Carderock Division
Naval Surface Warfare Center
West Bethesda, MD 20817-5700

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Survivability, Structures And Materials Directorate

Technical Report

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In order to understand the microstructure of 50V0 nickel – 50% chromium alloy produced using spray forming, 3 mm diameter disks of the alloy were cut from several samples. The disks were thinned by electrochemical jet polishing using a mixture of HJP04 and H2S04. The microstructure is very complex. Some areas showed a composite structure of spherical 5- (Cr-Ni) particles imbedded in a dimpled matrix of Cr-Ni. Some areas had a distribution of spherical 8- (Cr-Ni) and Cr-Ni imbedded in planar nickel matrix. The most interesting result is that the microstructure consisted of areas of fine disc shaped (Ni3C, Cr2C and CrC) carbide precipitates dispersed in a nickel matrix. These carbides always tend to orient in a preferred direction, and formed a concentric ring type structure.

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ABSTRACT

In order to understand the microstructure of 50 740 nickel – 50 YO chromium alloy produced using spray forming, 3 mm diameter disks of the alloy were cut from several samples. The disks were thinned by electrochemical jet polishing using a mixture of H3 P04 and H2 S04. The microstructure is very complex. Some areas showed a composite structure of spherical 8- (Cr-Ni) particles imbedded in a dimpled matrix of Cr-Ni. Some areas had a distribution of spherical 8- (Cr-Ni) and Cr-Ni imbedded in planar nickel matrix. The most interesting result is that the microstructure consisted of areas of fine disc shaped (Ni3C, Cr2 C and CrC) carbide precipitates dispersed in a nickel matrix. These carbides always tend to orient in a preferred direction, and formed a concentric ring type structure.

Administrative Information

The work described in this report was performed by the Metals Department (Code61) of the Survivability, Structures and Materials Directorate at the Naval Surface Warfare Center, Carderock Division (NSWCCD). The work was fimded by the Office of Naval Research, ONR 10 as part of the NS WCCD Research Ventures program of the FY 1999 6.1 and administered by the research director Code 0112, Dr. John Barkyoumb.

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Introduction

Background

The spray metal forming process involves the use of an inert gas to atomize a stream of molten metal. The atomized stream is then deposited on substrates for the production of billets or part preforms, e.g. tubes. The deposited material is characterized by a fine grain structure, that is often difficult, if not impossible, to achieve by conventional casting or powder metallurgy techniques. This fine grain structure results in alloys with both high strength and high ductility.

Recently, the process has been used to make spray formed versions of alloys that are of interest to the Navy. One of these is an alloy of *50* % nickel and 50 % chromium, 50Ni50Cr. This alloy is difficult to cast by conventional methods and to machine into finished parts. The alloy has excellent high temperature corrosion resistance and is a candidate for use as a shipboard incinerator liner. When spray formed, the alloy has a yield strength approaching 150 ksi and is a candidate for use as a high strength, corrosion resistant fastener. To further advance the alloy for fleet transition, data is needed on the reproducibility of the mechanical properties, the fracture toughness, and the crevice corrosion resistance of the alloy. In this report, the results on the microstructure of 50% nickel – 50% chromium alloy that was produced as Spray Metal Forming Run # 377 are presented.

Experimental Procedure

Spray forming was performed at the NSWCCD non-reactive pilot research facility using an 80 pound bottom pour melt system. Nitrogen was used as the melt cover gas, and as the scanning atomization gas. Mild steel tubes of 4 inches outer diameter and 0.065" wall thickness were used as substrate. A single pass motion plan was used to translate the rotating substrates

beneath the spray. Final dimensions of the spray formed tube were approximately six inches outer diameter (one inch wall thickness), and seven inches in length after end cropping. Gas to metal ratio (GMR) ranged from 0.45 at the beginning of the run to 0.6 at the end of the run.

Transmission Electron Microscopy

Sample Preparation

The samples for microstructural characterization were prepared as follows. A small block of approximately 1" X 1" X 0.5" was cut from a tube (Run # 377) of the 50 % nickel – 50 % chromium alloy produced using spray forming. A 1/25" (approximately 1 mm thick) thick strip of the sample was cut using a diamond saw. The thin sample strip was mounted in a metal block using hot glue. The sample was mechanically thinned first using 120 grit paper followed by 280 grit paper. After sufficient thinning, the foil was removed from the metal block and was cleaned free of the mounting hot glue. The thin foil was then cleaned using distilled water followed by alcohol. The sample was dried. The clean, thin 50 Ni-50 Cr foil was placed in a sample cutter and 3 mm discs were cut. The 3 mm discs were further carefully thinned on 450 grit paper. The foils were cleaned using distilled water. One disc at a time was then introduced into an electrochemical jet polishing sample holder. The sample holder was introduced into an electrochemical jet polishing unit. The unit was filled with an acid mixture of 60 % H_3PO_4 and 40 % H_2SO_4. The acid mixture in the cell was maintained at room temperature. A constant potential of 15 V was applied to the system. During the jet polishing, the sample current was ~ 100 milli-ampere. The 50 Ni – 50 Cr samples were electrochemically thinned until a fine perforation was observed. Once a small hole was observed the electrical potential was switched off. The sample holder was removed from the electrochemical cell and was cleaned thoroughly using distilled water. The thin 3 mm disk with a fine hole in the center was removed from the

sample holder and was cleaned in an ultrasonic bath. The sample was later cleaned using alcohol and was dried.

