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General paper

Neutron Diffraction Study of Thermal Residual Strain in Three Layered Materials Made by Self-propagating High-temperature Synthesis

Kazuko INOUE*, Tetsuya TSUJIKAMI*, Manshi OHYANAGI*, Mitsuhiro KAWAGAI *, Masaaki KOMATSU *, Masaki SUGIMOTO *, Nobuaki MINAKAWA **, Atsushi MORIAI **, Takashi KAMIYAMA*** and Kenichi OIKAWA***

* *Faculty of Science and Technology, Ryukoku University, Seta Ohoe-cyo, Otsu 520-2194, Japan*

** *Advanced Science Research Center, JAERI, Tokai, Ibaraki 319-1195, Japan*

*** *Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan*

Abstract: The thermal residual strain in the three layered materials, [WC-10mass%Ni]-[Ni]-[WC-10mass%Ni], [WC-10mass%Ni]-[SUS304(plate)]-[WC-10mass%Ni] and [WC-10mass%Ni]-[Ni(plate)]-[WC-10mass%Ni], has been investigated by neutron diffraction measurement. They were made by self-propagating high-temperature synthesis. Original materials of composite [WC-10mass%Ni] are powders of W, C and Ni, and those of the middle layers are the powders of Ni, a plate of SUS304 and a plate of Ni. The samples were 40mm in diameter and about 4mm in thickness of each layer. The result of the measurement shows that the middle layer made from powders of Ni has no strain, which suggests that it shrinks from high temperature freely from the existence of both side layers. On the other hand, the middle layer made from a plate material experiences complex stress according to each position and to each direction of the sample, which suggests that it shrinks from high temperature in a state of tight binding on both side layers. The Ni region in the composite material, [WC-10mass%Ni], has a large tensile strain of 0.6 to 1.0%, whereas WC region has a negligibly small compressive strain. In this case, the Ni region shrinks under the hard connection with the WC region, of which the thermal expansion coefficient is relatively small.

Key words: *Thermal residual strain, Neutron diffraction measurements, Three layered materials, Composite materials, Self-propagating High-temperature Synthesis*

1. INTRODUCTION

Reduction of the residual strain or stress of materials caused by thermal treatment is very important to avoid cracking or fracture of the materials. Neutron diffraction is one of the best tools to measure the inner residual strain of materials, because the neutron beam penetrates further into the material than X-ray. The neutron diffraction apparatus, RESA [1], at T2-1 port of JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI) was designed for the residual strain measurement of a small area of materials in three directions. While, a time-of-flight (TOF) neutron powder diffractometer, Sirius [2], installed at Neutron Science Laboratory (KENS) of High Energy Accelerator Research Organization (KEK), is suitable for the observation of strain from a whole diffraction peaks, because the resolution is extremely high.

Using RESA and Sirius, we investigated the thermal residual strain of the three layered materials, [WC-10 mass%Ni]-[Ni]-[WC-10mass%Ni], [WC-10mass%Ni]-[Ni(plate)]-[WC-10mass%Ni] and [WC-10mass%Ni]-[SUS304(plate)]-[WC-10mass%Ni]. They were made by self-propagating high-temperature synthesis (SHS) using the powders of W, C and Ni for composite material, and the powder of Ni, a plate of SUS304 or Ni for the middle layer material. The samples were 40mm in diameter and about 4mm in thickness of each layer. We used the composite material, [WC-10mass%Ni], as a substitute of a usual ultra hard alloy, [WC-10mass%Co], because the total absorption cross section for neutron beam, σ_a, of Co nucleus is large compared to that of Ni nucleus. The observation of the reflection from Co nucleus is comparatively difficult, because the intensity of the reflected beam is weak and an amount of Co in the composite material is small. Monolithic materials, [WC-10mass%Ni], [Ni], [SUS304(plate)] and [Ni(plate)], were prepared by the same synthesis and were used as a standard material, which has no macro-strain. The monolithic materials, [WC-10mass%Co] and [Co] were also prepared by the same method of synthesis and a neutron diffraction of these two materials was also made.

