

## Description

The present invention relates to a hearth roll for use in the continuous annealing of steel and a process for producing said roll.

This invention relates particularly to the problem of providing a hearth roll with a high wear and thermal shock resistant coating, for use in annealing steel, stainless steel and silicon steel sheet in a hearth (furnace). The hearth rolls carry the steel sheet through the hearth. The temperature in the hearth may vary from about 816°C (1500°F) to over 1093°C (2000°F) depending upon the type of steel, the travel speed of the sheet steel as it passes through the furnace and the duration of time in the furnace.

A major problem encountered in the annealing operation is the transfer or pick-up of material from the steel sheet to the hearth rolls. If pick-up occurs, it will accumulate on the hearth rolls and damage the steel sheet being processed. To avoid this problem frequent roll changes are required with concomitant costs for replacement and lost production. This problem has become more severe in recent years since thinner sheets are being used, along with higher speeds and temperature to increase productivity.

To suppress the transfer of material to the hearth roll and to increase wear resistance it is desirable to coat the hearth roll with a coating composition which is substantially chemically inert at elevated temperatures. An undercoating of metal or a ceramic-metal alloy is used to prevent spalling. Spalling may also be prevented using a graded coating in which the composition of the undercoating is gradually varied from 100% alloy to 100% ceramic. Unfortunately, the ceramic coatings presently available usually crack in thermal cycling due to a large difference in thermal expansion between the substrate, a heat resistant alloy, and the coating. The alloy undercoat at the interface is oxidized at or above 1000°C in the presence of oxygen leading to spalling of the ceramic layer. When a graded coating is used, the alloy component of the coating is also oxidized which, in turn, increases the volume of the coating. Upon cooling, the coating spalls due to excessive compressive stress created by the shrinkage of the substrate.

EP-A-230554 discloses a corrosion and wear resistant material produced by a thermal spray using a powder which may consist of zirconia and zirconium silicate. The zirconium silicate is used as a corrosion barrier to protect the zirconia by first producing a composite powder with the zirconia buried in the zirconium silicate. The application intended is high temperature wear resistance in an oxidising environment typical of a gas turbine engine.

Fr-A-1536493 teaches the use of a combination of zirconia and zirconium silicate within this disclosure of all oxides with melting points higher than 1000°C. This combination could be used to produce the outer layer of a multi-layer coating system, which it is intended to use as a protective layer in the production of acetylene or the cracking of hydrocarbons.

According to the present invention there is provided a hearth roll having a metal surface coated with a wear resistant refractory oxide coating which comprises particles of zirconium silicate and/or its decomposition products  $\text{SiO}_2$  and  $\text{ZrO}_2$ , in a mixture with particles of zirconia fully or partially stabilized with an oxide selected from  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  and  $\text{HfO}_2$ .

According to a further aspect of the present invention there is provided a process for forming a wear resistant and thermal shock resistant refractory oxide coating on a metal hearth roll for use in the continuous annealing of steel, which process comprises:

formulating a powder feed composition comprising mixing powder particles of zirconium silicate with powder particles of zirconia at least partially stabilized with an oxide selected from  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  and  $\text{HfO}_2$ ; and

thermally spraying the powder feed composition on the metal roll to form an as-deposited coating composition which, by x-ray phase analysis, comprises:  $\text{ZrO}_2 \cdot x$  where x is one of the stabilizing oxides;  $\text{ZrSiO}_4$  and/or its decomposition products  $\text{SiO}_2$  and  $\text{ZrO}_2$ , and  $\text{SiO}_2$ .

It has been found that a thermally sprayed coating formed as a hearth roll from a powder feed composition of zirconium silicate and at least partially stabilized zirconia possesses high resistance to thermal shock in thermal cycling. The powder feed composition of the present invention produces a coating particularly useful to protect the hearth roll in a continuous annealing line for annealing steel, stainless steel or silicon steel sheets. The powder feed composition is applied by a thermal spray technique to produce an as-deposited coating having a composition which by x-ray phase analysis comprises zirconia, silica and zirconium silicate. The major component of the powder composition is partially stabilized zirconia with the zirconium silicate preferably limited to a maximum of 60 wt%. For plasma spray application the powder feed composition should comprise at least 65 wt% stabilized zirconia with the remainder substantially zirconium silicate whereas for detonation gun application the powder feed composition should comprise at least 40 wt% stabilized zirconia and up to 60 wt% zirconium silicate. The zirconia may be either fully or partially stabilized although partially stabilized zirconia is preferred.