TEM Parameters

The transmission electron microscope parameters for the examination of the small samples were as follows: The operating voltage for the electron microscope was 100 keV. The electron wavelength for the electrons operating at 100 keV is 3.7×10^{-3} nm.

Electron Diffraction Pattern Analysis

The most convenient method of interpreting the electron diffraction patterns is by means of the reciprocal lattice construction. The reciprocal lattice is determined in size and shape by means of defining the unit vectors of a crystal unit cell. The first step is to determine the geometry and orientation of the crystal reciprocal lattice.

The reflecting sphere construction effectively gives the direction of the diffracted beam. For a conventional electron diffraction camera, with no electron lens after the specimen, the position of a diffraction spot (for planes of spacing d) on the photographic plates or screen is given by[1]

$$\lambda L = Rd$$

Where λL is the camera constant;
λ is the electron wavelength (for electrons operating at 100 keV, $\lambda = 3.7 \times 10^{-3}$ nm);
L is the camera length in mm;
R is the distance measured between a diffraction spot and the center;
and d is the lattice spacing.

Indexing the Diffraction Spot Patterns

One of the simplest ways of plotting the crystal diffraction patterns is to make use of an appropriate reciprocal lattice model. All the diffraction spots can be indexed by simple vector

addition or by measuring the angle between the lines connecting the central spot to the other diffraction spots. First, by inspection, the low index points were indexed. The next point was indexed using the magnitude of vectors (1/d). Table 1 shows typical electron diffraction d-spacings and the corresponding (hkl) planes for nickel, chromium and nickel chrome alloys.

Most of the time, the diffraction patterns show extra spots. The extra diffraction spots are due to either double diffraction and /or due to the presence of multiple phases. The double diffraction spots can be indexed by translating the primary diffraction patterns without rotation.

Results

In the solid state, Ni-Cr alloys with a range of 30-50% Cr can have either a single γ Ni phase or a dual phase microstructure of γ Ni plus α Cr [2]. A Ni-Cr equilibrium phase diagram is shown in Figure 1. The eutectic composition is 49Ni-51Cr, and a solubility limit of 47% chromium in nickel occurs at 1345°C (2453 °F). Alloys having greater than 47% Cr are expected to solidify into the two phase region of α-Cr + γ-Ni. This includes the 50 % Ni – 50% Cr alloy that is being investigated here.

Figure 2 (A) – (B) shows a typical optical microstructure of 50% Ni – 50% Cr alloy. The dark regions represent the eutectic structure consisting of α-chromium phase and the γ-nickel phase and the surrounding area represents the γ-nickel phase. It can also be noted from the higher magnification optical micrograph (Figure 2 (B)) that the eutectic phase has the typical lamellar type of structure. The results suggest that the spray formed 50% Ni– 50% Cr alloy has an average grain size of 50 μm for the γ-nickel phase and an average grain size of 10 μm for the eutectic phase (i.e. the α-chromium and the γ-nickel phase).

Table 1. Index of electron diffraction spots for possible (hkl) planes [3]

Metal / Alloy	Spot 1		Spot 2		Spot 3	
	d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)	d-spacing (nm)	(hkl)
Nickel (Ni)	20.34	111	17.62	200	12.46	220
Chromium (Cr)	20.39	110	11.77	211	14.42	200
Chromium Nickel (Cr_3Ni_2)	22.9	002	21.5	321	19.45	411
Chromium Nickel δ-(Cr-Ni)	18.66	211	22.9	200	20.44	210
Nickel Nitride (Ni_3N)	20.35	111	13.33	300	11.55	220
Nickel Nitride (Ni_4N)	21.60	111	18.70	200	13.20	220
Chromium Carbide (CrC)	23.30	111	20.17	002	14.27	022
Chromium Carbide (Cr_3C_2)	23.06	121	22.40	230	19.48	211
Chromium Carbide (Cr_2C)	21.14	101	11.83	112	11.66	201
Nickel Carbide (NiC_x)	30.37	111	22.56	204	24.81	114
Nickel Carbide (Ni_3C)	20.19	113	13.23	300	12.77	306

The microstructural examination using the transmission electron microscopy revealed that the alloy microstructure is varied from one section of the bulk sample to the other. Two different structural morphologies are discernable. The morphologies can be identified as follows: 1). Microstructure that shows a uniform distribution of spherical δ - (Ni-Cr) particles distributed in a matrix of Ni-Cr alloy; 2). Microstructure that shows the distribution of both δ - (Ni-Cr) and Ni-Cr alloy phase dispersed in nickel phase.

Figure 3(A) shows a typical transmission electron micrograph (bright field image) obtained from thinned 50 % nickel – 50 % chromium sample. The surface of the sample in Figure 3(A) appears to have a rough and dimpled topography. It is possible that such a surface texture was due to the loss of some spherical particles, the dissolution of spherical particles during electrochemical thinning of the sample, or a combination of both.

