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(54) **Aluminiumbased coating for metallic products.**

(57) The invention relates to an aluminiumbased coating for metallic products and in particular metal sheet.

The aluminising bath for making said coating comprises:

- Si in amounts ranging between 6% and 10% by weight,
- Mn in amounts ranging between 0.5% and 2% by weight,
- Fe in amounts ranging between 0% and 1% by weight,
- Al and impurities to reach 100% by weight.

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Field of the invention

The present invention relates to an aluminium-based coating for metallic products and in particular metal sheet.

Prior art

Aluminiumbased coatings for metallic products are employed to protect said products from corrosion. In particular, for aluminised metal sheet, it is widely used in applications which call for exposure to high temperatures and, in the automotive industry, for the manufacture of tubing and silencers for exhaust gases.

The latest antipollution standards are leading to a gradual but still massive use of catalysts in newly manufactured vehicles.

The changes made to new motor vehicles (catalyst, lean combustion and increasing in explosion chamber temperatures) are reflected in an increase in the temperature of the exhaust gases and a change in their composition.

The entire exhaust system thus operates under more severe temperature conditions and with more corrosive condensation.

It was thus deemed necessary to improve the performance of the aluminised material in terms of resistance to hot oxidation and wet corrosion.

Summary of the invention

There has accordingly been provided and it is an object of the present invention a new aluminising bath making it possible to produce products with improved properties of resistance to hot oxidation and wet corrosion.

Another object of the present invention is the coating obtainable with said aluminising bath.

Still another object of the present invention is the aluminising process.

Additional objects of the present invention are clarified by the detailed description of the present invention.

Description of the invention

The aluminising bath according to the present invention, comprising in a known manner Si up to 10% by weight and Fe up to 1% by weight, is characterised by a manganese content ranging between 0.5% and 2% by weight and the rest being Al and minor impurities up to 100% by weight.

Preferably the aluminising bath in accordance with the present invention contains:

- Si in amounts ranging between 6% and 10% by weight,
- Fe in amounts ranging between 0% and 1% by weight,
- Mn in amounts ranging between 0.5% and 2% by weight,
- Al and impurities to reach 100% by weight.

For continuous aluminising processes the metallic products to be treated are in general in the form of continuous elongated bodies like for example metal sheet in strip form.

The strip, which can consist of crude steel from cold rolling, pickled hot rolled, cold annealed rolled steel, after conventional surface preparation (e.g. chemical degreasing, electrochemical degreasing, rinsing and drying) is continuously heat treated in order to bobtain the metallurgical properties required for the final product in a reducing atmosphere ($N_2 + H_2$) for reduction of the oxides. The strip is brought to the temperature of the aluminising bath, then immersed therein.

The temperature of the bath is usually between 620 °C and 660 °c and the immersion times vary typically between 1 and 6 seconds.

At the tank outlet the coating in excess, still in liquid state, is removed by air blades and then air cooled to T ~300 °C and then water cooled (the final temperature of the strip is ~40 °C), then wrung and, if required, skinpassed and passivated.

The compositions of the coatings obtained are typically:

- Si between 5% and 9% by weight,
- Mn between 0.3% and 1.5% by weight,
- Fe between 0.1% and 0.7% by weight,
- Al and impurities up to 100%.

In the process economics however the optimal cost/performance ratio is obtained with coatings having the following composition:

- Si between 6.5% and 7.5% by weight,
- Mn between 0.4% and 0.85% by weight,
- Fe between 0.5% and 0.6% by weight,
- Al and impurities up to 100%.

Coatings thus obtained have generally a thickness between 10μ and 30μ. They are highly homogeneous and bright and give excellent results when tested for adherence, acid corrosion and hot oxidation at 800 °C.

Brief description of drawings

The following drawings are given which illustrate the examples hereinbelow.

Fig. 1 illustrates a specimen prepared according to the invention and subjected to impact test. It did not display any exfoliation or detachment of the coating.

Fig. 2 illustrates the behaviour with respect to the weight increse of the new aluminised material, subjected to hot oxidation test according to the examples.

Fig. 3 illustrates the results obtained at the end of ten cycles (200 immersions) in synthetic condensate vapours according to the examples and after removal of the corrosion products.

Fig. 4A and Fig. 4B illustrate the metallographic crosssection of the aluminum coating with an Electron Scanning Microscope before and after hot oxidation.

Fig. 4A shows the metalographic crossection of the specimen as is, there can be observed a homogeneous coating with formation of a homogeneous and continuous interphase.

Fig. 4B shows the metallographic crosssection performed on the material subjected to hot oxidation, there can be observed a controlled growth of the grain and absence of oxidation zones at the interphase.