It was further discovered in accordance with the present invention that spalling of the coating may be prevented at elevated temperatures exceeding 1150°C by thermally spraying a metallic undercoat. The preferred undercoat is a cobalt based metal matrix comprising Co-Cr-Al-Ta-Y with a dispersion of  $\text{Al}_2\text{O}_3$ .

The present invention is based upon the discovery that a starting powder feed composition consisting essentially of a mixture of zirconium silicate and zirconia with the zirconia being stabilized with a stabilizing oxide such as, for example, yttria, calcia, or magnesia may be thermally sprayed to form a coating possessing the characteristic of being resistant to thermal shock and resistant to steel or steel oxide pick-up from a continuous annealing line. Any conventional thermal spray technique may be used to form the coating including detonation gun deposition and plasma spray deposition. The chemical composition of the thermally sprayed coating should consist of a mixture of at least about 40 wt% zirconia ( $\text{ZrO}_2$ ), including a stabilizer for the zirconia selected from the group consisting of  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  and  $\text{HfO}_2$  with the balance zirconium silicate ( $\text{ZrSiO}_4$ ) and/or its decomposition products  $\text{SiO}_2$  and  $\text{ZrO}_2$ . The preferred weight percent of the component oxides in the coating is 55 to 85% stabilized  $\text{ZrO}_2$  and 15 to 45%  $\text{ZrSiO}_4$  and/or its decomposition products  $\text{SiO}_2$  and  $\text{ZrO}_2$ . The optimum weight percent of the component oxides in the coating is 70 to 85% stabilized  $\text{ZrO}_2$  and 15 to 30%  $\text{ZrSiO}_4$  and/or its decomposition products. The stabilizer should be between 2 and 20 wt% of the zirconia component.

The coatings are preferably applied by detonation gun deposition or plasma spray deposition. A typical detonation gun consists essentially of a water-cooled barrel which is some metres (several feet) long with an inside diameter of about 2.5mm (1 inch). In operation, a mixture of oxygen and a fuel gas, e.g., acetylene, in a specified ratio (usually about 1:1) is fed into the barrel along with a charge of coating material in powder form. Gas is then ignited and the detonation wave accelerates the powder to about 730 m/sec (2400 ft./sec), while heating the powder close to or above its melting point. After the powder exits the barrel, a pulse of nitrogen purges the barrel and readies the system for the next detonation. The cycle is then repeated many times a second.

The detonation gun deposits a circle of coating on the substrate with each detonation. The circles of coating are about 25mm (1 inch) in diameter and several micrometres (a few ten thousandths of an inch) thick. Each circle of coating is composed of many overlapping microscopic thin lenticular particles or splats corresponding to the individual powder particles. The overlapping splats interlock and bond to each other and the substrate without automatically alloying at the interface thereof. The placement of the circles in the coating deposition are closely controlled to build-up a smooth coating of uniform thickness and to minimize substrate heating.

In the plasma arc spray process, an electric arc is established between a non-consumable electrode and a second non-consumable electrode spaced therefrom. Gas is passed in contact with the non-consumable electrode such that it contains the arc. The arc-containing gas is constricted by a nozzle and results in a high thermal content effluent. The powders used to produce the coatings are injected into the effluent nozzle and are deposited onto the surfaces to be coated. This process, which is described in US-A-2 858 411, produces a deposited coating which is sound, dense and adherent to the substrate. The applied coating also consists of irregularly shaped microscopic splats or leaves which are interlocked and bonded to one another and also the substrate.

In general the coating composition for the plasma arc spray process will be substantially equivalent to its corresponding starting material composition. When using the detonation gun to apply the starting material evaporation of the components may result in a significantly different ratio of constituents in the as deposited coating. Thus some change in chemistry may occur during deposition, using any thermally sprayed process. Such changes can be compensated for by adjusting the powder composition or deposition parameters.

