

Rapidly Solidified Thick Nickel Base Alloy Deposit with Carbide Particles Produced by Plasma Spraying

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Ni-1.5 wt.% C, Ni-1.5 wt.%C-14 wt.%Cr, and Ni-1.5 wt.%C-29 wt.%Cr alloy powders were low-pressure plasma sprayed to produce nickel-base composite deposits with dispersed carbide particles. The constituent of the as-sprayed deposit formed on a water-cooled substrate from the Ni-1.5 wt.%C alloy powder is a nickel phase that is supersaturated with carbon. The deposit heat-treated at 673 K in vacuum consists of a nickel phase, nickel carbide, and graphite. In the case of the Ni-1.5 wt.%C-14 wt.%Cr alloy powder, the as-sprayed deposit produced on a water-cooled substrate is made up of a nickel phase that is supersaturated with chromium and carbon, and subsequent heat-treatment of the deposit leads to the formation of chromium carbide and graphite. When the non-cooled substrate is used, the as-sprayed deposit consists of a nickel phase, chromium carbide, and graphite. The as-sprayed deposit formed on a non-cooled substrate from the Ni-1.5 wt.%C-29 wt.%Cr alloy powder is composed of a nickel phase, chromium carbide, and graphite.

Keywords carbide, low-pressure plasma spray, nickel base alloy deposit, rapidly solidification, supersaturation

1. Introduction

In thermal spraying process, spray material is heated, melted, and accelerated by a high-temperature flame. Thermal spraying of metallic materials in an air atmosphere results in the reaction of the spray material with atmospheric gases (e.g., oxygen or nitrogen) and the variation in composition of the spray material (Ref 1). These problems can be solved by plasma spraying in a chamber filled with a low-pressure inert (Ar) gas. In this process, the amount of gas incorporated in the deposit can be minimized, yielding dense deposits. Thermal spraying can produce rapidly solidified thick materials, because the alloy droplets that accumulate successively on the substrate solidify at a cooling rate in the range of 10^5 – 10^8 K s⁻¹ (Ref 2). Depending on the cooling condition of the substrate and on the alloy composition, coatings are produced with metastable phases or extremely fine crystalline phases (Ref 1).

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Thermal spraying is an attractive method for the production of composite deposits with in-situ formed fine particles.

Nickel-based deposits with carbide particles are commonly used for wear and corrosion resistance applications at elevated temperatures (Ref 3-6). In the future, such deposits are expected to find application to structural parts for use in high-temperature environments (Ref 3). In the present work, Ni-1.5 wt.%C, Ni-1.5 wt.%C-14 wt.%Cr, and Ni-1.5 wt.%C-29 wt.%Cr alloy powders are low-pressure plasma sprayed onto water-cooled and non-cooled substrate to produce rapidly solidified composite deposits based on a nickel phase with finely dispersed carbide particles, and structures and mechanical properties of the deposits are examined.

2. Experimental Procedure

2.1 Plasma Spraying

Ni-1.5 wt.%C, Ni-1.5 wt.%C-14 wt.%Cr, and Ni-1.5 wt.%C-29 wt.%Cr alloy powders of 32–53 μ m diameter formed by argon atomization were low-pressure plasma sprayed in an Ar gas (53.3 kPa) on an alumina grit-blasted steel (SS400) substrate of 100 mm diameter and 3 mm thickness using a Metco 7MB plasma spray gun. The plasma spraying conditions are listed in Table 1. Plasma spraying was carried out at spray distance of 0.3 m for 120 s without gun movement. Two types of substrates were used in the present work: a water-cooled substrate and a non-cooled substrate.

