DOI 10.1007/s11182-017-1106-7

Russian Physics Journal, Vol. 60, No. 3, July, 2017 (Russian Original No. 3, March, 2017)

THE USE OF HARD SYNCHROTRON RADIATION FOR DIFFRACTION STUDIES OF COMPOSITE AND FUNCTIONAL MATERIALS

A. I. Ancharov

UDC 53.08

Potential use of hard synchrotron radiation (SR) with the quantum energy above 25 keV is discussed aiming to solve a number of research tasks on investigation of structural changes taking place in materials. The advantages and limitations of the use of hard SR for diffraction studies are evaluated. A review of the principal techniques is made wherein application of hard SR both promotes certain experimental investigations and frequently allows obtaining new structural data unavailable with X-ray tubes.

Keywords: synchrotron radiation, diffraction methods of structure investigations, composite materials.

INTRODUCTION

Composite materials are solid materials consisting of two and more components with distinct boundaries. The phases making a composite may differ in their physical-chemical composition. One of the first articles in the history of mankind was a wicker basket. When tempered by the fire the wicker became charred and burnt, while the clay sintered forming a ceramic vessel. Another example of a composite material is damask steel. The articles were manufactured by multiple rolling of the ribbons of low- and high-carbon steel grades. In present-day engineering composite materials are used quite extensively. These are concrete iron, glass- and carbon-fiber plastics, and eutectic alloys. Eutectic alloys are natural composite materials.

Let us agree to refer the term "hard" synchrotron radiation to electromagnetic radiation with the quantum energy higher than 25 keV. This delineation is quite conventional but is associated with the fact that the proper hard characteristic X-ray radiation is generated by X-ray tubes with silver anodes, and the resulting quantum energies are 22.16 and 24.94 keV. The elements, which follow silver, have either high melting temperatures or high vapor pressure and cannot be used as X-ray tube materials. Other elements following silver with high ordinal numbers, which are applicable as anodes, are hafnium, tantalum, and tungsten. In order to generate high-intensity hard characteristic radiation from the hafnium, tantalum, and tungsten tubes, a voltage of 100–150 keV has to be supplied to them. Commercial diffractometers are not equipped with such high-voltage sources, and there are no commercially produced tubes for structural analysis either.

Since 1970-s, synchrotron radiation has been widely utilized in X-ray diffraction studies. Synchrotron radiation is generated when relativistic particles (primarily electrons) move along curvilinear trajectories. It propagates in the directions tangential to their motion paths. In contrast to the radiation from X-ray tubes, having a low-intensity bremsstrahlung spectrum, synchrotron radiation has a continuous, monotonous spectrum ranging from infrared to hard X-ray radiation region. Unlike radiation from X-ray tubes propagating in all directions and limited by the tube design only, synchrotron radiation is collimated in the plane of the charged-particle orbit. Synchrotron radiation is polarized linearly, while that from X-ray tubes has random polarization. The intensity of synchrotron radiation is by a few orders

Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia, e-mail: ancharov@mail.ru. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 3, pp. 150–156, March, 2017. Original article submitted January 12, 2017.

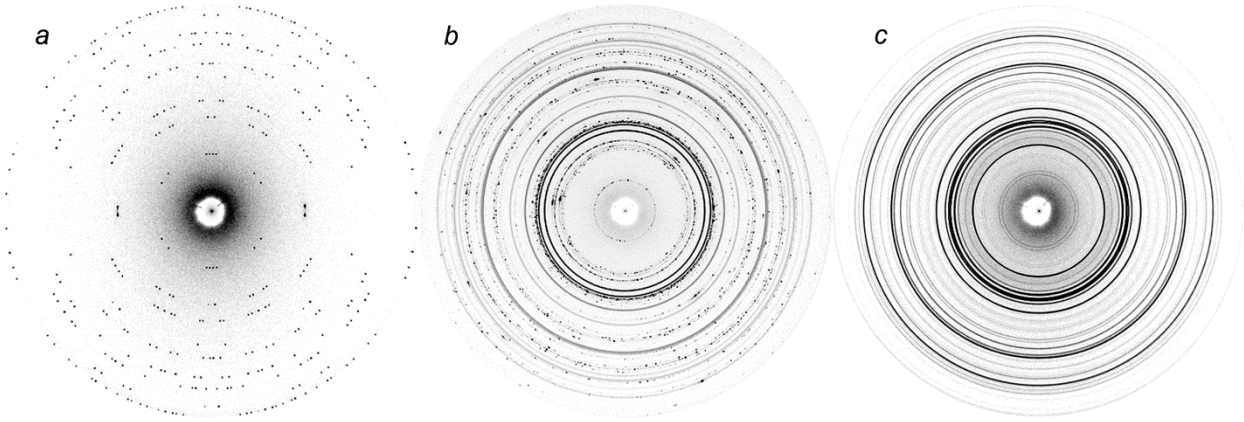

Fig. 1. Rotation diffraction patterns obtained for different materials: a single crystal (*a*), a multiphase material (*b*), and a fine-crystalline material *(c).*

of magnitude higher than that of characteristic radiation from X-ray tubes. For practical calculations of the SR beam parameters it is convenient to use the results obtained in [1].

