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(54) **Powder of chromium carbide and nickel chromium**

Pulver aus Chromkarbid und Nickel-Chrom

Poudre de carbure de chrome et de nickel-chrome

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- 'Synthesis of Nanostructured Cr<sub>3</sub>C<sub>2</sub>-25(Ni<sub>2</sub>O<sub>2</sub>Cr) Coatings, Jianhong He et al.', vol. 31 A, part 2 2000, METALLURGICAL AND MATERIALS TRANSACTIONS A pages 555 - 564

**Description**

**[0001]** This invention relates to thermal spray powders of chromium carbide and nickel chromium alloy according to the preamble of the independent claim 1.

**BACKGROUND**

**[0002]** Thermal spraying, also known as flame spraying, involves the melting or at least heat softening of a heat fusible material such as a metal or ceramic, and propelling the softened material in particulate form against a surface which is to be coated. The heated particles strike the surface where they are quenched and bonded thereto. In a plasma type of thermal spray gun, a high temperature stream of plasma gas heated by an arc is used to melt and propel powder particles. Other types of thermal spray guns include a combustion spray gun in which powder is entrained and heated in a combustion flame, such as a high velocity, oxygen-fuel (HVOF) gun.

**[0003]** One type of thermal spray powder is formed of chromium carbide and nickel chromium alloy. The carbide does not melt well and would be too brittle alone in a coating, so the alloy, typically nickel with 20% by weight chromium, is incorporated in each powder particle to provide a matrix. Chromium carbide and nickel chromium alloy are selected for high temperature, corrosive and oxidizing environments such as in a gas turbine engine, up to about 815°C.

**[0004]** There are three forms of chromium carbide,  $Cr_3C_2$ ,  $Cr_7C_3$  and  $Cr_{23}C_6$  according to a standard phase diagram. The first,  $Cr_3C_2$ , is most wear resistant and stable, melting at 1811°C. The second melts at 1766°C. The third,  $Cr_{23}C_6$ , is least wear resistant and stable, melting at 1576°C. The first and second form have orthorhombic structure, and the third form is cubic.

**[0005]** Present commercially available powders of chromium carbide with nickel-chromium commonly are produced by blending, or by chemical or mechanical cladding of the alloy onto grains of the carbide, or by mixing, sintering and crushing. Such methods are relatively expensive and effect particles with relatively large grains of carbide. During spraying these grains are exposed to oxidizing conditions which decarburize the carbide and introduce oxides into the coatings. Also the larger grains in coatings can cause scuffing of mating surfaces.

**[0006]** EP-A-0 843 585, the publications "Reardon, J.D. et.al. Plasma- and vacuum-plasma-sprayed chromium carbide composite coating / Thin Solid Films (1981), 83(3), 345-51" and "Mor, F. et.al. Tribological behavior of different HVOF spray carbide coatings; Adv. Powder Metall. Part. Mater. (1996), (VOL. 5), 18/55-18/68" and "Guilemany J.M. et al. Characterisation of  $Cr_3C_2$ -NiCr cermet powder for high velocity oxyfuel spraying. Powder Metallurgy, 1994, UK, vol. 37, no. 4, pages 289-292 disclose thermal spray powders according to the preamble of the independent claim 1. L. Russo et al. "A Structural Evaluation of HVOF Sprayed N.Cr-Cr<sub>3</sub>C<sub>2</sub> Coatings," Proceedings of ITSC 195, kobe, may 1995, p. 681 to 686 discloses powders containing only two phases; NiCr and  $Cr_3C_2$ . US 5747163 describes powders prepared from  $Cr_3C_2$  powder and a nickel-chromium alloy powder.

**[0007]** A group of chromium carbide powders were introduced recently by Praxair Surface Technologies, Indianapolis, Indiana, according to a brochure "CAT Powders - Introducing A Whole New Breed of CrC-NiCr Powder Technology" (undated). These are CRC-410 (70CrC-30 NiCr), CRC-425 (60CrC-40 NiCr) and CRC-415 (35CrC-65 NiCr). The present inventors obtained an x-ray diffraction analysis of these powders which showed the carbide to be in the form of  $Cr_{23}C_6$ , and a chemical analysis which determined a ratio (by weight) of chromium to carbon in the powders to be 22.2 for powders designated CRC-410-1 and CRC-425-1, and 37.6 for CRC-415-1.