2.2 Evaluation of Deposits

Sprayed deposits were mechanically separated from the substrate and heat-treated in a vacuum at temperatures of

Table 1 Plasma spraying conditions

Plasma gases	
Primary gas, Ar	$3.9 \times 10^{-4} \text{ m}^3/\text{s}$
Secondary gas, H ₂	$2.9 \times 10^{-5} \text{ m}^3/\text{s}$
Voltage-current	60 V-500 A
Chamber	
Gas	Ar
Pressure	53.3 kPa
Spraying distance	0.30 m
Substrate traverse	
Span	$3.5 \times 10^{-2} \text{ m}$
Traverse speed	$5.0 \times 10^{-2} \text{ m/s}$
Pre-heating time	60 s
Spraying time	120 s

673, 873, and 1073 K for 7.2 ks, followed by furnace-cooling to room temperature. The deposits formed from the Ni-1.5C and Ni-1.5C-14Cr alloy powders are called deposit A and deposit B, respectively. The as-sprayed deposit produced on a water-cooled substrate, the deposit heat-treated at 673, 873, 1073 K and the as-sprayed deposit formed on a non-cooled substrate will hereafter be referred to as deposits X0, X1, X2, X3 and NX (X = A, B). The as-sprayed deposit formed on a non-cooled substrate from the Ni-1.5C-29Cr alloy powder will be called deposit NC. Cross sections of the deposit B and NC were etched in a reagent (aqua regia) consisting of one part HNO₃ and three parts HCl at room temperature for 120-180 s, and then were examined by scanning electron microscope (SEM). The x-ray diffraction identification of the deposits was carried out using CuK α radiation. The Vickers microhardness of polished cross section was measured under a load of 2.94 N.

3. Results and Discussion

3.1 Spray Materials

Carbon contents of Ni-C and Ni-C-Cr alloy powders analyzed by carbon determinator (LECO Corporation, USA) are 1.5 wt.% (range of 1.54-1.57 wt.%). The Ni-C alloy powder consists of a nickel phase that is supersaturated with carbon ($\underline{\text{C}}$) due to high cooling rate during atomization, graphite, and Ni₃C. The constituents of the Ni-C-Cr alloy powders are Ni, Cr₃C₂, and Cr₇C₃. Figure 1 shows SEM micrographs of Ni-1.5C-29Cr alloy powder. The alloy powders have a predominantly spherical morphology. Carbon contents of Ni-C and Ni-C-Cr as-sprayed deposits analyzed by carbon determinator range from 1.54 to 1.57 wt.%.

3.2 Deposits Produced from Ni-C Alloy Powder

Figure 2 shows the x-ray diffraction patterns of the Ni-C deposits. The constituent of the as-sprayed deposit A0 formed on a water-cooled substrate is a nickel phase that is supersaturated with carbon due to high cooling rate during solidification of the melt. Heat treatment of the deposit at above 873 K leads to the decomposition of the metastable nickel carbide (Ref 7, 8), which forms in the deposit A1, to a nickel phase and graphite.