In case of the measurements by Sirius, Rietveld analysis of the diffraction patterns was made and the strain determined from the obtained lattice constants were compared with that obtained by RESA.

We discuss the difference between the strain in three layered sample with a middle layer made from powders and that with a middle layer made from a plate-type material.

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2. EXPERIMENTS

2.1. Sample Preparation

The samples were made by Self-propagating High-temperature Synthesis / Static Pseudo Isostatic Compaction (SHS/SPIC) equipment as the following. The original source materials were the powders of W, C and Ni with an average diameter of 5-8 μm, or a plate of SUS304 or Ni. The powders were mixed with an automatic mortar by dry blending for 1 h. They were formed using a cylindrical mold of 40 mm diameter by hand press of 70 MPa during 30 s, and then were formed to a green compact by cold isostatic press (CIP) with 200 MPa during 120 s. After drying by vacuum pump, the green compact was wrapped by carbon sheet and was synthesized by SHS/SPIC equipment, which is shown in Fig. 1. In the equipment, isotropic press of the sample by commercial sand was made. The pressure was 25 MPa. The carbon sheet was ignited by an induction heating. Then, the combustion wave of about 1800 K propagated toward the center of the sample with a speed of 1-100 mm/s. The sample cooled down rapidly after the combustion wave passed.

The synthesized [WC-10mass%Ni]-[Ni]-[WC-10 mass%Ni] and [WC-10mass%Ni]-[SUS304(plate)]-[WC-10mass%Ni] are shown in Fig.2. We see that in case of [WC-10mass%Ni]-[Ni]-[WC-10mass%Ni] the middle [Ni] layer shrinks from the edge to inside, whereas in case of [WC-10mass%Ni]-[SUS304(plate)]-[WC-10mass%Ni] the middle [SUS304(plate)] layer is forced out from the edge. In the case of a middle [Ni(plate)] layer, the situation is the same as that of the middle [SUS304(plate)] layer.

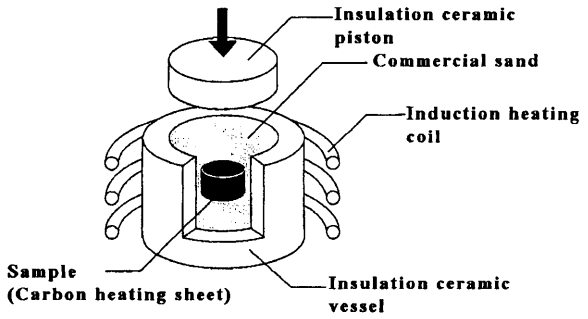
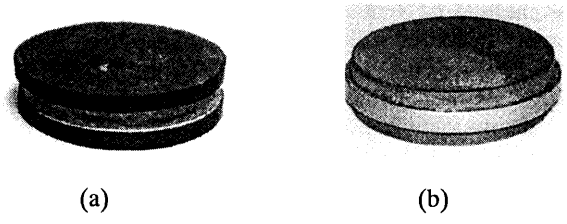


Fig.1. Scheme of a SHS/SPIC equipment.



(a) (b)

Fig.2. (a) [WC-10mass%Ni]-[Ni]-[WC-10mass%Ni] and (b) [WC-10mass%Ni]-[SUS304(plate)]-[WC-10 mass%Ni] synthesized by SHS/SPIC.

The SEM image of the composite material, [WC-10 mass%Ni], is shown in Fig.3, where the white region is WC and the black region is Ni.

2.2. Neutron Diffraction by RESA

The three layered sample, [WC-10mass%Ni]-[SUS304(plate)]-[WC-10mass%Ni], installed on the apparatus, RESA, is shown in Fig.4. We see the incident beam tube with a slit on the upper right hand side and the collimator box in front of the counter with an adjustable slit on the left hand side.

In case of [WC-10mass%Ni]-[Ni]-[WC-10mass%Ni] sample, Ni 200 peak and WC 110 peak were observed for radial and axial direction of the sample. The wavelength was 0.20887 nm. As the size of slits was 2 mm$\times$ 10 mm for incident and reflected beams, we observed the [WC- 10mass%Ni] layer and the [Ni] layer simultaneously. A part of this experiment was published elsewhere [3,4].