**SUMMARY**

**[0008]** An object of the invention is to provide a novel thermal spray powder of chromium carbide and nickel-chromium, the powder having reduced cost and producing thermal sprayed coatings having high temperature properties comparable to or better than coatings from conventional powders of similar composition.

**[0009]** The foregoing and other objects are achieved by a thermal spray powder having the features of the characterizing part of claim 1. The chromium consists of a first portion and a second portion, the nickel being alloyed with the first portion in an alloy matrix. The second portion and the carbon are combined into chromium carbide substantially as  $Cr_3C_2$  and  $Cr_7C_3$ , with the chromium carbide being in the form of precipitates essentially between 0.1  $\mu$ m and 5  $\mu$ m distributed substantially uniformly in the alloy matrix. The chromium has a ratio by weight to the carbon between 6.5 and 10.

**BRIEF DESCRIPTION OF THE DRAWING**

**[0010]** The drawing is a photograph of a metallographic cross section of powder particles of the invention.

DETAILED DESCRIPTION

**[0011]** A thermal spray powder according to the invention has a size distribution within a range essentially between 10 μm and 125 μm, the size distribution being selected according to type of thermal spray process used for effecting a coating. For example, for a plasma gun with higher velocity spray a size distribution of 44 μm to 125 μm is suitable, or for a plasma gun with lower velocity spray) a size of 10 μm to 53 μm is suitable, or for an HVOF gun a size of 16 μm to 44 μm is suitable.

**[0012]** Each powder particle consists essentially of nickel, chromium and carbon. Typical powder particles are shown in the cross sectional photomicrograph. (The central particle is about 40 μm diameter.) A matrix phase (darker grey) is a nickel-chromium alloy. Precipitates (lighter grey) are formed of chromium carbide substantially as Cr<sub>3</sub>C<sub>2</sub> and Cr<sub>7</sub>C<sub>3</sub>. The alloy preferably is nominally 80:20 nickel to chromium but may contain more chromium to the extent that chromium is taken from the carbide. The proportion of nickel in the alloy is not critical to the invention and may be modified to enhance coating properties, for example 50:50 Ni:Cr alloy for special corrosive conditions (e.g. from fuel oil contaminants or additives). (All percentages and ratios set forth herein and in the claims are by weight except for atomic proportions in the chemical formulae for the carbide.)

**[0013]** Thus the chromium consists of a first portion and a second portion, the first portion being alloyed with the nickel, and the second portion being combined with carbon in the carbide. The nickel should be between about 10% and 90% of the total of the nickel, chromium and carbon. With such composition, the powder is for producing thermal sprayed coatings having the elevated , temperature wear resistance of the designated chromium carbides, and the oxidation and corrosion resistance of nickel-chromium alloy.

**[0014]** The carbide precipitates generally have a size of approximately 1 μm, essentially between 0.1 μm and 5 μm, and are distributed substantially uniformly in the alloy matrix. (This size is average cross-sectional diameter of the dendritic precipitates which may be elongated.)

**[0015]** To achieve this structure the powder should be formed by rapid solidification from a melt, preferably by conventional atomization, and more preferably by inert gas atomization. Air or water may used but would introduce oxides into the powder. Such production of the powder is by atomizing from a melt of the constituents nickel, chromium and carbon at about 1600°C for the lowest carbon content to 1460°C for the highest carbon content. Preferably the atomizing is with inert aspirating gas such as argon in a closed coupled gas atomization system. For example, the melt flows by gravity through an annular delivery tube with an annular opening of about 1.0 to 2.0 mm on a 2.4 cm diameter circle, and is atomized by choked flow from an annular nozzle of about 0.3 to 0.5 mm on a 3.0 cm diameter circle concentric with the delivery tube to cause aspirating conditions at the tip of the delivery tube to aid in atomization. The atomizing gas pressures are varied from 2.76 MPag (400 psig) for the lowest carbon content to 3.45 MPag (500 psig), flows are 212 to 236 sl/sec (450 to 500 scfm).