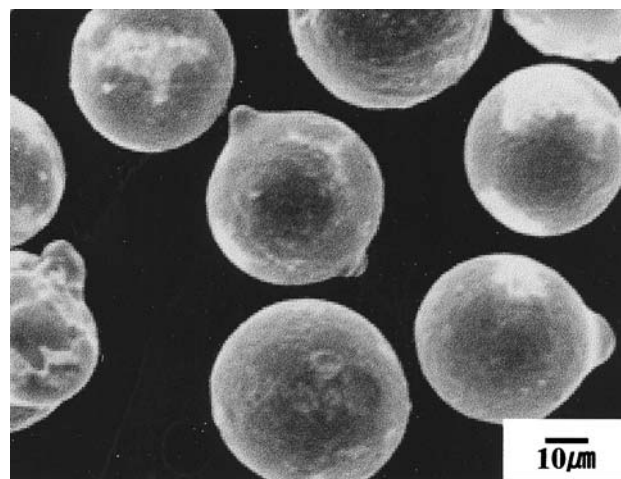


Fig. 1 Scanning electron micrograph of Ni-1.5 wt.%C-29 wt.%Cr alloy powder

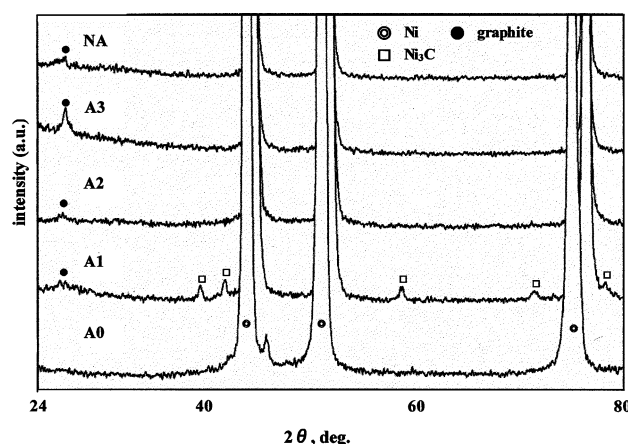
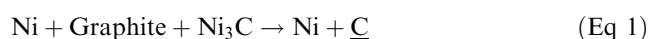


Fig. 2 X-ray diffraction patterns of deposit A—A0: as-sprayed deposit formed on a water-cooled substrate; A1: heat-treated at 673 K; A2: heat-treated at 873 K; A3: heat-treated at 1073 K; NA: as-sprayed deposit formed on a non-cooled substrate

During spraying, the following non-equilibrium reaction occurs:



Heat treatment of as-sprayed deposit results in the following reaction:



The temperature of the non-cooled substrate during plasma spraying (about 1000 K) is higher than that of the water-cooled substrate, and graphite forms in the deposit NA. Figure 3 shows SEM micrographs of cross sections of the Ni-C deposits. The dark-colored particle area coarsens with increasing heat treatment temperature up to 1073 K. Figure 4 shows the EPMA images of the deposit heat-treated at 1073 K for 604.8 ks. The particle of about 1.6 μm in diameter, indicated by an arrow in the figure, is graphite. Figure 5 shows the lattice parameter of the