The selected area diffraction patterns were obtained from a rough, dimpled sample surface topography. A typical diffraction pattern is shown in Figure 3(B). The diffraction pattern was analyzed. The d-spacing for all the major diffraction spots were identified and the results are given in Table 2. By comparing the d-spacing values shown in Table 2 with the

Table 2. The d-spacing obtained from different electron diffraction spots

d- spacing (nm) Sample area shown in Figure 3	**d- spacing (nm) Sample area shown in Figure 4**	**d- spacing (nm) Sample area shown in Figure 5**
22.96 20.81 20.18 18.56	22.62 20.02 18.07 16.02 14.48 13.15 11.17	23.48 21.95 20.18 17.90 13.15 12.82 12.22 12.01 11.46

standard values shown in Table 1, the structural composition of the areas shown in the electron micrographs was determined. The results suggest that the pattern corresponds to two mixed phases (viz. chromium – nickel alloy and δ - (Ni-Cr) phase). The indexed (hkl) planes correspond to (002), (321), (202) planes of chromium- nickel and (211), (200) and (210) planes of δ - (Ni-Cr) phase, respectively. From the brightest diffraction spots, (002) and (330), two dark field images of the area were obtained. The diffraction spot (C) corresponds to the (002) reflection and the diffraction spot (D) corresponds to the (330) reflection. Figures 3 (C) and (D)

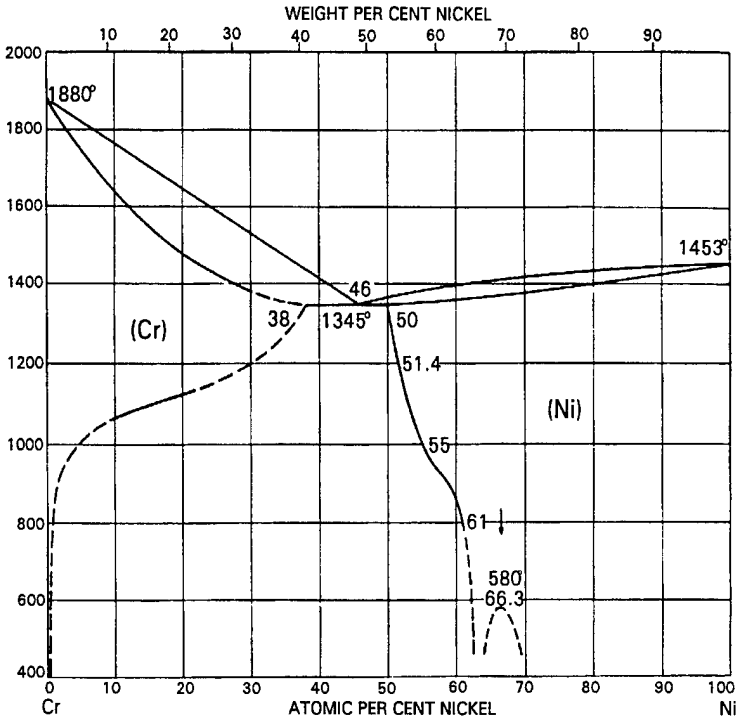

Figure 1: Nickel -chromium Phase Diagram.

show the dark field image of the 50 – 50 Ni-Cr sample. The results suggest that the sample contains fine 20-40 nm size spherical shaped particles and / or precipitates with different orientations and / or compositions. Since most of the precipitates correspond to both diffraction spots, it is possible that the spherical particles and /or precipitates shown in Figure 3 (C) and (D) represent the particles of δ - (Ni-Cr) phase and the uneven surface corresponds to chromium-nickel alloy composition. Since the surface topography shown in Figure 3(A) indicates that the spherical particles and or the precipitates were imbedded in a soft matrix, it is possible that δ-(Ni-Cr) phase particles are harder than the chromium-nickel alloy.

Figure 4(A) shows a transmission electron micrograph (bright field image) obtained from a second foil made from the 50 Ni-50 Cr alloy. The surface of the sample once again appears to have a rough and dimpled topography.

Selected area diffraction patterns were obtained from the above sample surface. A typical diffraction pattern is shown in Figure 4(B). The diffraction pattern was analyzed and the results are given in table 2. The diffraction pattern indexing suggests that the pattern corresponds to three components - (a) pure nickel phase, (b) Ni-Cr alloy phase, and (c) the δ - (Ni-Cr) phase. The indexed (hkl) planes correspond to (111), (200) and (220) planes of nickel, (002), (321), (202) planes of Ni-Cr alloy phase, and (211), (200) and (210) planes of δ - (Ni-Cr) phase respectively.

From the brightest diffraction spots [(C) and (D) in Figure 4B], two dark field images of the area were obtained. The diffraction spot (C) corresponds to the (002) reflection of Ni-Cr alloy, and the diffraction spot (D) corresponds to the (330) plane of δ - (Ni-Cr) phase. Figures 4 (C) and (D) show the dark field image of the 50 Ni – 50 Cr sample. The results suggest that the sample contains fine 20-40 nm size spherical shaped particles and /or precipitates with different orientations or compositions. Since the reflections corresponds to the two different compositions, it is possible that the spherical particles and / or precipitates shown in Figure 4(C) represent the Ni-Cr alloy, while those shown in Figure 4(D) represent the particles of δ - (Ni-Cr) phase. Since the surface topography shown Figure 4(A) indicates that the spherical particles and