**[0016]** Other conventional or other desired configurations for the atomizing may be used, such as a non-aspirating, gravity flow atomizing nozzle system. Other powder production techniques for rapid solidification may be used, such as centrifugal with rotating disk or rotating electrode.

**[0017]** Also, one or more other elements may be added to enhance production or powder properties or coating properties, such as 1% to 5% manganese (e.g. 2% or 4%) to enhance manufacturability. However, the additive should not interfere significantly with the presence of Cr<sub>3</sub>C<sub>2</sub> and Cr<sub>7</sub>C<sub>3</sub> or significantly lower the melting point of the powder.

**[0018]** Table 1 shows several compositions over a range encompassed by the invention. These were produced for testing (except No. 1 not in accordance with the invention). The column "Ratio Cr:C" indicates the ratio of total chromium to carbon in the powder. It may be seen that the ratios are relatively low in a range between 6.5:1 and 10:1.

Table 1 -

Powders				
No.	Ni(%)	Cr(%)	C(%)	Ratio Cr:C
1	64	33.3	2.7	12:1
2	56	40	4	10:1
3	40	53.3	6.67	8:1
3A		(No. 3 heat treated)*		
4	20	70	10	7:1
5	19.2	67.2	9.6**	7:1

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(continued)

Powders				
No.	Ni(%)	Cr(%)	C(%)	Ratio Cr:C
10	85	13	2	6.5:1
* In nitrogen at 1038°C for 20 minutes.				
** Plus 4% manganese.				

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10 **[0019]** X-ray diffraction analysis of the powders in the table qualitatively showed the carbide to be substantially Cr<sub>3</sub>C<sub>2</sub> and Cr<sub>7</sub>C<sub>3</sub>. A free carbon analysis showed a small trace (less than 0.1%) of free carbon. The highest desirable ratio of Cr:C is 10, and lowest is 6.5. A significantly higher Cr:C ratio should be avoided as this is expected to yield a carbide containing a significant amount of Cr<sub>23</sub>C<sub>6</sub>. The nickel is provided for corrosion resistance and matrix purposes and, as it does not form a carbide, its relative content should not significantly affect the formation or type of chromium carbide.  
15 The photograph shows the No. 3 powder.

**[0020]** A portion of the No. 3 composition (No. 3A) was heat treated in nitrogen at 1038°C (1900°F) for 20 minutes. This increased the proportion of Cr<sub>3</sub>C<sub>2</sub> in the powder.

20 **[0021]** The powders in size 16 to 44 μm were sprayed with a Metco™ type DJ HVOF thermal spray gun of a type described in U.S. patent No. 4,865,252, using a DJ2603 nozzle and the following parameters: hydrogen combustion gas at 0/97 MPag (140 psig) pressure and 231 sl/min (489 scfh) flow rate, oxygen at 1.17 MPag (170 psig) and 685 sl/min (1450 scfh) flow, 1.8 to 2.2 kg/hr (4-5 lb/hr) spray rate, 22.5 cm spray distance, 75 cm/min traverse rate, coating thickness 0.1 to 0.5 mm. Dense, high quality coatings were obtained on mild steel prepared by grit blasting with -60 mesh alumina grit, with low porosity (less than 5%) and good substrate bonding.

25 **[0022]** Table 2 shows test results of hardness (Vickers hardness number VHN) and slurry wear using a conventional wear test with an aqueous slurry of alumina with a size of 11 μm to 45 μm, for a coating specimen sliding with the slurry against a mild steel plate for two 10-minute runs. "Slurry Wear" is weight loss in grams, and "Depth of Wear" is measured thickness loss in millimeters. For comparison, Diamalloy™ 3007 (sold by Sulzer Metco) is a conventional powder of Cr<sub>3</sub>C<sub>2</sub> clad with 20% Ni-20Cr and having size 5.5 μm to 44 μm; this powder has large grains of chromium carbide (Cr<sub>3</sub>C<sub>2</sub>) in each powder particle, generally of size about 25 μm.  
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Table 2 -