In case of [WC-10mass%Ni]-[SUS304(plate)]-[WC-10mass%Ni], the wavelength was 0.20995 nm. As the size of slits for incident and reflected beams were 2 mm $\times$2 mm, respectively, we observed the small area of the sample. On the mid plane of the thickness of [SUS304 (plate)], we observed 200 reflection of SUS304 from the small area at 0, 10, 15, 16, 17 and 18 mm position apart from the center, for axial, radial and hoop directions. On the interface between [WC-10mass%Ni] and [SUS304 (plate)], we observed 200 reflection of SUS304 from the small area at 0, 15 and 18 mm position apart from the center, for axial, radial and hoop directions.

To obtain the standard lattice spacing, d_0, for the estimation of the strain, we used the monolithic materials, [WC-10mass%Ni], [Ni] and [SUS304(plate)], made by the same synthesis method. During the observation of the reflection, these samples were rotated around the χ, ϕ

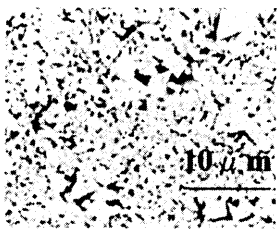


Fig.3. SEM image of [WC-10mass%Ni].

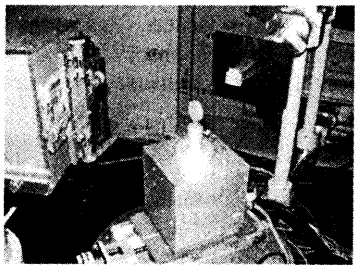


Fig.4. The three layered sample, [WC-10mass%Ni]-[SUS304(plate)]-[WC-10mass%Ni], installed on RESA.

direction using a small motor on the goniometer, to obtain the average lattice spacing for all directions.

2.3. Neutron Diffraction by Sirius

A sample installed on the sample holder of Sirius is shown in Fig.5. The backward scattering was observed for the axial direction of the sample. We observed the large area of the sample, as the slit of incident beam is 20 mm × 40 mm. The sample holder inside the neutron beam was covered with a thin plate of Cd. The lattice constants were determined by Rietveld analysis using the computer program, RIETAN-2001T [5]. The three layered material, [WC-10mass%Ni]-[Ni(plate)]-[WC-10 mass%Ni] and monolithic materials, [Ni(plate)], [WC-10 mass%Co] and [Co], were observed only by Sirius.

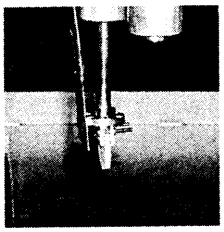


Fig.5. Sample installed on the sample holder of Sirius.

3. EXPERIMENTAL RESULTS

3.1. Residual Strain of [WC-10mass%Ni]-[Ni]-[WC-10mass%Ni]

As a result of the measurements by RESA, a difference of the strain according to the different positions and to the different direction of the sample was scarcely observed. It is presumably due to the fact that the original materials before synthesis are all powders and the pressure during the synthesis is isotropic. As an example, the reflections in the radial direction at 14 mm position from the center of the sample and the Gauss fitting of the peaks are shown in Fig.6. A large peak of the Ni 200 reflection corresponds to the reflection from the middle [Ni] layer and a small one corresponds to the reflection from the Ni region in [WC-10mass%Ni]. The position and the width of large peak is almost the same as those of Ni 200 reflection from monolithic [Ni] material made by the same synthesis. This fact indicates that the middle

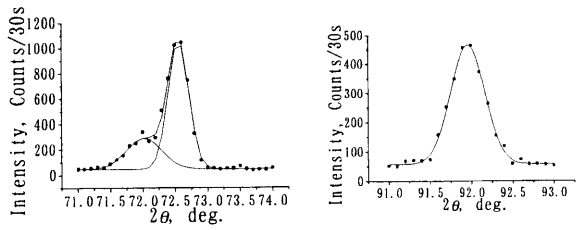


Fig.6. Data plot and the Gauss fitting of Ni 200 reflection and WC 110 reflection for radial direction at 14 mm position from the center of sample, for three layered [WC-10mass% Ni]-[Ni]-[WC-10mass%Ni] material.