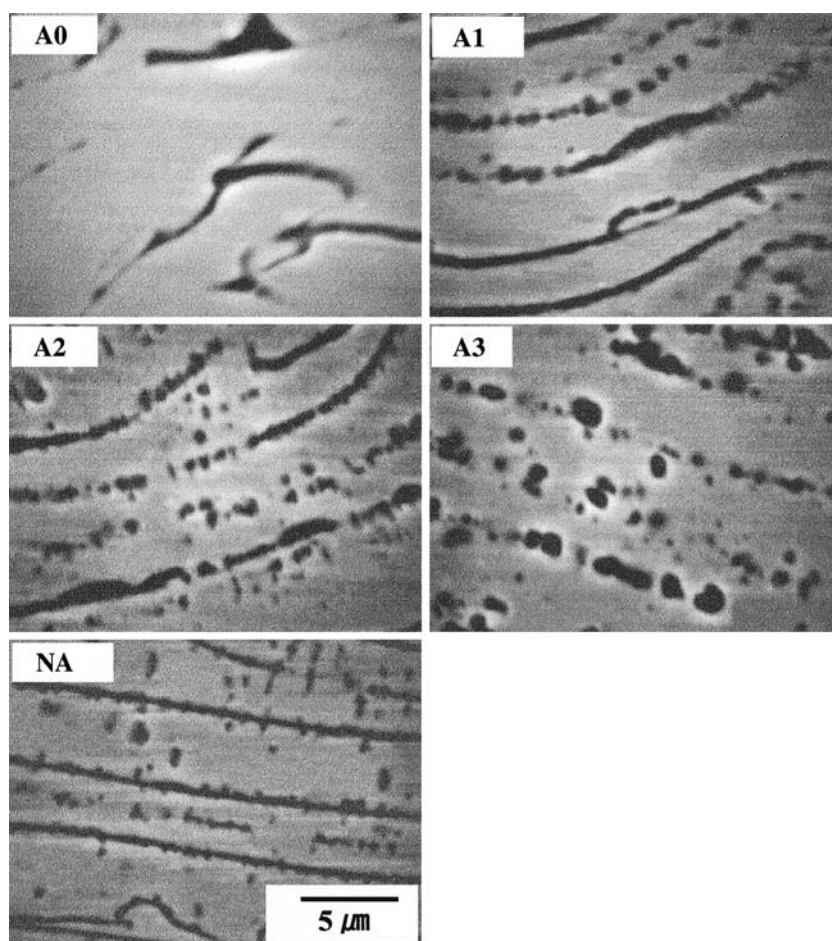


Fig. 3 Scanning electron micrographs of cross sections of deposit A (aqua regia etching)—A0: as-sprayed deposit formed on a water-cooled substrate; A1: deposit heat-treated at 673 K; A2: deposit heat-treated at 873 K; A3: deposit heat-treated at 1073 K; NA: as-sprayed deposit formed on a non-cooled substrate

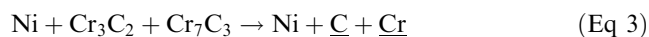
nickel phase in the Ni-C deposits. Upon heat treatment of the deposit A0 at above 673 K, the lattice parameter of the nickel phase in the deposit A decreases sharply, on account of the formation of nickel carbide and graphite, which results in the elimination of the supersaturation of matrix with carbon in the as-sprayed deposit. Figure 6 shows the Vickers microhardness of the Ni-C deposits. The hardness of the deposit A decreases with increasing heat treatment temperature. As known from the lattice parameter of the nickel phase in Fig. 5, the supersaturation of matrix with carbon in the deposit is eliminated upon heat treatment, which leads to softening of the matrix. As heat treatment temperature increases, coarsening of graphite results in lowered hardness of the deposit. The hardness of the deposit NA is higher than that of deposit A3, because spray time is much shorter than heat treatment time.

3.3 Deposits Produced from Ni-C-Cr Alloy Powders

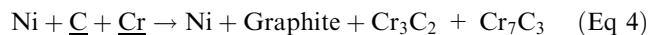
Figure 7 shows the x-ray diffraction patterns of the deposit B. The as-sprayed deposit produced on a water-

cooled substrate from Ni-1.5C-14Cr alloy powder is composed of a nickel phase that is supersaturated with chromium and carbon. Upon heat treatment above 873 K, chromium and carbon supersaturated in the matrix due to extremely high cooling rate of sprayed droplets during solidification combine to form chromium carbide.

During spraying, the following non-equilibrium reaction occurs:



Heat treatment of as-sprayed deposit results in the following reaction:



Chromium carbide and graphite exist in the deposits NB and NC, owing to the increase of the temperature of the substrate. Figure 8 shows SEM micrographs of cross sections of the deposits. The deposit B0 has a lamellar structure arising from the successive impingement and spreading of the sprayed droplets. The fine precipitates of about 0.3 μm in the deposit B1 are chromium carbide, though no diffraction peak due to the chromium carbide is seen in the x-ray diffraction pattern of the deposit B1. As