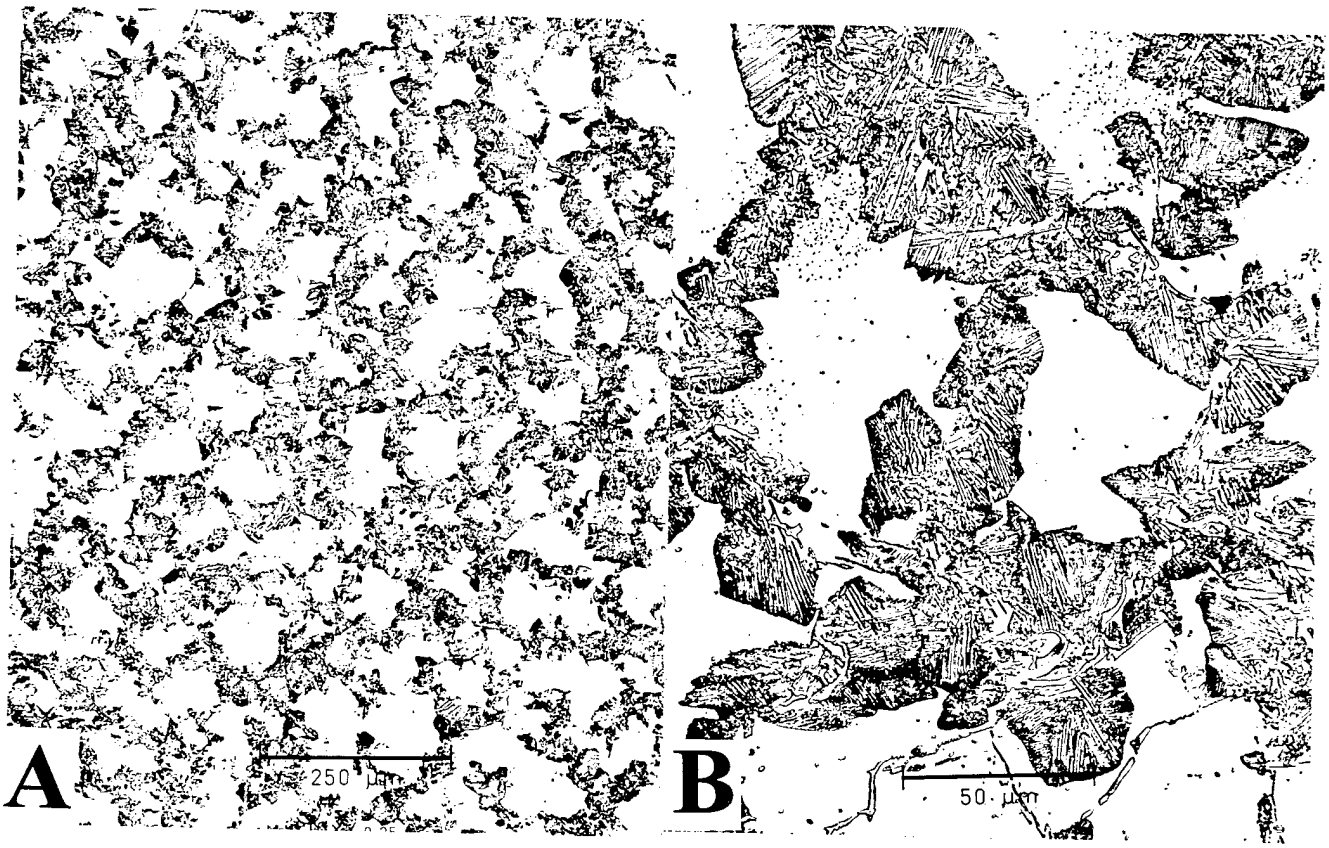

Figure 2. Typical optical micrograph showing the microstructure of 50% nickel – 50% chromium alloy produced using spray forming method. (Run # 377).

