New Ordered State Between Crystalline and Amorphous in Ni-Cr Particles

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A new ordered state characterized by sharp electron diffraction spots showing an arrangement with a twelvefold symmetry axis inconsistent with the existence of a Bravais lattice has been found in small particles in Ni-Cr. Electron-microscopic high-resolution structure images of these particles reveal that this ordered state has no translational symmetry but has far-reaching orientational order.

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Recently, metallic materials with long-range orientational order and no translational symmetry have been reported in two different alloy systems. Small particles of Ni-Cr showed twelvefold symmetry in diffraction patterns.[1] Quenched specimens of an alloy with composition Al-(14 at.% Mn) showed sharp tenfold diffraction symmetry.[2,3] In both cases, these unusual symmetry properties are inconsistent with the translational symmetry of a crystal. In this paper, we present a structural analysis of the new ordered state in small particles of Ni-Cr, using the many-beam structure-imaging technique.

Small Ni-Cr particles were made by evaporation of Ni-(70.6 at.% Cr) alloy in Xe gas. Details of the gas-evaporation technique are described elsewhere.[4] The majority of the particles were found to have the $A15$- or the σ-phase structure.[5] Neither the $A15$ nor the σ phase occurs in samples of this alloy when synthesized in the bulk state.[6] The object of this paper is to describe one type of these particles which contain regions of multiply twinned σ-phase domains as well as another region with highly disordered structural state. Many-beam structure images were made with the beam oriented along the [001] direction as defined by the σ-phase domains. A JEOL TEM 200CX electron microscope operating at 200 kV with a high-resolution objective lens ($Cs = 1.2$ mm) was used. The images were recorded at a magnification of 2.5×10^5 after insertion of an objective aperture at the center of the diffraction pattern, corresponding to a limiting radius of 3.9 nm^{-1}.

An electron micrograph of one Ni-Cr particle and its diffraction pattern are presented in Fig. 1. The external shape of the particle tends to be a polyhedron in spite of its highly disordered internal structure. It was found from image details in high magnification made from the film negative corresponding to Fig. 1(a) that the marginal region is composed of small twin domains with σ-phase structure which have a common c axis and are rotated by 30° around the c axis.[7] This twin relation is very similar to that observed in the bulk state.[8] The distribution and the sizes of the σ-phase domains could also be determined from the high-magnification image. Their sizes range between 9 and 2.3×10^2 unit cells, and they occur in the region between the edge of the particle and approximately 12 nm inside. In the region further inside the particle, σ-phase domains are not apparent.

The diffraction pattern [Fig. 1(b)] consists of groups of four diffraction spots each. Three of these sets have diffuse maxima which are arranged on tetragonal net planes rotated 30° against each other. These sets correspond to the multiple-twin domains of the σ-phase material, all of which are oriented with their c axes along the electron beam. The fourth set comprises all spots which satisfy a twelvefold diffraction symmetry. They are loacted at the center of the triplets of diffuse maxima originating from the multiple-twin domains of σ-phase material. An optical diffraction pattern [Fig. 1(c)] of the interior region of the particle [obtained from the same negative film as that used for Fig. 1(a)] shows the fourth set of diffraction spots only. In Fig. 1(c) the diameter of the area selected for the diffractogram was 40 nm. Even when the diameter of the selected area was reduced to 4 nm, the spots in twelvefold symmetric arrangement could be observed. The triplets corresponding to the σ-phase reflections reappeared when the diameter was increased to 48 nm. These optical diffraction results as well as the electron diffraction pattern are definite evidence of the existence of the structure with the twelvefold diffraction symmetry in the interior of the particle.

It is emphasized that the twelvefold symmetric reflections cannot be indexed as any reflections originating from the σ-phase structure located at the outer part of the particle. The dark-field imaging technique was also applied for similar particles. The center reflection with the surrounding triplet was used for the dark-field observations because these reflections could not be separated by the smallest objective aperture. In dark-field images obtained in this way, a complicated