Coatings			
Powder No.	Hardness (VHN)	Slurry Wear	Depth of Wear
1	675		
2	870	1.5	0.14
3	1060	0.6	0.09
5	975	0.53	0.085
Diamalloy 3007	1000	0.35	0.05

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40 **[0023]** Powders of the invention may be mixed with other powder compositions. Specific mixtures were prepared with by mixing the No. 3 composition with other powders designated in Table 3. The other powders are conventional: Diamalloy 4006 is nickel alloy containing 20 Cr, 10 W, 9 Mo and 4 Cu, size 11 to 53 μm; Diamalloy 1006 is nickel alloy containing 19 Cr, 18 Fe, 3 Mo, size 11 to 45 μm; Metco™ 70F-NS is crushed Cr<sub>3</sub>C<sub>2</sub>, size 5 to 45 μm; and Metco 43F is nickel alloy containing 20 Cr, size 11-53 μm. Table 3 shows such blends. (Powder set forth in the claims may be a blend comprising such additional powders.)  
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Table 3 -

Mixtures				
Powder No.	Component A	% A	Component B	% B
6	No. 3	75%	4006	25%
7	No. 3	80%	1006	20%
8	No. 3	85%	70F-NS	15%
9	No. 3	80%	43F	20%

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**[0024]** These mixtures were thermal sprayed with the same type of gun and spray parameters as described above. Coatings were finished by grinding using a 150 grit diamond wheel. Deposit efficiency, percentage of carbon in the coating, macro-hardness (Rockwell C - Rc), micro-hardness (DPH Vickers, 300 gram load) and ground surface finish were measured. Table 4 shows results compared with conventional coatings Diamalloy 3007 (described above) and 3004 which is a blend of  $\text{Cr}_3\text{C}_2$  with 25% nickel 20% chromium alloy of size 5.5 to 45  $\mu\text{m}$ . These conventional powders are of generally similar composition but with larger carbide grains, and were sprayed with the gun and parameters set forth above.

Table 4 -

Results					
Powder No.	Dep. Eff.	% C	Rc	DPH	Finish ( $\mu\text{m}$ )
3	65-70%	6.2%	64	1060	0.41
8	55-60%	6.3%	64	1060	0.38
7	50-55%	5.1%	60	880	0.38
6	50-55%	4.5%	62	900	0.36
9	50-55%	5.0%	61	930	0.33
3004	40-45%	3.4%	64	990	0.41
3007	40-45%	6.4%	66	1000	0.41

**[0025]** In the conventional coatings of 3004 and 3007 the size of the carbides is substantially the size of the carbide grains in the powder which is about 5 to 53  $\mu\text{m}$ . The carbides in the coatings produced from the powders of the invention are in the 1  $\mu\text{m}$  range. Presence of carbide (primarily  $\text{Cr}_7\text{C}_3$ ) in the coating from the No. 3 powder was confirmed by x-ray diffraction analysis. The fine carbide grain size should provide benefits of low scuffing of mating surfaces with improved sliding wear, and less particle pullout. Also, there was high carbon retention of about 80% compared with 35% to 65% in conventional chromium carbide coatings of similar composition, and relatively low oxygen content. The high carbon and low oxygen reflect reduced oxidation during spraying.

**[0026]** Deposit efficiency for the present powders is higher than for the conventional powders of similar composition. Thus not only is the powder itself lower in cost by way of the manufacturing method (atomization), but coating costs are even less due to the deposition efficiency. Carbon retention, hardnesses and finishes may be seen to be comparable to or better than the conventional coatings.

**[0027]** Other types of powders may be mixed with the chromium carbide powder of the invention to attain other properties. An example is a powder of nickel clad onto 20% graphite of size 30 to 90  $\mu\text{m}$ .

**[0028]** While the invention has been described above in detail with reference to specific embodiments, various changes and modifications which fall within the scope of the appended claims will become apparent to those skilled in this art. Therefore, the invention is intended only to be limited by the appended claims.