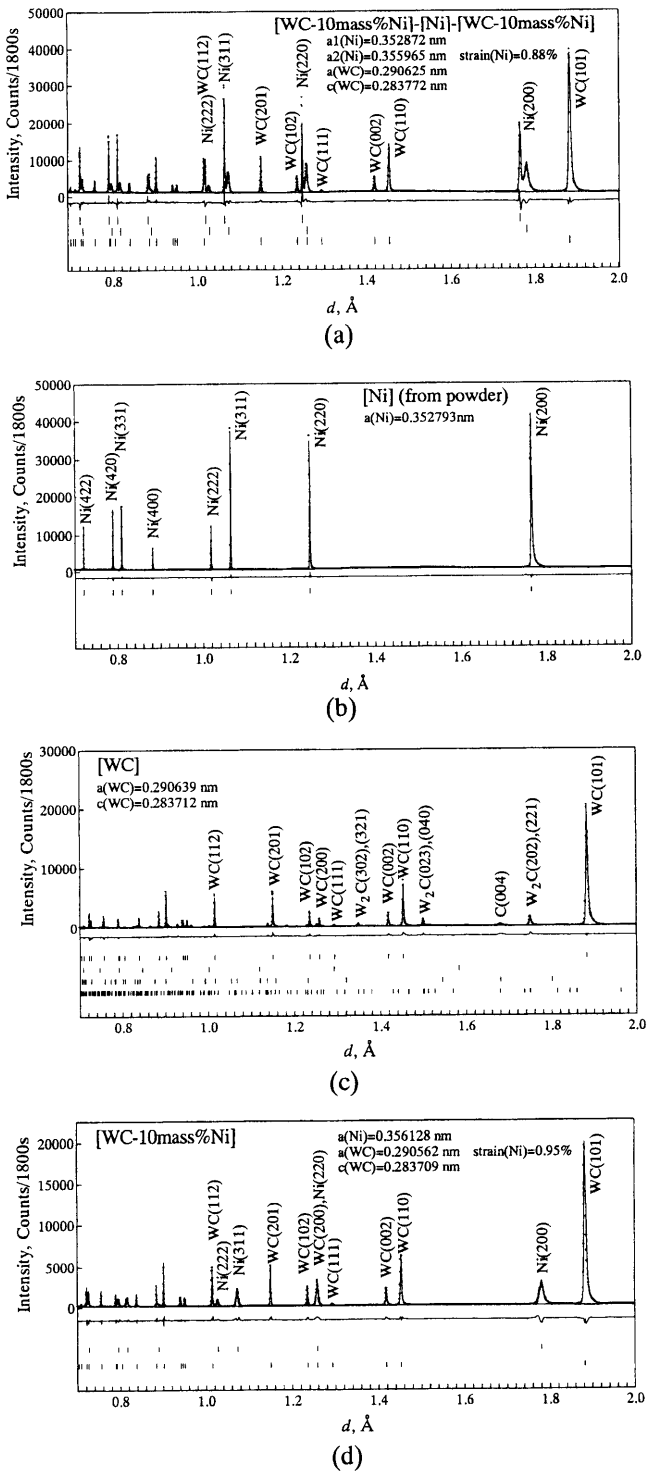


Fig.7. Diffraction patterns observed by Sirius and the results of Rietveld analysis, for (a) three layered [WC-10mass%Ni]-[Ni]-[WC-10mass%Ni], (b) monolithic [Ni], (c) monolithic [WC] and (d) monolithic [WC-10mass%Ni].

[Ni] layer experiences almost no strain. On the other hand, the positions and the width of a small Ni 200 peak are almost the same as those of a peak from Ni region of monolithic [WC-10mass%Ni] material. It means that the strain of the Ni region of composite material, [WC-10mass%Ni], is not affected by the existence of the middle [Ni] layer. The Ni region experiences only the tensile force originated from the adjacent WC region. The width of the small 200 peak, which is wide compared to that of the large peak, indicates that the strain of Ni region of composite [WC-10mass%Ni] material is not uniform. The average strain of this Ni region is 0.72-0.80% according to the different directions and positions of the sample.