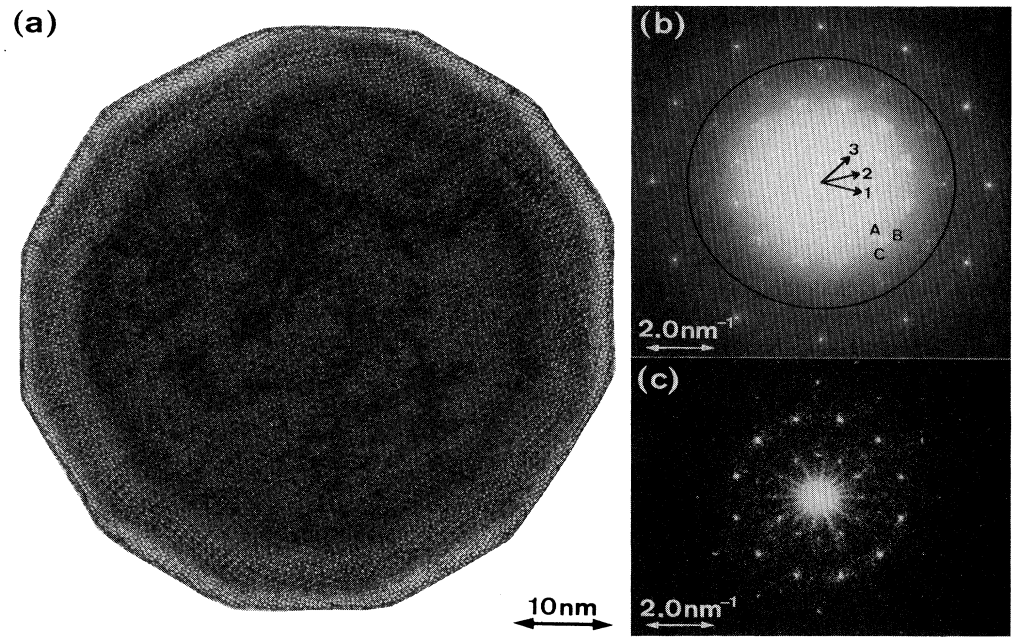

FIG. 1. (a) Structure image of a small particle of Ni-Cr. This particle contains a highly disordered structure in the interior. (b) Electron diffraction pattern corresponding to the whole particle shown in (a). The vectors 1, 2, and 3 indicated in the center of the figure represent reciprocal-lattice vectors a^* for three orientations of the tetragonal σ phase. The lattice parameter a of the σ phase is 0.88 nm. The indices of reflections A, B, and C which compose one triplet are $0\bar{2}0$ for orientation 3, $2\bar{1}0$ for orientation 1, and $1\bar{2}0$ for orientation 2, respectively, of the σ phase. The black circle corresponds to the outline of the objective aperture used for the structure image in (a). (c) Optical diffraction pattern corresponding to the disordered region of the particle's interior shown in (a).

arrangement of many bright spots was observed in the highly disordered region. The size of these bright spots is approximately 2.0 nm in diameter. Even if these spots would correspond to small domains of σ-phase structure, these domains contain only four unit cells of the σ phase. (The lattice parameter a of the σ-phase structure is 0.88 nm.) This domain size is smaller than that estimated in the Al-Mn quasicrystal from weak beam images.[3] Accordingly, the highly disordered structure cannot be regarded as an ordinary twin structure containing many unit cells in each twin domain, such as the σ-phase material located at the outer part of the particle.

In Fig. 2(a), another example of the highly disordered structure is presented in a highly magnified image. In this micrograph the disordered structure is located in a thin marginal region of the particle. Contrast details can be recognized here within the second equal-thickness fringe, which corresponds to a thickness suitable for investigation of this σ-phase–related structure by the many-beam structure-imaging technique. In the highly disordered region, the arrangement of the bright spots is not periodic, i.e., no long-range translational symmetry can be found in the region. This structure has several other remarkable features. Many bright spots are arranged on the vertices of regular dodecagons, as indicated in Fig. 2(b) by thick lines. A bright spot can also be observed in the centers of the dodecagons. The distances between nearly all adjacent bright spots are equal to the edge length of the dodecagons, and also inside these dodecagons. The orientations of the lines connecting the bright spots are very restricted and correspond to the twelve edge directions of the dodecagons. Thus this structure has long-range orientational order. This orientational order is considered to be the cause of the twelvefold diffraction symmetry in the diffraction pattern.

Our detailed interpretation of the arrangement of the bright spots inside the dodecagonal areas is also indicated in Fig. 2(b) by thin lines. In this model two geometric units are frequently observed. One is a regular triangle and the other a square, and both of them have same edge length. In the regular σ-phase region, which is located near the highly disordered structure, the same two geometric units are also observed in the second equal-thickness fringe. They are arranged in a periodic pattern corresponding to a semiregular tessellation which can be represented by the Schläfli symbol $3^2.4.3.4$. From a calculation of the image contrast of the σ-phase structure, it was found that the regular triangles and squares correspond to one-half of the unit