## Claims

1. A thermal spray powder comprising powder particles each consisting essentially of nickel, chromium and carbon, the chromium consisting of a first and a second portion, the nickel being alloyed with the first portion in an alloy matrix, the second portion and the carbon being combined into chromium carbide substantially as  $\text{Cr}_3\text{C}_2$  and  $\text{Cr}_7\text{C}_3$  wherein the chromium has a ratio to the carbon between about 6.5 and 10, and the chromium carbide being in the form of precipitates essentially between 0.1  $\mu\text{m}$  and 5  $\mu\text{m}$  distributed substantially uniformly in the alloy matrix.
2. The powder of claim 1 wherein the nickel is between 10% and 90% of the total of the nickel, chromium and carbon.
3. The powder of claim 1 having a size distribution essentially between 10  $\mu\text{m}$  and 125  $\mu\text{m}$ .
4. The powder of claim 1 wherein each particle further contains between 1% and 5%, manganese based on the total of the nickel, chromium, carbon and manganese.
5. The powder of claim 1 wherein the powder particles are gas atomized powder particles.
6. The powder of claim 1, wherein the nickel is 40%, the chromium is 53.3% and the carbon is 6.67%.

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7. The powder according to claim 6, wherein the powder is heat treated in nitrogen at 1038°C for 20 minutes.
8. The powder according to claim 7, wherein the powder is heat treated to increase the proportion of  $\text{Cr}_3\text{C}_2$ .
- 5 9. Powder composition comprising 75% of the powder according to claim 6 and 25% of a nickel alloy powder containing 20 Cr, 10 W, 9 Mo and 4 Cu, size 11 to 53  $\mu\text{m}$ .
- 10 10. Powder composition comprising 80% of the powder according to claim 6 and 20% of a nickel alloy powder containing 19 Cr, 18 Fe, 3 Mo, size 11 to 45  $\mu\text{m}$ .
11. Powder composition comprising 85% of the powder according to claim 6 and 15% of a  $\text{Cr}_3\text{C}_2$  crushed powder, size 5 to 45  $\mu\text{m}$ .
- 15 12. Powder composition comprising 80% of the powder according to claim 6 and 20% of a nickel alloy powder containing 20 Cr, size 11 to 53  $\mu\text{m}$ .

### Patentansprüche

- 20 1. Pulver zum Thermospritzen mit Partikeln, von denen jedes im wesentlichen aus Nickel, Chrom und Kohlenstoff besteht, wobei der Chrom aus einem ersten und einem zweiten Teil besteht, der Nickel mit dem ersten Teil in einer Legierungsmatrix legiert ist, der zweite Teil und der Kohlenstoff im wesentlichen zu Chromkarbid  $\text{Cr}_3\text{C}_2$  und  $\text{Cr}_7\text{C}_3$ , verbunden ist, wobei das Verhältnis Chrom zu Kohlenstoff zwischen etwa 6.5 und 10 liegt und das Chromkarbid in der Form von Niederschlag von der Grösse zwischen hauptsächlich 0.1  $\mu\text{m}$  und 5  $\mu\text{m}$ , im wesentlich gleichmässig in der Legierungsmatrix verteilt ist.
- 25 2. Pulver nach Anspruch 1, bei welchem der Nickel zwischen 10% und 90% des gesamten Anteils von Nickel, Chrom und Kohlenstoff beträgt.
- 30 3. Pulver nach Anspruch 1 mit einer Verteilung der Grösse der Partikel zwischen 10  $\mu\text{m}$  und 125  $\mu\text{m}$ .
4. Pulver nach Anspruch 1, bei welchem jedes Partikel zwischen 1 % und 5 % Mangan enthält, bezogen auf den gesamten Teil von Nickel, Chrom, Kohlenstoff und Mangan.
- 35 5. Pulver nach Anspruch 1, bei welchem die Pulverpartikel gasatomisierte Partikel sind.
6. Pulver nach Anspruch 1 mit 40 % Nickel, 53.3% Chrom und 6.67% Kohlenstoff.
7. Pulver nach Anspruch 6 das während 20 Minuten bei 1038° C mit Stickstoff wärmebehandelt wurde.
- 40 8. Pulver nach Anspruch 7 bei welchem das Pulver wärmebehandelt wurde, um **dadurch** den Anteil von  $\text{Cr}_3\text{C}_2$  zu erhöhen.
9. Pulvermischung aus 75 % Pulver nach Anspruch 6 und 25 % und aus Pulver einer Nickellegierung die 20 Teile Cr, 10 Teile W, 9 Teile Mo und 4 Teile Cu enthält und die Grösse der Partikel 11 bis 53  $\mu\text{m}$  ist.
- 45 10. Pulvermischung mit 80 % Pulver nach Anspruch 6 und aus 20 % Pulver einer Nickellegierung die 19 Teile Cr, 18 Teile Fe und 2 Teile Mo enthält und die Grösse der Partikel 11 bis 45  $\mu\text{m}$  ist.
- 50 11. Pulvermischung mit 85 % Pulver nach Anspruch 6 und 15 % verkleinertes  $\text{Cr}_3\text{C}_2$  und einer Grösse der Partikel von 5 bis 45  $\mu\text{m}$ ,
- 55 12. Pulvermischung mit 80 % Pulver nach Anspruch 6 und 20 % Pulver einer Nickellegierung, die 20 Teile Cr enthält und mit einer Grösse der Partikel von 11 bis 53  $\mu\text{m}$ .