The peak position of WC indicates that the strain of WC is negligibly small compressive one. The average values distribute from -0.00 to -0.08% according to the different position and direction of the sample.

The diffraction patterns of three layered [WC-10 mass%Ni]-[Ni]-[WC-10mass%Ni] material, and monolithic [Ni], [WC] and [WC-10mass%Ni] materials, observed by the TOF-type diffractometer, Sirius, and the results of Rietveld analysis, are shown in Figs.7(a), 7(b), 7(c) and 7(d). All of the materials were made from the powders. On the Rietveld analysis, we excluded Ni 111 peak, because this peak includes the magnetic reflection, which is not important for the present purpose. However, it was difficult to obtain a sufficient fitting of the intensity of the whole peaks, especially for three layers material. This is presumably originated from the texture made in the process of synthesis of three layers.

In Fig.7 (a), we observe two kinds of explicitly different Ni peaks. The left large peaks come from the middle [Ni] layer and the right small peaks come from the Ni region in [WC-10mass%Ni] layer. The fact that the position and the width of large Ni peaks are almost the same as those of Ni peaks in Fig.7 (b) indicates that the middle [Ni] layer in three layered material has no strain. The result is consistent with that obtained by RESA. On the other hand, the positions of small Ni peaks in Fig.7 (a) are apparently shifts toward right hand side, and the width is large compared to that of large Ni peaks. These facts are consistent with the results by RESA, which indicate that the strain in Ni region of composite material is tensile and is not uniform inside the region. The obtained average value of the strain of 0.88% is slightly large compared to that obtained by RESA.

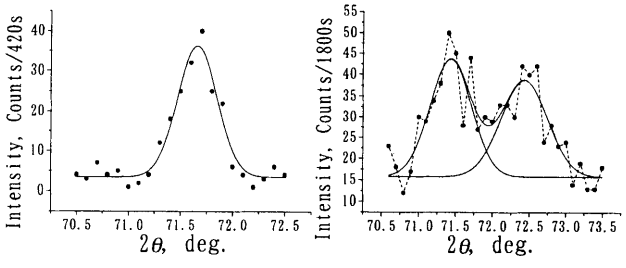
In Fig.7 (c), we observe small amount of graphite peaks and the W_2C peaks, whereas the main material is WC. The peak positions and width of this WC is not so different from those of WC in Fig.7 (a). This fact indicates that the WC in three layered material has almost no strain. The fact is also consistent with the result by RESA.

In case of monolithic composite material, [WC-10mass%Ni], as shown in Fig.7 (d), we see the same WC peaks as those in Figs. 7(a) and 7(c). The fact indicates that the strain of WC is scarcely affected by the existence of Ni region. On the other hand, the strain determined from the small Ni peaks is 0.95%, which is slightly larger than the value of 0.88% determined using Fig.7 (a).

3.2. Residual Strain of [WC-10mass%Ni]-[SUS304 (plate)]-[WC-10mass%Ni]

As the examples of the peaks of 200 reflection of SUS304 observed by RESA, the peak for axial direction from the center of mid plane of the [SUS304(plate)] layer and that from the center of the boundary between [SUS304(plate)] layer and [WC-10mass%Ni] layer, are shown in Fig. 8(a) and 8(b). In Fig. 8(b), we see the Ni 200 reflection on the right hand side, which comes from the Ni region of composite [WC-10mass%Ni] layer. To obtain the standard lattice spacing, d_0, we used the 200 reflection from the monolithic [SUS304(plate)]. To estimate the stress, we used Young' s modulus of 113.6 GPa and the Poisson' s ratio of 0.262, which were obtained from the 200 reflection of SUS304 under tensile test [6]. The residual stress at each position of the middle [SUS304 (plate)] layer is shown in Fig. 9. We see that the middle [SUS304(plate)] layer shows a very complex stress according to each position and direction. At the interface between two layers, SUS304 has a large tensile stress in the three directions, whereas at the mid plane of the thickness, SUS304 has a weak tensile stress in the radial and hoop directions and a weak compressive stress in the axial directions. We see that the stresses of [SUS304(plate)] alter drastically at the radial position of 14-18mm from the center especially on the mid plane. They have a tendency to become more compressive.