Because of the complex phase diagram for Zr-Si-O, the solidifying  $\text{ZrSiO}_4$  powder particles may contain  $\text{ZrSiO}_4$  as a crystallographic phase and/or  $\text{ZrO}_2 + \text{SiO}_2$  as the decomposition products of the molten  $\text{ZrSiO}_4$  in separate crystallographic phases within individual splats. Thus the  $\text{ZrO}_2$  and  $\text{SiO}_2$  are intimately associated within each splat which had previously been  $\text{ZrSiO}_4$  in the powder form. By "associated" is meant the extremely fine and intermixed crystalline structure of  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and/or  $\text{ZrSiO}_4$  crystallites within the splat.

Although the coatings of the present invention are preferably applied by detonation or plasma spray deposition, it is possible to employ other thermal spray techniques such as, for example, high velocity combustion spray (including hypersonic jet spray), flame spray and so called high velocity plasma spray methods (including low pressure or vacuum spray methods). Other techniques can be employed for depositing the coatings of the present invention as will readily occur to those skilled in the art.

The thermal spray coating may be applied directly to the metal substrate. However, an undercoat compatible with the substrate and resistant to oxidation is preferred. An undercoat of a ceramic-metal alloy

mixture having a cobalt based metal matrix containing alumina is preferred. Optimum coatings are a cobalt based alloy with alumina dispersions described in US-A- 4 124 737. The refractory oxide coating reacts with the preferred undercoat to produce an impervious thin layer of aluminium and/or zirconium oxide phases at the interface which prevents oxidation of the undercoat as well as to provide good bonding between the undercoat and the ceramic layer. The impervious layer may be less than 0.005mm (5 microns) and is produced as a result of interdiffusion or oxidation in an environment at an elevated temperature in the presence of oxygen. A similar layer may form in an inert atmosphere as a result of reaction between the oxide overcoat and the metallic undercoat.

The present invention will now be further illustrated with reference to, but in no manner limited to, the following Examples.

Such illustration of the invention in the Examples (particularly Example 3) is shown in the accompanying drawings, wherein the single Figure is a schematic representation of the equipment used to test the propensity of the as-deposited coating on a hearth roll for pick-up of metal or metal oxides under dynamic and static local conditions.

### Example 1

To substantiate the superiority of the coating composition of the present invention, various powder mixtures containing a yttria stabilized zirconia ( $ZrO_2 \cdot 8\% Y_2O_3$ ) and zirconium silicate ( $ZrSiO_4$ ) were mechanically blended into the blend ratios identified in Table I and fed to a plasma torch in a conventional manner to produce a coating on a 304 stainless steel bar. The ceramic coating was applied on one face of the 304 stainless steel bar 6.99x1.91x1.27cm (2 3/4" x 3/4 x 1/2" height) which was first coated with a detonation gun with an undercoat of 0.05 to 0.075mm (50 to 75  $\mu m$ ) of a cobalt-based coating undercoating of 90 (Co-25Cr-7.5Al-0.8Y-10Ta) + 10%  $Al_2O_3$ . Then the ceramic coating was ground to a 100 micrometre thickness before heat cycling.

The coating specimens were heated in air to 1150°C to 1200°C and held for a minimum of six (6) hours followed by air cooling. After five (5) cycles, the specimens were water quenched on the sixth cycle. If no spalling or partial spalling occurred, the coating was described as acceptable. The results are shown below in Table I.

TABLE I

| Coating No. | Powder Mixture % |     | Test Result Spalling After WQ | Hardness HV 0.3 |
|-------------|------------------|-----|-------------------------------|-----------------|
|             | A*               | B*  |                               |                 |
| 1           | 100              | 0   | No                            | 402             |
| 2           | 85               | 15  | No                            | 587             |
| 3           | 75               | 25  | No                            | 539             |
| 4           | 65               | 35  | Partial Spalling*             | 532             |
| 5           | 50               | 50  | Spalled                       | 482             |
| 6           | 25               | 75  | Spalled                       | 535             |
| 7           | 0                | 100 | Spalled Before WQ             | 481             |

\* Powder A-yttria stabilized zirconia ( $ZrO_2 \cdot 8\% Y_2O_3$ )

\* Powder B-zirconium silicate ( $ZrSiO_4$ )

\* Partial spalling indicates a lifting of the ceramic layer at edges.