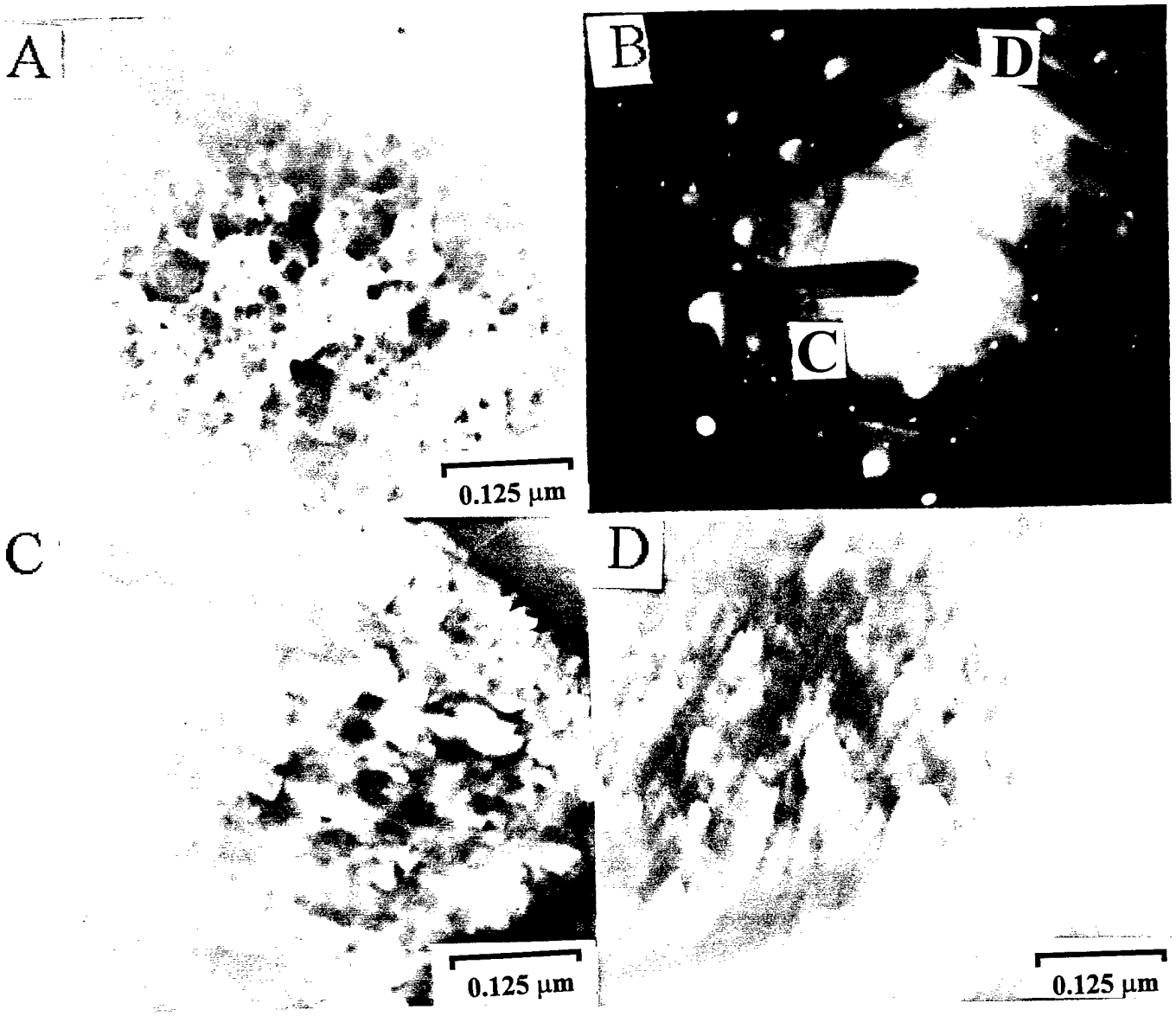

Figure 3. Transmission electron micrograph of 50 % nickel – 50 % chromium alloy sample produced using spray forming. Spray forming run # 377. (A) Bright field image, (B) selected area diffraction pattern, (C- D) dark field images taken from (002) and (330) reflections.