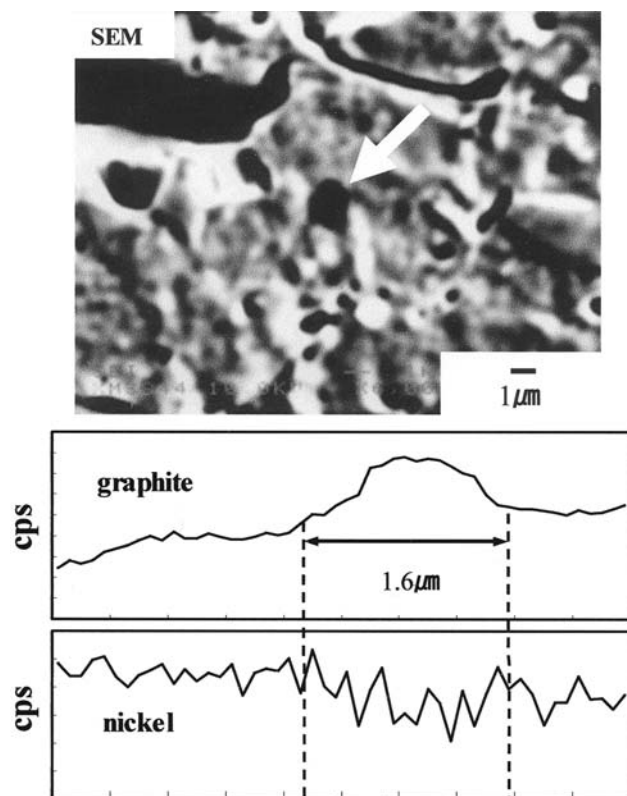


Fig. 4 EPMA image of deposit heat-treated at 1073 K for 604.8 ks (Ni-C) (aqua regia etching)

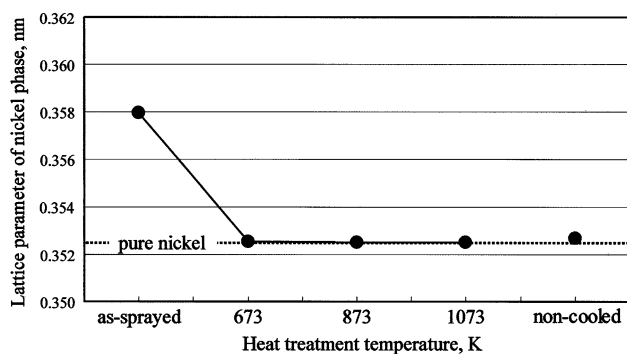


Fig. 5 The lattice parameter of nickel phase in deposit A

heat treatment temperature increases up to 1073 K, the chromium carbide precipitates coarsen. The number of the precipitates is less in the deposit NB than in the deposit B2, because spray time is much shorter than heat treatment time. Figure 9 shows the EPMA images of the deposit heat-treated at 1073 K for 604.8 ks. The coarse precipitate particles (about 1.0 μm in diameter) indicated by arrows in Fig. 9 are chromium carbides. Figure 10 shows the lattice parameter of the nickel phase in the Ni-C-Cr deposits. As heat treatment temperature increases up to 1073 K, the lattice parameter of the nickel phase in

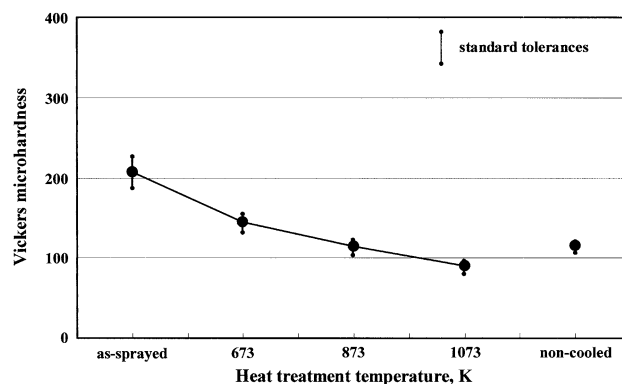


Fig. 6 Dependence of Vickers microhardness of deposit A on heat treatment temperature

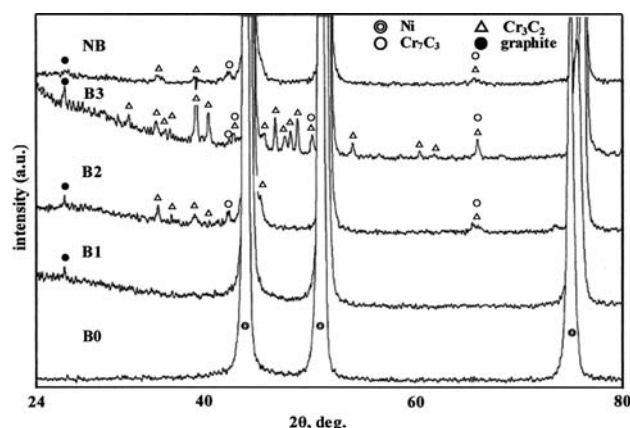


Fig. 7 X-ray diffraction patterns of deposit B—B0: as-sprayed formed on a water-cooled substrate; B1: heat-treated at 673 K; B2: heat-treated at 873 K; B3: heat-treated at 1073 K; NB: as-sprayed formed on a non-cooled substrate