It is apparent from Table I that for plasma torch applications spalling did not occur using a starting powder composition of greater than 65 wt.% zirconia with above about 75 wt. % zirconia being optimum.

### Example 2

Similar tests were conducted using a powder feed composition of calcia stabilized zirconia ( $ZrO_2 \cdot 5CaO$ ) and zirconium silicate in a mechanical blend at the various powder ratios labelled 8 to 12 as reflected in the following Table II. The powder feed composition was applied through a detonation gun over a preferred cobalt-based metal matrix undercoat of (Co-25Cr-7.5Al-10Ta-0.8Y) + (30%  $Al_2O_3$ ). The wear performance, thermal shock resistance and anti-pickup performance was optimum for coatings made with

mixture number 8.

TABLE I

| Coating | $\text{ZrSiO}_4/\text{ZrO}_2$ | Water Quench from 900°C | *Coating Chemistry, wt%                      |
|---------|-------------------------------|-------------------------|----------------------------------------------|
| 8       | 50/50                         | 20 cycles OK            | $\text{ZrSiO}_4$ 43.5<br>$\text{ZrO}_2$ 56.5 |
| 9       | 15/85                         | 20 cycles OK            | 21 79                                        |
| 10      | 30/70                         | 5 cycles 50% spall      | 34 66                                        |
| 11      | 70/30                         | 1 cycles 50% spall      | 46.5 53.5                                    |
| 12      | 85/15                         | 20 cycles OK            | 45 55                                        |

\*Coating chemistry - based on metallic element concentration measured by Electron Microprobe Analyzer

Additional tests as set forth in Examples 3, 4 and 5 were conducted to substantiate the superiority of a detonation gun coating formed from a thermal spray powder feed composition comprising zirconium silicate and partially stabilized zirconia ( $\text{ZrO}_2 \cdot 5\text{CaO}$ ) on a hearth roll based on its anti-pickup characteristics compared to detonation gun coatings of a conventional composition of (Co-25Cr-7.5Al-0.8Y-10Ta) + 10%  $\text{Al}_2\text{O}_3$ , a coating from a feed composition of  $\text{ZrSiO}_4$ , and bare steel. It should be noted that while a detonation gun coating of (Co-25Cr-10Ta-7.5Al-0.8Y) + 10%  $\text{Al}_2\text{O}_3$  powder is a preferred undercoat for the ceramic coatings of this invention it has been used in the past as a hearth coating by itself and for

comparison purposes is designated as coating number 13 in Table III.

### Example 3

The following anti-pickup test was conducted.

Evaluation Method: A semicircular roll simulator as depicted in Figure 1 was used. The rocker 6 is rotated about pivot point 7 by reciprocating arms 8 and 9. Two coated specimens 10, 12 were mounted under the roll for simulating reciprocating sliding motion over the specimens and static reaction under load. A powdered  $\text{Fe}_2\text{O}_3$  and/or Fe powder 14 is placed on specimen 10 for dynamic pickup evaluation and powdered  $\text{Fe}_2\text{O}_3$  or Fe powder 16 is placed on specimen 12 for static pickup evaluation. The test measures the propensity of Fe or  $\text{Fe}_2\text{O}_3$  to stick to surface faces A, B and C respectively under a load of 8.5kg.

Test Conditions Temperature: : 900 °C

Duration Time : 4 hours

Atmosphere : Nitrogen 98% + Hydrogen 2%

Pickup source : Fe &  $\text{Fe}_2\text{O}_3$

Anti-Pickup Index: is determined by the sum of the anti-pickup points (AP) for faces A, B and C based on the following Table III.

Table III

|           | Graded Value | Description                                             |
|-----------|--------------|---------------------------------------------------------|
| Good<br>↑ | 3            | No adhesion                                             |
|           | 2            | Adhesion can be removed by 6kg/cm <sup>2</sup> air blow |
|           | 1            | Adhesion can be removed by hand-rubbing                 |
| ↓<br>Bad  | 0            | Adhesion cannot be removed by the above methods         |