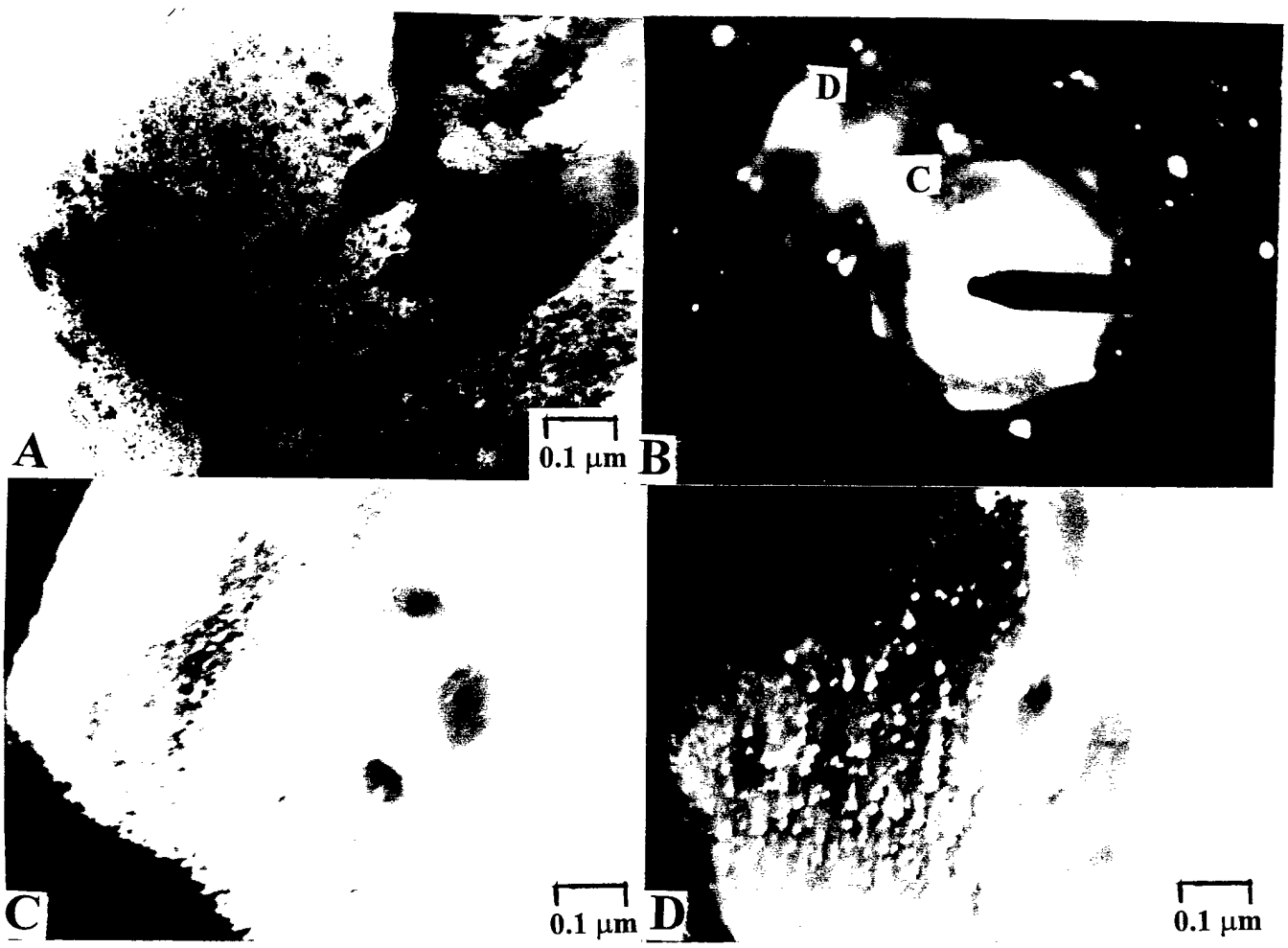

Figure 4. Transmission electron micrograph of 50 % nickel – 50 % chromium alloy sample produced using spray forming. Spray forming run # 377. (A) Bright field image, (B) selected area diffraction pattern, (C- D) dark field images taken from (330) and (211) reflections.

/ or the precipitates were imbedded in a soft matrix, it is possible that both the Ni-Cr alloy, and δ-(Ni-Cr) phase form as spherical particles during the melting process.

It is interesting to note that in some areas, two different particles and or precipitates were observed. Figure 5(A) shows a typical transmission electron micrograph of these features. The selected area diffraction pattern obtained from the area is shown in Figure 5(B). The electron micrograph shown in Figure 5(A) suggests the sample consisted of fine 10 – 20 nm sized precipitates. The presence of these features produced significant strain field. The diffraction pattern shows diffused rings and also double diffraction spots. The diffused ring pattern indicates the presence of fine crystallite structure. The double diffraction pattern may be due to multiple phase and or structures.

Figure 6(A) shows a magnified view of the area shown in Figure 5(A) and the corresponding diffraction pattern. The structure indicates that the defects are fine disc shaped precipitates. The diffraction pattern suggests that the precipitates are very fine and the crystal is very complex. From careful electron diffraction analysis, it was found that the diffraction spots represent nickel [Ni - (111), (200) and (220) planes], nickel carbide [Ni_3C - (306), (300) and (113) planes], chromium carbide [Cr_2C - (101), (103), (112) planes] and chromium carbide [CrC – (111), (113), (100), (022) and (222) planes].

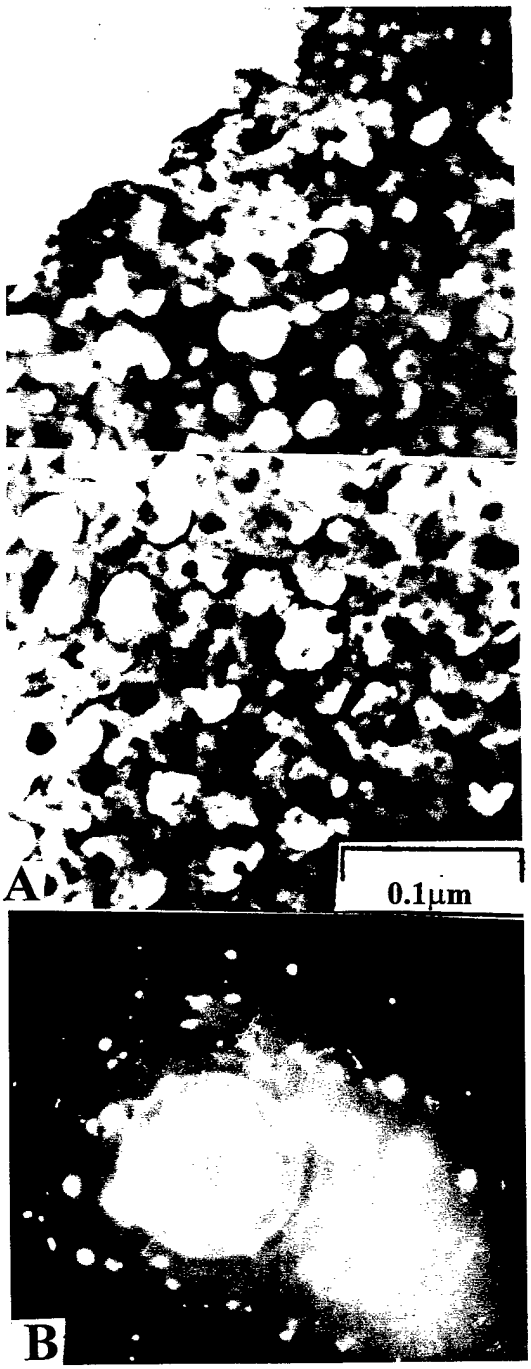

Figure 5. Transmission electron micrograph of 50 % nickel – 50 % chromium alloy sample produced using spray forming. Spray forming run # 377. (A) Bright field image showing the precipitates, (B) selected area diffraction pattern.

Figure 7 shows a typical morphology of the disc shaped precipitates in 50% Ni – 50 % Cr sample. The interesting feature is that the precipitates orient in a concentric ring type pattern. While most of the precipitates lied flat and were oriented in a circular orientation, a few precipitates tended to align edge-on. The contrast on the precipitates oriented edge-on suggests that the shape of the precipitates is more like that of a disc rather than that of of a cylinder. The electron diffraction patterns indicate that the precipitates consist of nickel carbide [Ni_3C], and chromium carbide [Cr_2C and CrC]. Figure 8(A) shows a lower magnification view of the area shown in Figure 7. The corresponding diffraction pattern is shown in Figure 8 (B). From the diffraction spot C [(113) plane] in Figure 8 (B), a dark field image was obtained (Figure 8(C)). The dark field image indicates that the precipitates are oriented in a circular pattern and that the features in bright field image that were thought to represent individual precipitates are actually a group of 3 to 4 fine (size < 10 nm) precipitates.

