- 40 1. Une composition d'addition pour alliages à base de fer destinée à améliorer leur résistance, caractérisée en ce que, outre les impuretés et éléments accidentels, elle contient 16 à 30% de Ca et/ou Na, 13 à 30% de Si, 2 à 28% de V et/ou Mo, 2 à 25% de Nb et/ou Ta, 2 à 15% de Zr et/ou Ce, 2 à 14% de Ti, 1 à 15% d'Al et/ou Ba, 0,1 à 3,0% de B et/ou Be, 1 à 5% de C, 5 à 20% de Fe et 1 à 10% de N.
- 45 2. Un procédé de production d'acier, caractérisé en ce que la composition telle que revendiquée dans la revendication 1, est ajoutée à l'acier liquide en une proportion de 5 à 17 kg/t d'acier au cours de la phase finale de production de l'acier, préalablement à la solidification de l'acier.
3. Un procédé tel que revendiqué dans la revendication 2, caractérisé en ce que la composition est
50 ajoutée à l'acier au cours de la coulée en poche de l'acier.
4. Un procédé tel que revendiqué dans la revendication 2, caractérisé en ce que la composition est injectée par soufflage dans l'acier fondu.
- 55 5. Une électrode de sondage à noyau pulvérulent, caractérisée en ce que l'électrode est formée d'une composition telle que revendiquée dans la revendication 1.