In all present-day centers of synchrotron radiation there are experimental stations for structural research using hard synchrotron radiation. The entire volume of the matter within the radiation beam path takes part in photon scattering.

At the Siberian center for synchrotron and terraherz radiation, there is an experimental station for performing diffraction studies [2]. To do so, the radiation with a fixed wavelength is used – 0.368 Å. Detection is carried out using a two-coordinate detection system based on MAR 345 imaging plates. The use of a two-coordinate detector allows registering the entire diffraction pattern with all its features. This makes it possible to investigate the material structure by different methods (Fig. 1).

Classically, soft X-rays are utilized in the X-ray diffraction analysis, especially in the case of copper-anode tubes. Now there is a question: what are the prospects of using hard synchrotron radiation?

IMPROVED PENETRABILITY

It is well known that with an increase in the quantum energy the coefficient of absorption of radiation by matter decreases, except for the regions of X-ray absorption jumps. The radiation wavelength also decreases with an increase in the quantum energy and, in accordance with the Wolf-Bragg equation, the diffraction angle decreases. As the wavelength of the utilized synchrotron radiation decreases, the diffraction angles decrease and all diffraction maxima shift towards the region of small angles. Hence it becomes possible to register the principal set of diffraction maxima using a two-coordinate imaging plate. As it is known, the radiation diffracted from the specimen propagates in the form of so-called diffraction cones. Recall also that present day diffractometers register a small part of the diffracted radiation only. In order to obtain a complete set of the diffraction data it is necessary to scan over the required range of diffraction angles. A two-coordinate imaging plate detects all the radiation scattered by a specimen. The use of this detector makes it possible to obtain the information not only about the position and intensity of diffraction rings but also about the diffracted radiation intensity distribution over the ring. In the case of an immobile specimen, reflections from fine crystallites merge into rings. From the shape of the rings one can estimate the size and texture of the crystallites. When the specimen is rotated, the reflections from small crystallites merge into rings. If the specimen contains crystallites comparable with the radiation beam size or bigger than the latter, then moving progressively over the reflecting position the diffracting planes would yield a set of high-intensity diffraction reflections, forming a symmetrical pattern, in other words, a rotation diffraction pattern for a single crystal. It becomes possible now to use the Laue transmission approach. Smaller diffraction angles allow for experiments in peculiar conditions, in apparatus

with a low angular aperture. The use of two-coordinate plate detectors offers registering the entire diffraction pattern in a wide range of wave vectors or interplanar distances. Most of classical diffractometers use a diverging radiation beam and the Bragg-Brentano focusing scheme. Scattering in this case occurs from the outer powder sample surface. The depth of surface layer examination is on the order of dozens of microns and, with heavy elements, even smaller. In the case of the Laue transmission approach, we obtain a diffraction pattern from the entire bulk of the material irradiated with the primary beam. Hard synchrotron radiation offers a means for structural investigations on real objects such as machine components and mechanisms during their operation. Due to its low angular divergence, the object of examination can be located at a comparatively large distance from both the radiation point and the diagnostic apparatus. This is especially critical during investigations of large-sized components and mechanisms. These useful features have found their applications in investigating the stresses developed in materials.

Stresses of different origin give rise to different changes in the diffraction pattern, which allows investigating the internal stresses using synchrotron radiation. Macrostresses shear the diffraction lines. Microstresses result in line broadening.

A beam of monochromatic synchrotron radiation, collimated or focused to the size within 0.4–0.2 mm, penetrates both the openings made in the turbine casing and the turbine blade. Moving the turbine casing with respect to the radiation beam, it is possible to obtain a distribution map of the stresses developed in the blade under different operating modes of the turbine [3]. Since the turbine blades operate under conditions of high temperatures and corroding gases, using synchrotron radiation it becomes possible to investigate the structural transformations and chemical reactions taking place in the bulk of the blades [4, 5].

STRUCTURE INVESTIGATIONS AT HIGH PRESSURES AND TEMPERATURES

During structure investigations under conditions of high temperatures and pressures, high-pressure chambers with diamond anvils are used. The specimen is inserted into an opening measuring about 100 μm in the metal gasket squeezed between the diamond pyramids (anvils) with truncated vertices. Due to its design, the high-pressure chamber has low input and output apertures. The use of hard synchrotron radiation decreases absorption in the diamond anvils and reduces diffraction angles. This advantage together with the high intensity of the focused hard synchrotron radiation allow performing structural investigations up to the pressures of a few megabar and in the cases where IR-laser is used to heat the specimen up to 6000 K. These pressures and temperatures correspond to those existing in the Earth's center. This approach is most frequently used to solve geophysical tasks.