The following examples are given to better illustrate the invention and are not to be considered as limiting the scope thereof.

Examples

Preparation of samples

Four types of coating were prepared on metal strip of type PH 10 with titanium.
Bath temperature: 645 °C-650 °C.
Four types of coating were obtained as follow:

(1) Al-Si 8% by weight (for comparison).
(2) Si = 7% by weight,
Mn = 0.52% by weight,
Fe = 0.6% by weight,
Al and impurities up to 100%.
(3) Si = 7.5% by weight,
Mn = 0.85% by weight,
Fe = 0.4% by weight,
Al and impurities up to 100%.
(4) Si = 7% by weight,
Mn = 1.2% by weight,
Fe = 0.3% by weight,
Al and impurities up to 100%.

Impact test

All coatings had a thickness of approximately 22μ.
For this test the following equipment was used:
male punch dia. 12mm and height 6mm
plate with hole 18mm in dia. 10mm deep
height of fall of punch: 400mm
weight of punch: 19kg.

Specimens prepared as stated and subjected to impact test display no exfoliation nor detachment of the coating (see FIG. 1).

Hot oxidation test

Specimens 3cm x 7cm approximately were weighed after cleaning and then placed in a muffle at a temperature of 800 °C for 48 hours at the end of which the weight was again noted.

This cycle was repeated five times for a total of 240 hours of heating.

The behaviour of the new aluminised material subjected to hot oxidation test is shown in FIG. 2.

As can be seen in the figures the specimens coated with AlSi/Mn alloy, samples (2), (3) and (4) in accordance with the present invention, had better behaviour than those aluminised with a conventional bath (less weight increase), control sample (1).

Wet corrosion resistance test

The approximately 3cm x 7cm specimens were cleaned, weighed and then subjected to the wet corrosion resistance test.

This test consists of 10 cycles of 20 hours each divided as follows:

- exposure of the specimens to synthetic condensate vapours (HBr 48% : 1.14 ml/l; H_2SO_4 96% : 0.56 ml/l) at 80 °C for 60 minutes;
- immersion of specimens in said synthetic condensate vapours for 5 seconds;
- heating in an oven at 250 °C for 90 minutes every 20 hours of exposure.

At the end of the ten cycles (200 immersions) and after removal of the corrosion products the specimens were again weighed.

The results obtained are given in FIG. 3.

The lesser weight loss found for the materials obtained with the new alloy, samples (2), (3) and (4) in accordance with the present invention, in comparison with the specimens aluminised in a conventional bath, sample (1), denotes better wet corrosion resistance.

Observation of coating crosssection with SEM-EPMA before and after hot oxidation

The coated steel samples were analysed with an Optical Microscope (M.09 and with an Electron Scanning Microscope (SEM-EPMA) before and after hot oxidation.

From the metallographic crosssection of the specimen as is, there can be observed a homogeneous coating with formation of a homogeneous and continuous interphase (FIG. 4A).

The metallographic crosssection performed on the material subjected to hot oxidation (FIG. 4B) shows a controlled growth of the grain and absence of oxidation zones at the interphase.

Claims

1. Aluminising bath for treatment of metallic products comprising Si up to 10% by weight and Fe up to 1% by weight and characterised by a manganese content ranging between 0.5% and 2% by weight and the rest being Al and minor impurities up to 100% by weight.

2. Aluminising bath for treatment of metallic products comprising:
   - Si in amounts ranging between 6% and 10% by weight,
   - Mn in amounts ranging between 0.5% and 2% by weight,
   - Fe in amounts ranging between 0% and 1% by weight,
   - Al and impurities to reach 100% by weight.

3. Aluminising process for the treatment of metallic products comprising the following sequence of steps:
   - surface preparation of the product consisting of chemical or electrochemical degreasing, rinsing and drying;
   - heat treatment adequate for the metallurgical properties required for the final product in a reducing atmosphere ($N_2 + H_2$) for reduction of the oxides;
   - immersion in an aluminising bath comprising:
     - Si in amounts ranging between 6% and 10% by weight,
     - Mn in amounts ranging between 0.5% and 2% by weight,
     - Fe in amounts ranging between 0% and 1% by weight,
     - Al and impurities to reach 100% by weight;

     bath temperature ranging between 620 °C and 660 °C and immersion times ranging between 1 and 6 seconds.

4. Process according to claim 3 wherein the product consists of crude steel cold rolled, hot rolled and pickled steel, and cold rolled and annealed steel.