### Results

|                     | AP Point with Fe Powder |   |   |       | AP Point with $\text{Fe}_3\text{O}_4$ Powder |   |   |       | Grand Total |
|---------------------|-------------------------|---|---|-------|----------------------------------------------|---|---|-------|-------------|
| Coating             | A                       | B | C | Total | A                                            | B | C | Total |             |
| 9                   | 0                       | 3 | 1 | 4     | 0                                            | 2 | 3 | 5     | 9           |
| 13                  | 0                       | 1 | 1 | 2     | 0                                            | 0 | 1 | 1     | 3           |
| 14*                 | 0                       | 0 | 0 | 0     | 0                                            | 3 | 2 | 5     | 5           |
| uncoated**<br>steel | 0                       | 0 | 0 | 0     | 0                                            | 0 | 0 | 0     | 0           |

\* Coating 14 was made with a powder consisting of only zirconium silicate ( $\text{ZrSiO}_4$ ).

\*\* Bulk Material for reference: Refractory Cast Steel

**Example No. 4****Test: Wear Resistance under elevated temperature****Equipment: High Temperature Ball on Disk Wear Tester****Test Conditions:**

Temperature: 900 °C

Atmosphere: N<sub>2</sub> 98% + H<sub>2</sub> 2%

Ball size: 9.252mm in diameter

Weight: 2 kg

Sliding Speed: 0.2m/sec

Track: 35 mm in diameter

Total Sliding length: 720m

Ball: High carbon chromium bearing steel, SUJ2

Disk: Coated sample

**Wear Rate Calculation:**

The normalized wear rate is calculated by the following procedure.

a. The wear volume is calculated from area of cross section of scar measured from a profilometer chart multiplied by the circumference of the scar.

b. Wear volume is then divided by applied load and total sliding distance.

| Results        |                               |
|----------------|-------------------------------|
| Coating        | Wear rate mm <sup>2</sup> /kg |
| 8              | $1.2 \times 10^{-8}$          |
| 13             | $7.2 \times 10^{-8}$          |
| 14             | $280 \times 10^{-8}$          |
| uncoated steel | $850 \times 10^{-8}$          |

**Example No. 5****Heat shock Test:**

1000 °C - 15 minute heating from ambient to 1000 °C, water quench for 15 minutes - 1 cycle.

The sample substrate material had a thick plate shape with a dimension of 50x50x10 mm, one 50x50 side coated. The sample substrate was 304 stainless steel.

Thermal shock resistance is evaluated by counting how many cycles the coating can survive without spalling off.

| Sample | No. of Cycles               |
|--------|-----------------------------|
| 8      | no spalling after 20 cycles |
| 13     | no spalling after 20 cycles |
| 14     | spalling after 6 cycles     |

As is apparent from the Tables and all of the above Examples the optimum starting powder blend will necessarily vary depending upon the stabilizer and thermal spray technique used. The as-deposited coating should preferably have at least about 40 wt% stabilized zirconia and up to 60 wt% zirconium silicate. The preferred concentration of the component oxides in the coating independent of crystalline structure should be between about 55 to about 85 wt% stabilized ZrO<sub>2</sub> and 15 to 45% ZrSiO<sub>4</sub> and/or its decomposition products SiO<sub>2</sub> and ZrO<sub>2</sub> with 70 to 85 wt% stabilized ZrO<sub>2</sub> being optimum. The concentration of stabilizer in the as-deposited coating composition should preferably be between 2 to 20 wt% of the zirconia component.

**Claims**

1. A hearth roll for use in the continuous annealing of steel comprising a roll having a metal surface coated with a wear resistant refractory oxide coating which comprises particles of zirconium silicate and/or its decomposition products SiO<sub>2</sub> and ZrO<sub>2</sub>, in a mixture with particles of zirconia fully or partially

**Example No. 4****Test: Wear Resistance under elevated temperature****Equipment: High Temperature Ball on Disk Wear Tester****Test Conditions:**

Temperature: 900 °C

Atmosphere: N<sub>2</sub> 98% + H<sub>2</sub> 2%

Ball size: 9.252mm in diameter

Weight: 2 kg

Sliding Speed: 0.2m/sec

Track: 35 mm in diameter

Total Sliding length: 720m

Ball: High carbon chromium bearing steel, SUJ2

Disk: Coated sample

**Wear Rate Calculation:**

The normalized wear rate is calculated by the following procedure.