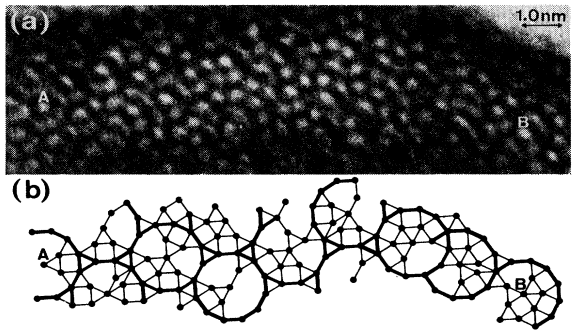

FIG. 2. (a) High-magnification structure image of the highly disordered Ni-Cr structure. (b) Schematic structure model corresponding to (a). Black points indicate positions of bright spots in the structure image. Thicker lines represent an arrangement of regular dodecagons. Positions A and B correspond to those indicated in (a). This figure may be used as a transparent overlay on (a).

cell of the Zr_4Al_3-type structure and to one unit cell of the $A15$-type structure, respectively.[9] Therefore, it may be reasonable to assume the same correspondence between the geometric units and the structural units in the highly disordered structure.

From the observations and arguments given above, it is concluded that the ordered state in the particular kind of Ni-Cr particles described here constitutes a state of order intermediate between the crystalline and the amorphous state. The new state is characterized by twelvefold diffraction symmetry which is assumed to be due to far-reaching orientational order and by the lack of a Bravais lattice and thus of any translational symmetry. The far-reaching orientational order may be caused by the shape of the two geometric units. This new state corresponds to the crystalloid state as defined by Mackay.[10]

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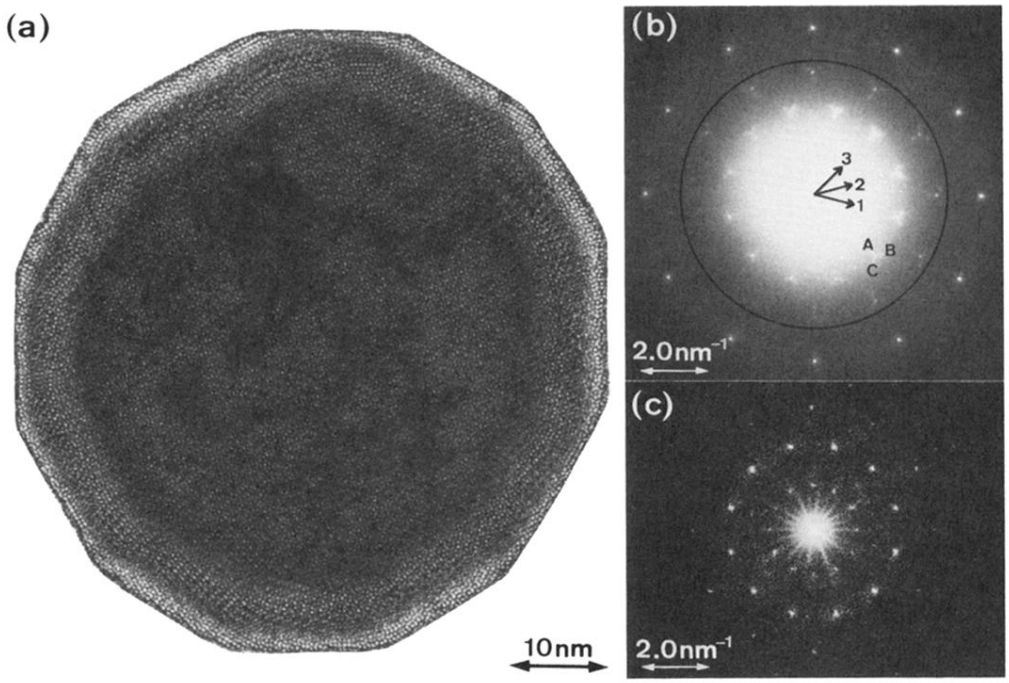

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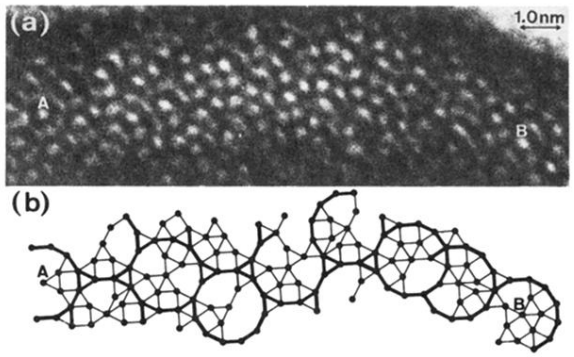

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