the deposit B decreases due to the formation of chromium carbide and graphite. The lattice parameter of the nickel phase is less in the deposit B3 than in the deposit NB, because spray time is much shorter than heat treatment time. The lattice parameter of the nickel phase is higher in the deposit NC than in the deposit NB, because the deposit NC has the highest chromium content of all deposits. Figure 11 shows the ratio of the integrated intensities of the diffraction peaks of the chromium carbide (Cr_3C_2 and Cr_7C_3) to those of all components; nickel phase, graphite, and chromium carbide. The integrated intensity for the deposit NB is lower than that for the deposit B2. The number of the precipitates is less in the deposit NB than in the deposit B2, because spray time is much shorter than heat treatment time. The integrated intensity for the deposit NC is the highest of the deposits, because the deposit NC has the highest chromium content of the deposits. Figure 12 shows the Vickers microhardness of the Ni-C-Cr deposits. The deposit B1, which is precipitates-hardened by the formation of fine chromium carbide and is solid solution-hardened by the supersaturation of matrix with

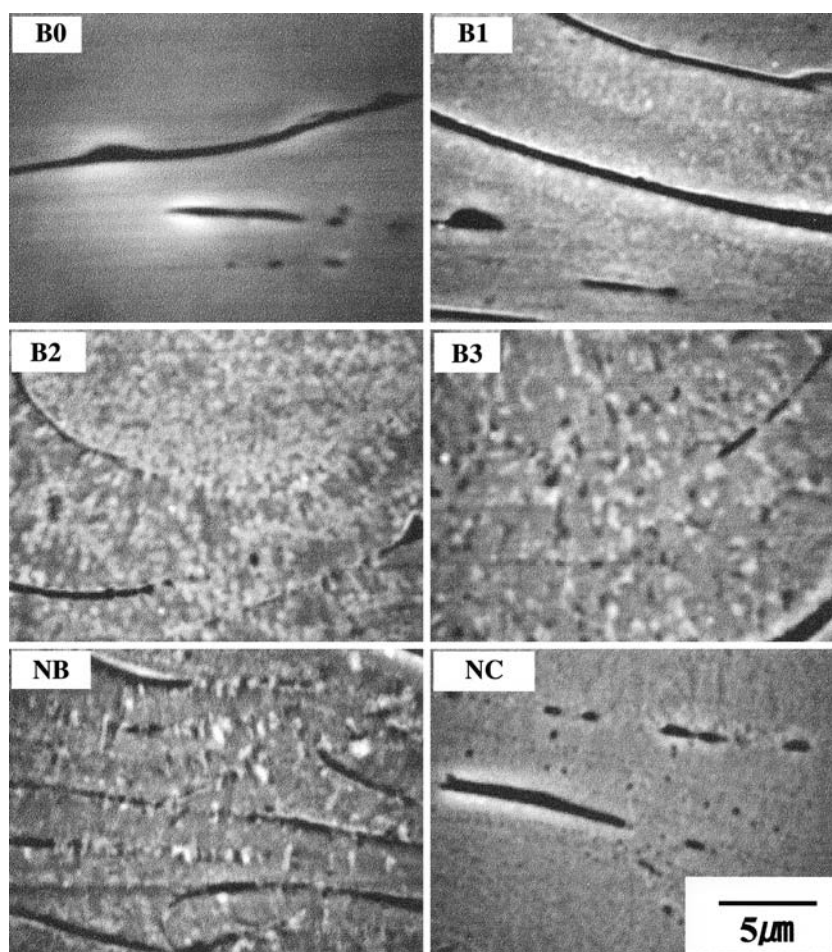


Fig. 8 Scanning electron micrographs of cross sections of deposit Ni-C-Cr (aqua regia etching)—B0: as-sprayed deposit formed on a water-cooled substrate; B1: deposit heat-treated at 673 K; B2: deposit heat-treated at 873 K; B3: deposit heat-treated at 1073 K; NB: as-sprayed deposit formed on a non-cooled substrate; NC: as-sprayed deposit formed on a non-cooled substrate