5. Process according to claim 3 wherein the degreasing is of chemical type.

6. Process according to claim 3 wherein the degreasing is of electrochemical type.

7. Process according to claim 3 wherein at the bath outlet the coating in excess, still in liquid state, is removed with air blades and then aircooled to T 300 °C and then water cooled for a final temperature of the strip of 40 °C.

8. Aluminiumbased coating for metallic products comprising:
   - Si between 5% and 9% by weight,
   - Mn between 0.3% and 1.5% by weight,
   - Fe between 0.1% and 0.7% by weight,
   - Al and impurities up to 100%.

9. Aluminiumbased coating for metallic products comprising:
   - Si between 6.5% and 7.5% by weight,
   - Mn between 0.4% and 0.85% by weight,
   - Fe between 0.5% and 0.6% by weight,
   - Al and impurities up to 100%.

10. Coating according to claim 8 having a thickness between 10μ and 30μ.

11. Metallic products coated with a coating having the following composition comprising:
    - Si between 5% and 9% by weight,
    - Mn between 0.3% and 1.5% by weight,
    - Fe between 0.1% and 0.7% by weight,
    - Al and impurities up to 100%.

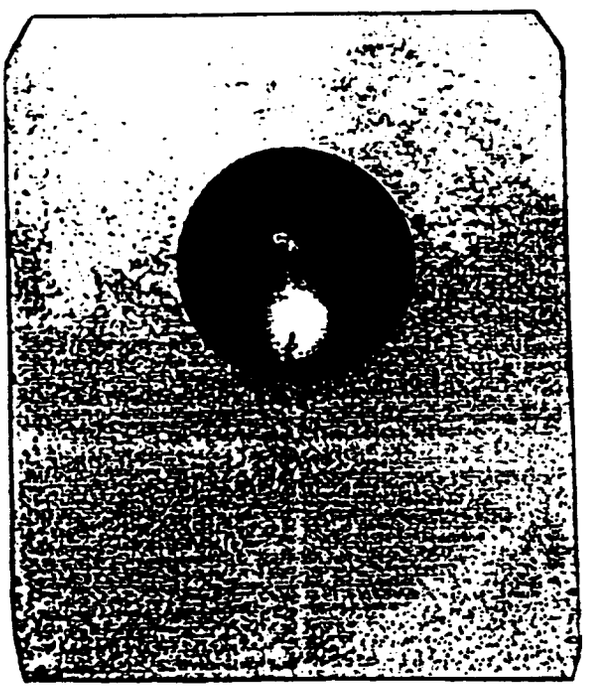


Fig. 1

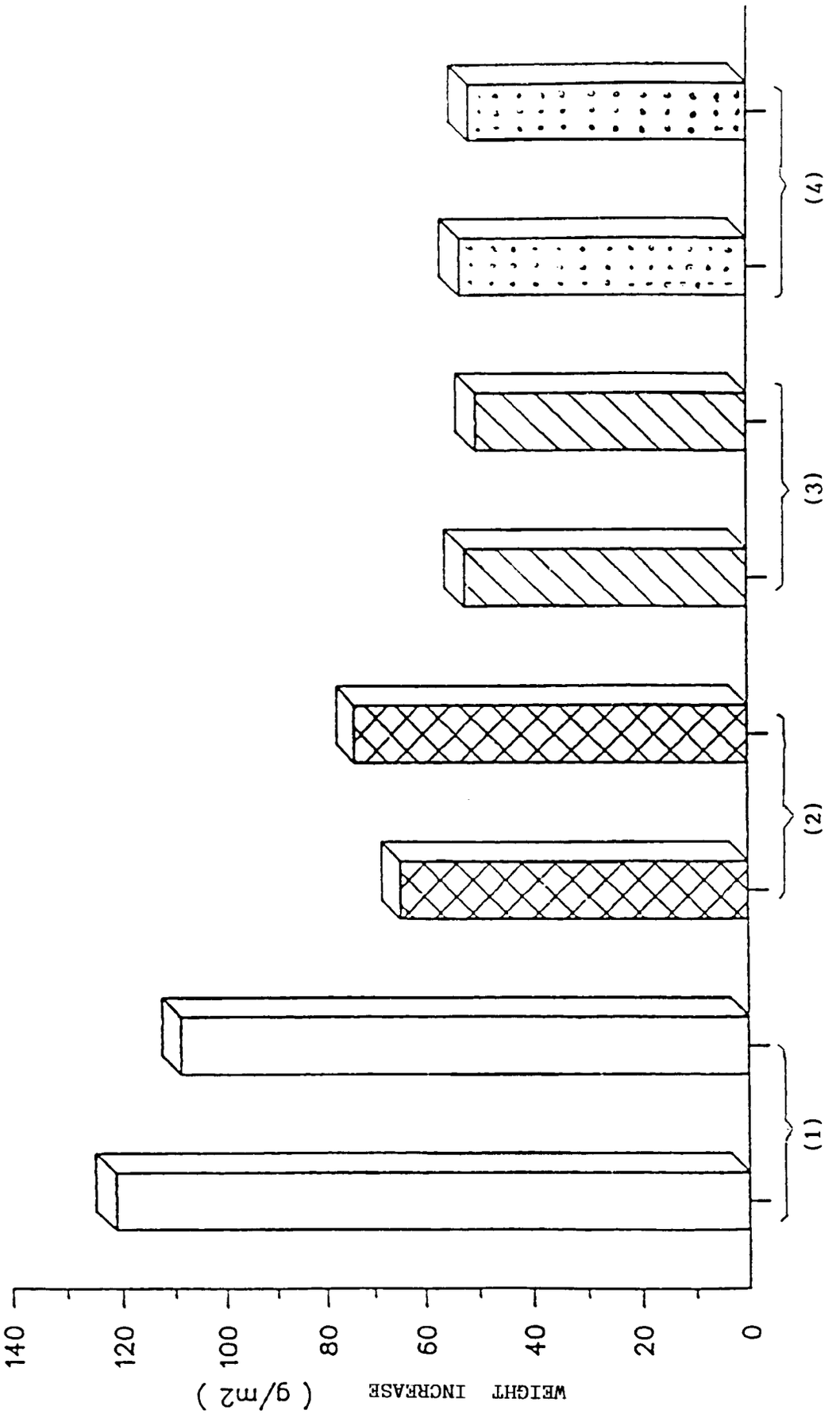


Fig. 2

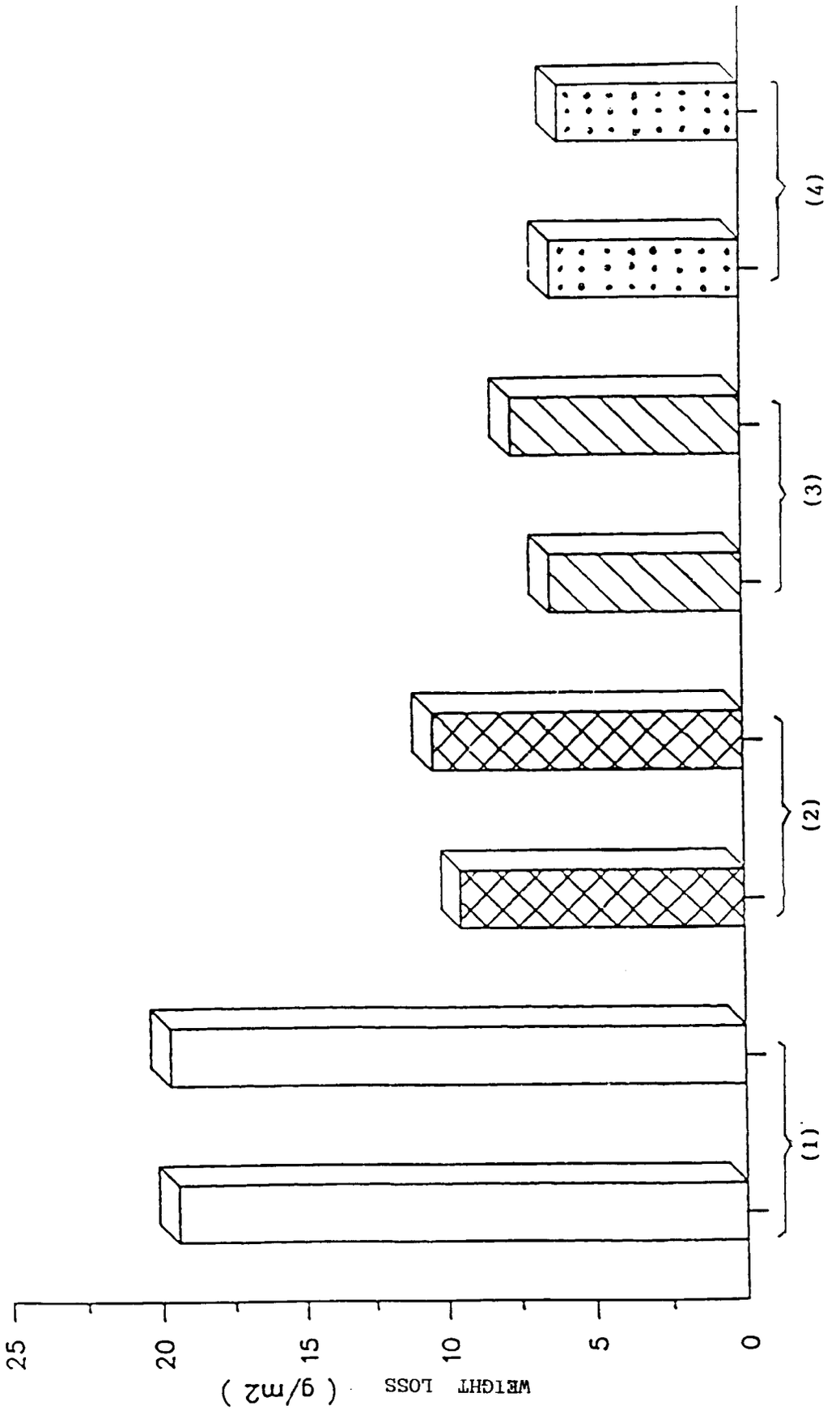
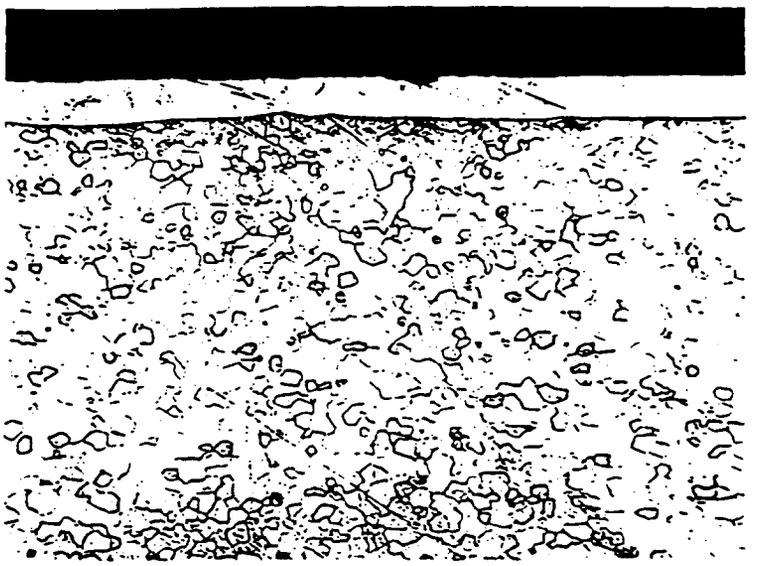
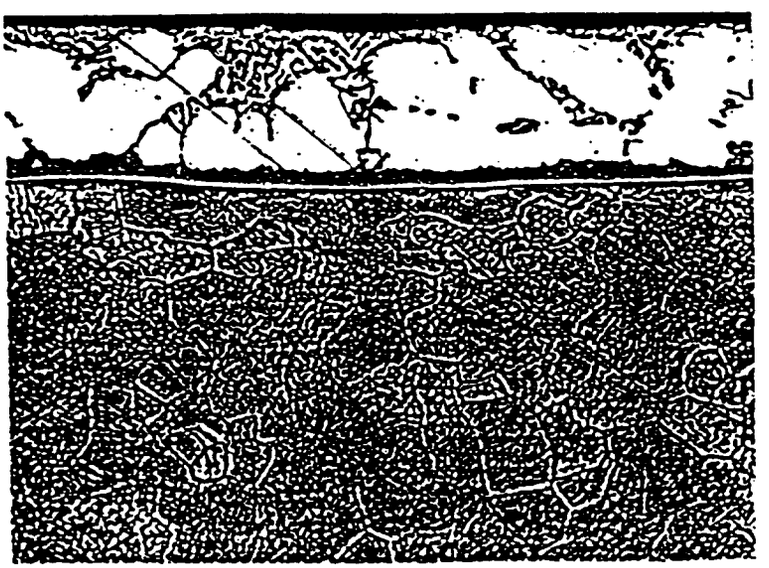


Fig. 3



125 X

Fig. 4A



500 X

Fig. 4B

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EUROPEAN SEARCH REPORT

Application Number

EP 93 10 9844

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-2 200 373 (USS ENGINEERS AND CONSULTANTS) * claims 1-8 *	1-9,11	C23C2/12
A	EP-A-0 489 427 (SUMITOMO METSL INDUSTRIES) * page 3, line 14 - line 18; claims 1,5,7 *	1	
A	US-A-3 639 107 (CHARLES B. THOMPSON) * claims 1,2 *	1-11	
P,X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 046 (C-1021)28 January 1993 & JP-A-42 59 363 (NIPPON STEEL CORP) 14 September 1992 * abstract *	1-11	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 SEPTEMBER 1993	ELSEN D.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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