- a. The wear volume is calculated from area of cross section of scar measured from a profilometer chart multiplied by the circumference of the scar.
- b. Wear volume is then divided by applied load and total sliding distance.

| Results        |                               |
|----------------|-------------------------------|
| Coating        | Wear rate mm <sup>2</sup> /kg |
| 8              | $1.2 \times 10^{-8}$          |
| 13             | $7.2 \times 10^{-8}$          |
| 14             | $280 \times 10^{-8}$          |
| uncoated steel | $850 \times 10^{-8}$          |

**Example No. 5****Heat shock Test:**

1000 °C - 15 minute heating from ambient to 1000 °C, water quench for 15 minutes - 1 cycle.

The sample substrate material had a thick plate shape with a dimension of 50x50x10 mm, one 50x50 side coated. The sample substrate was 304 stainless steel.

Thermal shock resistance is evaluated by counting how many cycles the coating can survive without spalling off.

| Sample | No. of Cycles               |
|--------|-----------------------------|
| 8      | no spalling after 20 cycles |
| 13     | no spalling after 20 cycles |
| 14     | spalling after 6 cycles     |

As is apparent from the Tables and all of the above Examples the optimum starting powder blend will necessarily vary depending upon the stabilizer and thermal spray technique used. The as-deposited coating should preferably have at least about 40 wt% stabilized zirconia and up to 60 wt% zirconium silicate. The preferred concentration of the component oxides in the coating independent of crystalline structure should be between about 55 to about 85 wt% stabilized ZrO<sub>2</sub> and 15 to 45% ZrSiO<sub>4</sub> and/or its decomposition products SiO<sub>2</sub> and ZrO<sub>2</sub> with 70 to 85 wt% stabilized ZrO<sub>2</sub> being optimum. The concentration of stabilizer in the as-deposited coating composition should preferably be between 2 to 20 wt% of the zirconia component.

**Claims**

1. A hearth roll for use in the continuous annealing of steel comprising a roll having a metal surface coated with a wear resistant refractory oxide coating which comprises particles of zirconium silicate and/or its decomposition products SiO<sub>2</sub> and ZrO<sub>2</sub>, in a mixture with particles of zirconia fully or partially



stabilized with an oxide selected from  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  and  $\text{HfO}_2$ .

- 5 2. A roll as claimed in claim 1, wherein the coating composition comprises at least 40 wt.% of the stabilized zirconia and up to 60 wt% zirconium silicate and/or its decomposition products  $\text{SiO}_2$  and  $\text{ZrO}_2$ .
3. A roll as claimed in claim 2, wherein the particle of stabilized zirconia represents the majority ingredient of the coating composition.
- 10 4. A process for forming a wear resistant and thermal shock resistant refractory oxide coating on a metal hearth roll for use in the continuous annealing of steel, which process comprises:  
     *formulating a powder feed composition comprising mixing powder particles of zirconium silicate with powder particles of zirconia at least partially stabilized with an oxide selected from  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  and  $\text{HfO}_2$ ; and*  
     *thermally spraying the powder feed composition on the metal roll to form an as-deposited coating composition which, by x-ray phase analysis, comprises:  $\text{ZrO}_2 \cdot x$  where x is one of the stabilizing oxides;  $\text{ZrSiO}_4$  and/or its decomposition products  $\text{SiO}_2$  and  $\text{ZrO}_2$ , and  $\text{SiO}_2$ .*
- 15 5. A process as claimed in claim 4, wherein the powder particle composition comprises at least 40 wt% stabilized zirconia and up to 60 wt% zirconium silicate and/or its decomposition products  $\text{SiO}_2$  and  $\text{ZrO}_2$ .
- 20 6. A process as claimed in claim 4 or 5, wherein an undercoat of a ceramic metal alloy is deposited upon the metal hearth roll before thermally spraying the powder feed composition.
- 25 7. A process as claimed in claim 6 wherein the ceramic metal alloy undercoat is a cobalt based metal matrix comprising Co-Cr-Al-Ta-Y and  $\text{Al}_2\text{O}_3$ .
- 30 8. A process as claimed in claim 4 or 7, wherein the as-deposited coating is formed by feeding the powder feed composition through a plasma torch with the powder feed composition comprising at least 65 wt% of the partially stabilized zirconia and up to 35 wt% zirconia silicate.
- 35 9. A process as claimed in claim 4 or 7 wherein the as-deposited coating is formed by feeding the powder feed composition through a detonation gun with the powder feed composition comprising at least 40 wt% of the partially stabilized zirconia and up to 60 wt% zirconia silicate.
10. A process as claimed in claim 9, wherein the powder feed composition comprises at least 50 wt.% partially stabilized zirconia.