chromium and carbon, has higher hardness than the deposit B0. As heat treatment temperature increases above 873 K, the coarsening of the chromium carbide precipitates and elimination of supersaturation of matrix with chromium and carbon in the coating result in lowered hardness of deposit B. The deposit NC has the highest hardness, because, as shown in Fig. 8, the deposit NC has many fine precipitates, and is supersaturated with chromium and carbon. Even the hardness of the deposit B3 which is softened upon heat treatment at 1073 K is slightly higher than that of the deposit plasma-sprayed on a water-cooled substrate from Ni-20 wt.%Cr alloy powder (Ref 9).

3.4 Influence of Chromium Content on the Deposits

When the substrate is not cooled, the deposit produced from Ni-1.5C alloy powder is composed of a nickel phase and graphite. In the case of the Ni-1.5C-14Cr alloy powder, the as-sprayed deposit formed on a non-cooled substrate is made up of a nickel phase, chromium carbide, and

graphite. The as-sprayed deposit formed on a non-cooled substrate from the Ni-1.5C-29Cr alloy powder is composed of a nickel phase, chromium carbide, and graphite. The number of the precipitates is less in the deposit NB than in the deposit NC. The deposit NC, which has many fine precipitates, has higher hardness than the deposit NB. The differences in constituents, structure, and hardness of the deposit results from the difference in chromium content of the deposit. The hardness of the deposits NB and NC is about 200-400 HV higher than that of the deposit plasma-sprayed on a water-cooled substrate from Ni-20 wt.%Cr alloy powder (Ref 9). Ni-1.5C-29Cr alloy powder is effective for producing rapidly solidified nickel base deposits with dispersed chromium carbide particles.

4. Conclusions

Ni-1.5 wt.%C, Ni-1.5 wt.%C-14 wt.%Cr, and Ni-1.5 wt.%C-29 wt.%Cr alloy powders are low-pressure plasma sprayed to produce nickel-base composite deposits with

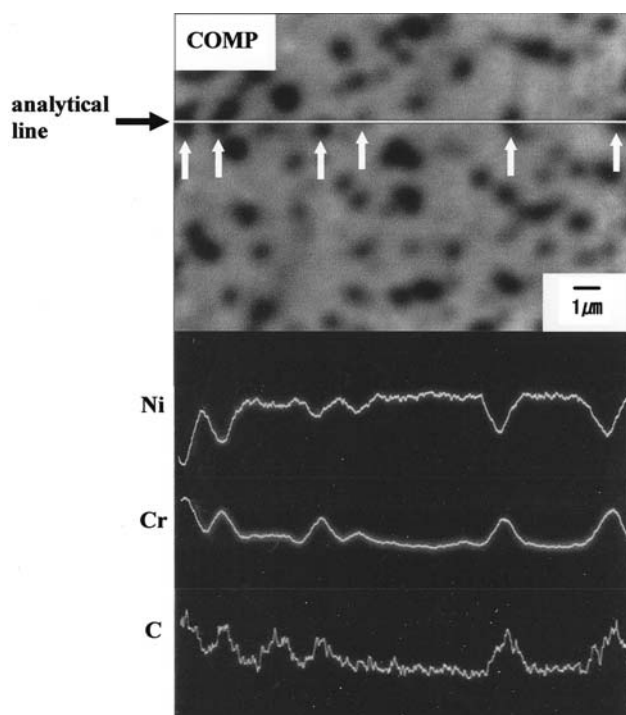


Fig. 9 EPMA images of deposit heat-treated at 1073 K for 604.8 ks (Ni-C-Cr) (aqua regia etching)