Diffraction patterns observed by Sirius for this three layered material and for monolithic [SUS304(plate)] material, are shown in Figs. 10(a) and 10(b). We recognize that the peak width of SUS304 for three layered material is wide compared to that of monolithic [SUS304]. This result is consistent with the fact obtained by RESA that the stress in the middle [SUS304(plate)] layer is not uniform.



(a) (b)

Fig.8. Data plot and the Gauss fitting of the 200 reflection of SUS304 for axial direction (a) from the center the mid plane of the [SUS304] layer and (b) from the center of the boundary of two layers. The peak on right side in figure (b) is Ni 200 reflection from the Ni region of composite [WC-10mass%Ni] material.

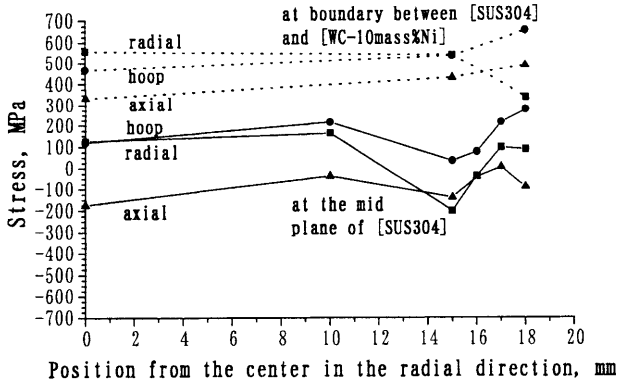


Fig.9. Stress for three directions at each position of the [SUS304] layer, estimated from the data by RESA.

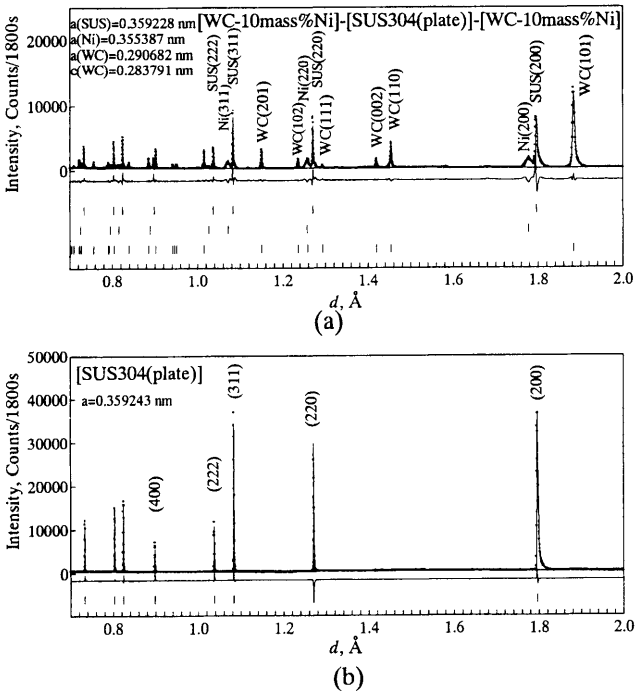


Fig.10. Diffraction patterns observed by Sirius and the results of Rietveld analysis, for (a) three layered [WC-10mass%Ni]-[SUS304(plate)]-[WC-10mass%Ni], and (b) monolithic [SUS304(plate)].