Discussion

Alloys of metals with different crystal structures often solidify into dual phase forms. The dual phase structure could result from the alloy composition and /or the processing. The situation becomes more complicated for the alloy compositions close to the eutectic composition. For the binary alloys of nickel and chromium the eutectic composition is at 49 % nickel and 51% chromium. The alloy samples studied were produced from a starting ingot with a composition of 50 % nickel – 50% chromium. It is therefore expected that the microstructure should show a lamellar type of eutectic structure (of α-chromium and the γ-nickel phase), surrounded by the α-chromium and / or the γ-nickel phase. The present optical microscopy results indicate that the structure of the spray formed material is similar to that discussed above.

The microstructures observed in the transmission electron micrographs revealed that the spray forming technique adds its own unique features to the final alloy structure. For example, the chromium-nickel (Cr-Ni phase) alloy topography was always found to have a sponge like structure in which hard and spherical δ-(Cr-Ni) particles were stuck. The distribution of the spherical δ-(Cr-Ni) particles in Cr-Ni phase gives an impression that the alloy can be classified as a composite in which δ-(Cr-Ni) spheres are the dispersed phase and the Cr-Ni phase is the matrix. A similar analogy can be made for the second sample area in which, the matrix is nickel and the dispersed phases are the spherical particles of Ni-Cr alloy and the δ-(Cr-Ni) phase.

The most intriguing observation is the presence of fine disc shaped carbide (Ni_3C, Cr_2C, CrC) precipitates. The carbides appeared to form a composite structure with nickel as the matrix phase. In addition, the precipitates tend to form an ordered concentric ring type structure. Although, the presence of nickel, chromium, Cr-Ni and δ-(Cr-Ni) are expected in the microstructure, it remains to be determined how the Ni_3C, Cr_2C, CrC carbides were formed.

Figure 6. Transmission electron micrograph of 50 % nickel – 50 % chromium alloy sample produced using spray forming. Spray forming run # 377. Insert is the selected area diffraction pattern