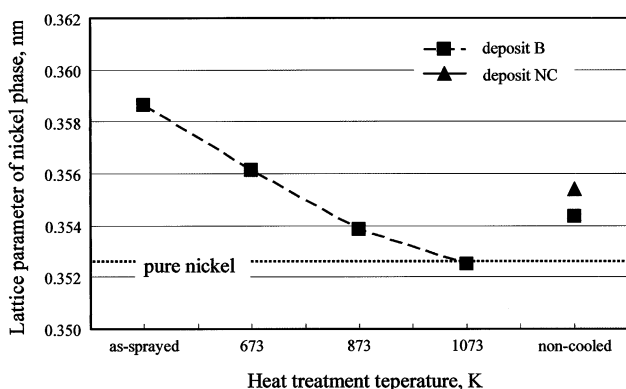


Fig. 10 The lattice parameter of the nickel phase in the deposit Ni-C-Cr

finely dispersed carbide particles. The constituent of the as-sprayed deposit formed on a water-cooled substrate from the Ni-1.5C alloy powder is a nickel phase that is supersaturated with carbon, and subsequent heat-treatment of the deposit leads to the formation of nickel carbide, which decomposes to nickel carbide and graphite at temperature above 873 K. In the case of the Ni-1.5C-14Cr alloy powder, the as-sprayed coating sprayed on a water-cooled substrate is made up of a nickel phase that is supersaturated with chromium and carbon. Upon heat treatment of the deposit at temperature above 873 K, chromium carbide and graphite form. The as-sprayed deposit produced on a non-cooled substrate using Ni-1.5C-29Cr alloy powders consists

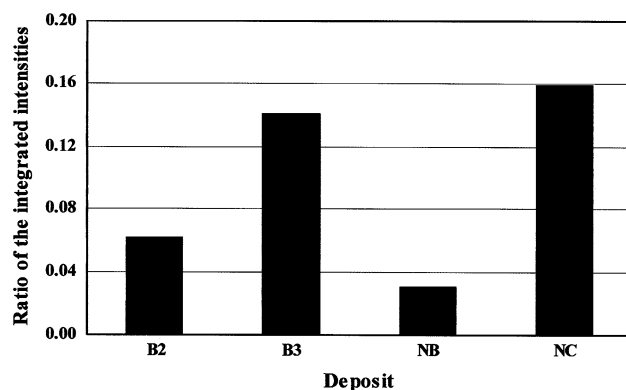


Fig. 11 The ratio of the integrated intensities for the deposit Ni-C-Cr

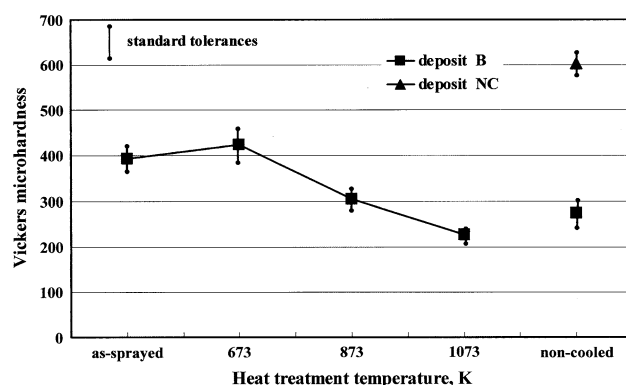


Fig. 12 Dependence of Vickers microhardness of deposit Ni-C-Cr on heat treatment temperature

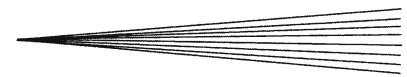
of a nickel phase, chromium carbide, and graphite, and is the hardest of the deposits.

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