3.3. Residual Strain of [WC-10mass%Ni]-[Ni (plate)]-[WC-10mass%Ni]

Diffraction patterns obtained by Sirius for three layered material [WC-10mass%Ni]-[Ni(plate)]-[WC-10 mass%Ni] and for monolithic [Ni(plate)], are shown in Figs. 11(a) and 11(b). From the result of Rietveld analysis, we recognize that the peak width of Ni in the middle [Ni(plate)] layer is wider than that of monolithic [Ni(plate)]. The situation is the same as that of the middle [SUS304 (plate)] layer of three layered material described in 3.2. This result suggests that the strain of the middle [Ni(plate)] layer is not uniform. The strain of Ni region in composite [WC-10mass%Ni], the average value of which is estimated to be 0.64 %, is slightly

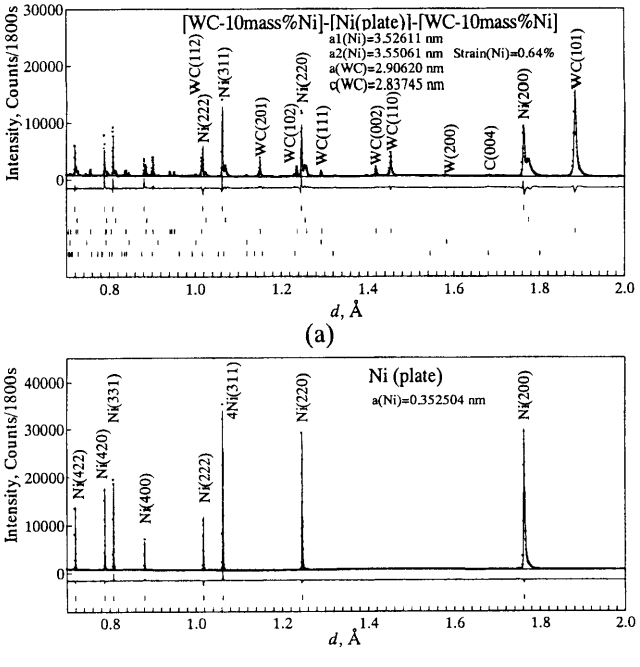


Fig.11. Diffraction patterns observed by Sirius and the results of Rietveld analysis, for (a) three layered [WC-10mass%Ni]-[Ni(plate)]-[WC-10mass%Ni] and (b) monolithic [Ni(plate)].

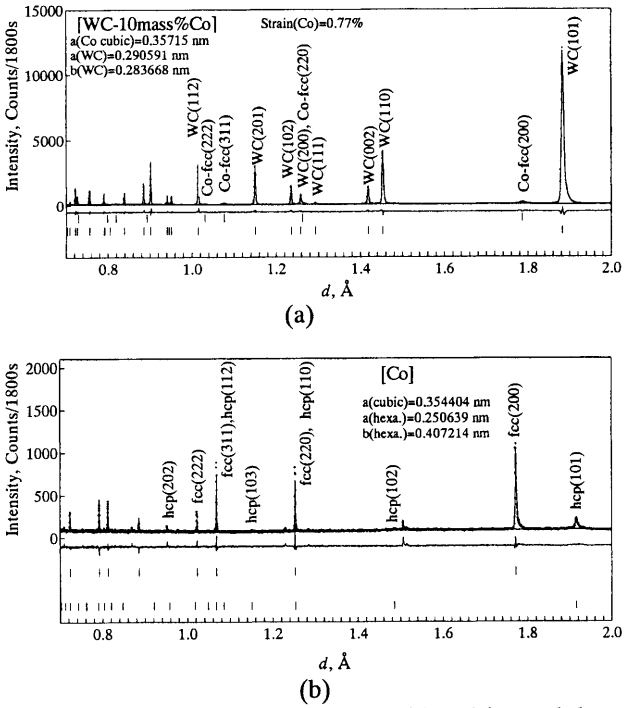


Fig.12. Diffraction patterns observed by Sirius and the results of Rietveld analysis, for (a) monolithic [WC-10mass%Co] and (b) monolithic [Co].

smaller than that of the other three layers case.