**Revendications**

- 5 1. Poudre pour jet thermique comprenant des particules de poudre, chacune consistant essentiellement en nickel, chrome et carbone, le chrome consistant en une première et une seconde portion, le nickel étant allié à la première portion dans une matrice d'alliage, la seconde portion et le carbone étant combinés en carbure de chrome sensiblement en tant que  $\text{Cr}_3\text{C}_2$  et  $\text{Cr}_7\text{C}_3$ , ou le chrome a un rapport au carbone entre environ 6,5 et 10 et le carbure de chrome est sous la forme de précipités essentiellement entre 0,1  $\mu\text{m}$  et 5  $\mu\text{m}$  distribués sensiblement uniformément dans la matrice de l'alliage.
- 10 2. Poudre de la revendication 1 où le nickel est compris entre 10% et 90% du total de nickel, chrome et carbone.
3. Poudre de la revendication 1 ayant une distribution granulométrique essentiellement entre 10  $\mu\text{m}$  et 125  $\mu\text{m}$ .
- 15 4. Poudre de la revendication 1 où chaque particule contient de plus entre 1% et 5% de manganèse en se basant sur le total du nickel, du chrome, du carbone et du manganèse.
5. Poudre de la revendication 1 où les particules de poudre sont des particules de poudre atomisées au gaz.
- 20 6. Poudre de la revendication 1, où le nickel représente 40%, le chrome représente 53,3% et le carbone représente 6,67%.
7. Poudre selon la revendication 6, où la poudre est traitée thermiquement dans l'azote à 1038°C pendant 20 minutes.
- 25 8. Poudre selon la revendication 7, où la poudre est traitée thermiquement pour augmenter la proportion de  $\text{Cr}_3\text{C}_2$ .
9. Composition de poudre comprenant 75% de la poudre selon la revendication 6 et 25% d'une poudre d'alliage de nickel contenant 20 Cr, 10 W, 9 Mo et 4 Cu, dimension de 11 à 53  $\mu\text{m}$ .
- 30 10. Composition de poudre comprenant 80% de la poudre selon la revendication 6 et 20% d'une poudre d'alliage de nickel contenant 19 Cr, 18 Fe, 3 Mo, dimension de 11 à 45  $\mu\text{m}$ .
- 35 11. Composition de poudre comprenant 85% de la poudre selon la revendication 6 et 15% d'une poudre broyée de  $\text{Cr}_3\text{C}_2$ , dimension de 5 à 15  $\mu\text{m}$ .
- 40 12. Composition de poudre comprenant 80% de la poudre selon la revendication 6 et 20% d'une poudre d'alliage de nickel contenant 20 Cr, dimension de 11 à 53  $\mu\text{m}$ .

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**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

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