#### 40 Patentansprüche

- 45 1. Herdrolle zur Verwendung bei der kontinuierlichen Wärmebehandlung von Stahl, mit einer Rolle, die eine metallische Oberfläche aufweist, die mit einem verschleißbeständigen, feuerfesten Oxidüberzug versehen ist, der Teilchen aus Zirkoniumsilikat und/oder dessen Zersetzungsprodukten  $\text{SiO}_2$  und  $\text{ZrO}_2$  in einem Gemisch mit Teilchen aus Zirkoniumoxid aufweist, das mit einem aus  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  und  $\text{HfO}_2$  ausgewählten Oxid voll- oder teilstabilisiert ist.
- 50 2. Rolle nach Anspruch 1, bei welcher die Überzugszusammensetzung mindestens 40 Gew.% des stabilisierten Zirkoniumoxids und bis zu 60 Gew.% Zirkoniumsilikat und/oder dessen Zersetzungsprodukte  $\text{SiO}_2$  und  $\text{ZrO}_2$  aufweist.
3. Rolle nach Anspruch 2, bei der die Teilchen aus stabilisiertem Zirkoniumoxid den Hauptbestandteil der Überzugszusammensetzung ausmachen.
- 55 4. Verfahren zur Bildung eines gegen Verschleiß und thermische Schocks beständigen feuerfesten Oxidüberzugs auf einer metallischen Herdrolle zur Verwendung bei der kontinuierlichen Wärmebehandlung von Stahl, bei dem:  
     eine Pulvereinsatzzusammensetzung zubereitet wird, indem Pulverteilchen aus Zirkoniumsilikat mit



Pulverteilchen aus Zirkoniumoxid gemischt werden, das mit einem aus  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  und  $\text{HfO}_2$  ausgewählten Oxid mindestens teilstabilisiert ist; und die Pulvereinsatzzusammensetzung auf die metallische Rolle thermisch aufgesprüht wird, um eine Überzugszusammensetzung zu bilden, die im aufgetragenen Zustand entsprechend einer Röntgenphasenanalyse  $\text{ZrO}_2 \cdot x$ , wobei  $x$  eines der stabilisierenden Oxide ist;  $\text{ZrSiO}_4$  und/oder dessen Zersetzungsprodukte  $\text{SiO}_2$  und  $\text{ZrO}_2$ , sowie  $\text{SiO}_2$  aufweist.

5. Verfahren nach Anspruch 4, bei dem die Pulverteilchenzusammensetzung mindestens 40 Gew.% stabilisiertes Zirkoniumoxid und bis zu 60 Gew.% Zirkoniumsilikat und/oder dessen Zersetzungsprodukte  $\text{SiO}_2$  und  $\text{ZrO}_2$  aufweist.
6. Verfahren nach Anspruch 4 oder 5, bei dem auf die metallische Herdrolle eine Zwischenschicht aus einer Keramik/Metall-Legierung aufgebracht wird, bevor die Pulvereinsatzzusammensetzung thermisch aufgesprüht wird.
7. Verfahren nach Anspruch 6, bei dem die Zwischenschicht aus einer Keramik/Metall-Legierung eine Metallmatrix auf Kobaltbasis ist, die  $\text{Co-Cr-Al-Ta-Y}$  und  $\text{Al}_2\text{O}_3$  aufweist.
8. Verfahren nach Anspruch 4 oder 7, bei dem der Überzug im aufgetragenen Zustand dadurch ausgebildet wird, daß die Pulvereinsatzzusammensetzung durch einen Plasmabrenner hindurch zugeführt wird, wobei die Pulvereinsatzzusammensetzung mindestens 65 Gew.% des teilstabilisierten Zirkoniumoxids und bis zu 35 Gew.% Zirkoniumsilikat aufweist.
9. Verfahren nach Anspruch 4 oder 7, bei dem der Überzug im aufgetragenen Zustand dadurch ausgebildet wird, daß die Pulvereinsatzzusammensetzung über eine Detonationskanone zugeführt wird, wobei die Pulvereinsatzzusammensetzung mindestens 40 Gew.% des teilstabilisierten Zirkoniumoxids und bis zu 60 Gew.% Zirkoniumsilikat aufweist.
10. Verfahren nach Anspruch 9, bei dem die Pulvereinsatzzusammensetzung mindestens 50 Gew.% teilstabilisiertes Zirkoniumoxid aufweist.