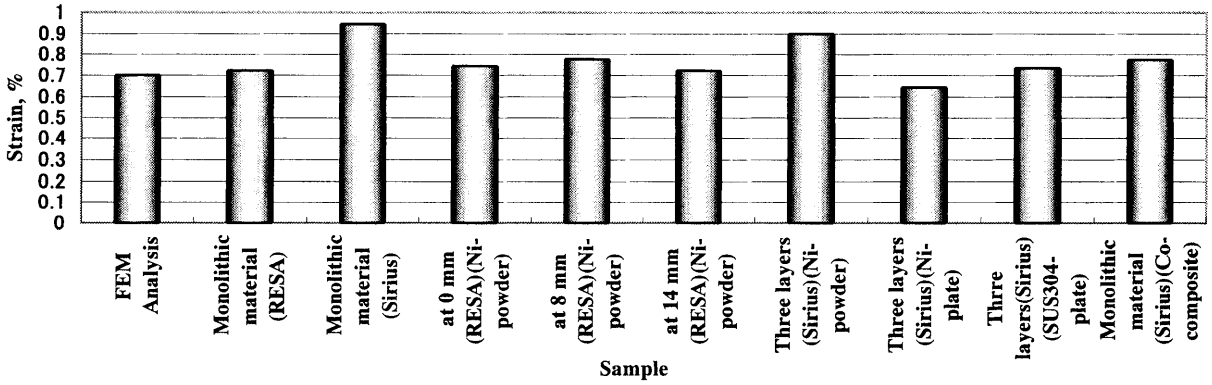


Fig.13. Strain of the Ni region in composite [WC-10mass%Ni]. At the most left side, a result of the calculation by FEM for monolithic material is shown. The second and the third bars show the experimental results for the monolithic material. From fourth to ninth, the experimental results for three layered materials are shown. In the first parentheses of the names on the horizontal axis, the neutron diffraction equipment is shown. In the second parentheses the state of original material of the middle layer is shown. At the most right side, the experimentally obtained strain of the Co region in composite [WC-10mass%Co] monolithic material is shown.

3.4. Residual Strain of Co Region in Composite [WC-10mass%Co] Monolithic Material

We tried to observe by Sirius the diffraction patterns of monolithic [WC-10mass%Co] and of monolithic [Co], as shown in Figs. 12(a) and 12(b). In Fig. 12(a) we are able to see very weak fcc Co peaks, whereas in Fig. 12(b) we see the peaks of fcc Co, hcp Co and others. The peak intensity of fcc Co is relatively large, which means that the main structure in [Co] is fcc. Comparing the lattice constants of fcc Co for two materials, we recognize that Co region in composite [WC-10mass% Co] material has a tensile strain, the average value of which is 0.77%. The value is similar to that of [WC-10mass%Ni]. We confirm that we can analogize the situation of super hard alloy, [WC-10mass%Co], from the data of [WC-10mass%Ni].

4. DISCUSSION

In the ultra hard alloys, which are the composite materials, [WC-10mass%Ni] or [WC-10mass%Co], the Ni region or the Co region experiences the strong tensile strain with the average value of 0.64-0.95%. Each strain in the axial direction is shown in Fig. 13. The distribution of the average value is presumably due to two reasons. First, it is difficult to make the same experimental condition in every SHS/SPIC synthesizing process, because the temperature of the combustion wave and the speed of cooling down after the combustion wave passed are different one by one according to the properties of original materials and according to the thickness of the sample. Secondly, the type of neutron diffraction and the method of analysis of the peak shape are quite different for RESA and Sirius.

In case of having a middle layer made from a powder-type original material, we found that there is no macro-stress due to the joint of two different materials, and the strength of the adhesive boundary is very strong. This is because the original materials before synthesis are all powders and the pressure during the synthesis is isotropic

In case which has a middle layer made from a plate-type original material, we found that the macro-stress due to the join is different according to each position and direction of the sample. We ascertained that the sample is brittle and has a complex fracture surface at the interface.

5.CONCLUSION

By neutron diffraction, we were able to investigate the thermal strain of the three layered materials synthesized by SHS/SPIC method, which include the joint surface between the ultra hard alloys and the usual popular metal such as Ni or SUS304.

We concluded that, to avoid the thermal stress and to obtain high strength, the use of original materials in the powder state for usual popular metal is extremely effective compared to the use of a block-type material.

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