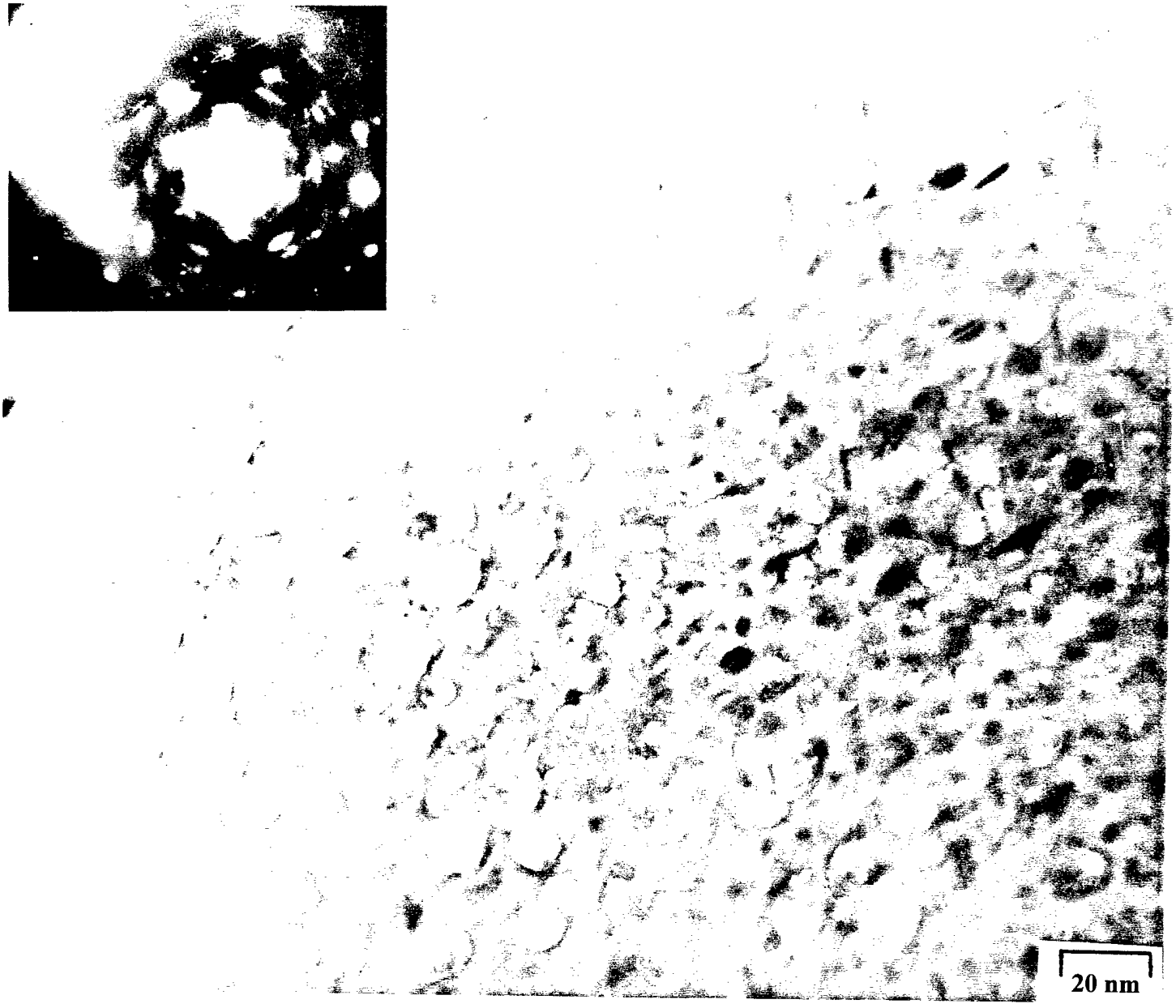

Figure 7. Transmission electron micrograph of 50 % nickel – 50 % chromium alloy sample produced using spray forming. Spray forming run # 377. Insert is the selected area diffraction pattern.

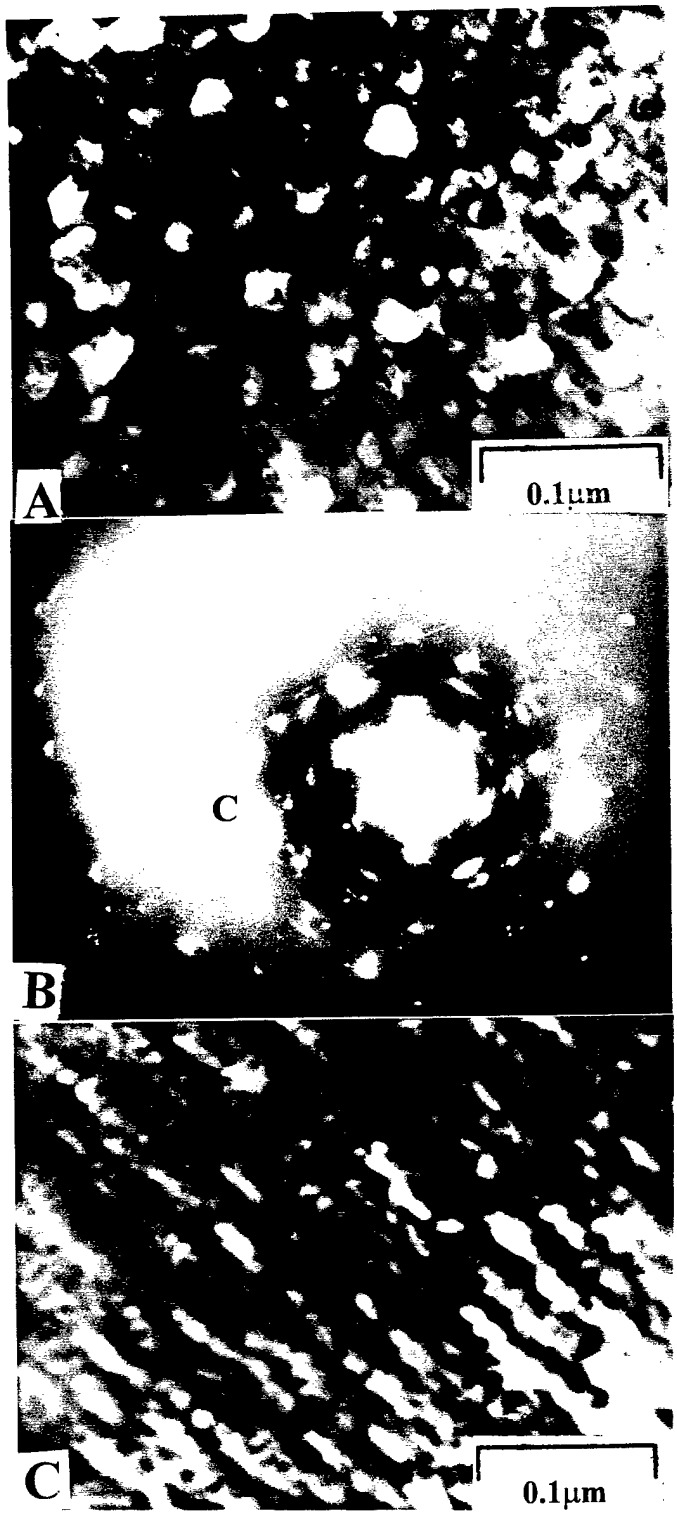

Figure 8. Transmission electron micrograph of 50 % nickel – 50 % chromium alloy sample produced using spray forming. Spray forming run # 377. (A) Bright field image, (B) selected area diffraction pattern and (C) dark field image from the diffraction spot C.

Summary and Conclusion

From the present investigation, the following conclusions can be derived:

1. The spray forming method alters the microstructure of the alloy. Although, the macro-structure represents a typical eutectic alloy structure, the fine microstructure shows at least three different types of structures:

   i. - Nickel rich matrix phase, and spheres of Ni-Cr alloy and δ- (Cr-Ni) as dispersed phase;

   ii. - Ni-Cr alloy as matrix phase and spheres of δ- (Cr-Ni) as dispersed phase; and

   iii. - microstructure with Ni_3C, Cr_2C, CrC carbide precipitates.

2. While the shape of Cr-Ni and / or δ- (Cr-Ni) is like spheres, the shape of Ni_3C, Cr_2C, CrC precipitates resemble that of thin discs.

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3. JCPDS- International Center for Diffraction Data - PDF-2 Data Base.

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