#### Revendications

1. Rouleau de soie destiné à être utilisé dans le recuit continu de l'acier, consistant en un rouleau ayant une surface métallique portant un revêtement d'oxyde réfractaire résistant à l'usure qui comprend des particules de silicate de zirconium et/ou de ses produits de décomposition  $\text{SiO}_2$  et  $\text{ZrO}_2$  en mélange avec des particules de zircone totalement ou partiellement stabilisée avec un oxyde choisi entre  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  et  $\text{HfO}_2$ .
2. Rouleau suivant la revendication 1, dans lequel la composition de revêtement comprend au moins 40 % en poids de la zircone stabilisée et jusqu'à 60 % en poids de silicate de zirconium et/ou de ses produits de décomposition  $\text{SiO}_2$  et  $\text{ZrO}_2$ .
3. Rouleau suivant la revendication 2, dans lequel la particule de zircone stabilisée représente l'ingrédient principal de la composition de revêtement.
4. Procédé pour former un revêtement d'oxyde réfractaire résistant à l'usure et résistant aux chocs thermiques sur un rouleau de soie en métal destiné à être utilisé dans le recuit continu de l'acier, procédé qui comprend :
  - la formulation d'une composition d'alimentation, sous forme de poudre, comprenant le mélange de particules de poudre de silicate de zirconium avec des particules de poudre de zircone stabilisée au moins partiellement avec un oxyde choisi entre  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CeO}_2$  et  $\text{HfO}_2$  ; et
  - la pulvérisation thermique de la composition d'alimentation, sous forme de poudre, sur le rouleau métallique pour former une composition de revêtement telle que déposée qui, par analyse des phases aux rayons X, comprend : du  $\text{ZrO}_2 \cdot x$  dans lequel  $x$  est un des oxydes stabilisants ; du  $\text{ZrSiO}_4$  et/ou ses produits de décomposition  $\text{SiO}_2$  et  $\text{ZrO}_2$  et du  $\text{SiO}_2$ .



5. Procédé suivant la revendication 4, dans lequel la composition de particules de poudre comprend au moins 40 % en poids de zircone stabilisée et jusqu'à 60 % en poids de silicate de zirconium et/ou de ses produits de décomposition  $\text{SiO}_2$  et  $\text{ZrO}_2$ .

5 6. Procédé suivant la revendication 4 ou 5, dans lequel une sous-couche d'un alliage matière céramique-métal est déposée sur le rouleau de sole en métal avant la pulvérisation thermique de la composition d'alimentation sous forme de poudre.

10 7. Procédé suivant la revendication 6, dans lequel la sous-couche d'alliage matière céramique-métal est une matrice métallique à base de cobalt comprenant du Co-Cr-Al-Ta-Y et du  $\text{Al}_2\text{O}_3$ .

15 8. Procédé suivant la revendication 4 ou 7, dans lequel le revêtement tel que déposé est formé en introduisant la composition d'alimentation, sous forme de poudre, à travers un chalumeau à plasma, ladite composition d'alimentation sous forme de poudre, comprenant au moins 65 % en poids de la zircone partiellement stabilisée et jusqu'à 35 % en poids de silicate de zirconium.

20 9. Procédé suivant la revendication 4 ou 7, dans lequel le revêtement tel que déposé est formé en introduisant la composition d'alimentation sous forme de poudre, à travers un canon à détonation, ladite composition d'alimentation sous forme de poudre, comprenant au moins 40 % en poids de la zircone partiellement stabilisée et jusqu'à 60 % en poids de silicate de zirconium.

10. Procédé suivant la revendication 9, dans lequel la composition d'alimentation sous forme de poudre, comprend au moins 50 % en poids de zircone partiellement stabilisée.

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