One of the processes for manufacturing composite materials is deformation under pressure. Using the method proposed in this work, one can manufacture such materials impossible to be produced under ordinary conditions as metastable solid solutions, which under heating decompose into a number of phases, and hence are composite materials. Moreover, hard synchrotron radiation made it possible to investigate the stage character of transformations in the course of deformation [6].

DIFFUSE SCATTERING

Diffuse scattering is the scattering of X-ray radiation by the matter along the directions for which the Wolf–Bragg condition is valid. In practice, use is made of diffuse scattering on single crystals and disordered systems.

Let us discuss scattering on single crystals only. The nature of diffuse scattering is elegantly interpreted by the Ewald structure. It is well known that if the reflection sphere crosses a certain reciprocal lattice node, a diffraction maximum is detected in this direction. Thus if we place an immobile single crystal in the radiation beam path, it is likely that we would not observe any reflections. During rotation of a single crystal and hence its reciprocal lattice, its nodes would cross the Ewald sphere and produce reflections in the respective directions.

As the radiation wavelength decreases, the Ewald sphere radius would be increasing and thus increasingly more reciprocal lattice nodes would be found near the Ewald sphere. A reciprocal lattice node represents a point in the case of a perfect lattice only. Actually, the size and shape of this node are affected by thermal vibrations of atoms about their

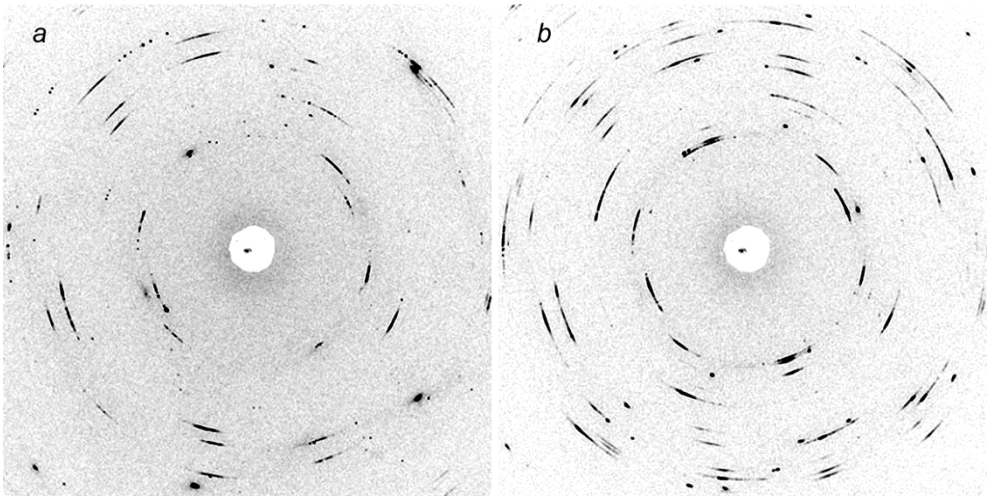

Fig. 2. Diffraction patterns from the zone of eutectic crystallization: from immobile (a) and rotating (b) specimens (rotation angle during exposure was 60°).

equilibrium positions. Thermal vibrations in a crystal cannot be isotropic, thus the shape of the reciprocal lattice node would be nonspherical. Crystal defects also influence the size and shape of the reciprocal lattice nodes, and a decrease in the crystallite size in one direction would give rise to a respective increase in the reciprocal lattice node in this direction. Scaly crystallites cause degeneration of the reciprocal lattice node to form a cylinder, while needle-like cause it to become a plane. In fact, diffuse scattering in the case of the use of synchrotron radiation represents an image of the reciprocal lattice cross section.

We investigated crystallization of a eutectic alloy of the In–Sn system. Ribbons made of indium and stannum were placed next to each other with an overlapping of 0.5 mm. They were then clamped between cover glasses and placed into a high-temperature chamber. The chamber temperature was increased by 2°C and remained constant for 3 h, while the region of contact melting widened up to 5 mm. When the specimen temperature decreased to below the eutectic point, single reflections were observed. Fifteen minutes later the diffraction pattern consisted of single reflections from the fine-crystalline phase of $InSn_4$ and two overlapping diffuse scattering patterns from the crystallites comparabe in size with the beam. The form of the diffuse scattering pattern suggests that a bicrysalline plate-like colony is involved itno crystallization. Cooling to 55°C does not virtually change the form of the pattern, and cooling to below 50°C gives rise to decomposition of large crystallites into fine ones, when low-angle boundaries appear. The positions of the diffraction maxima correspond to the $InSn_4$ and In_3Sn phases with a slightly deformed lattice [6].

In the new stage we investigated a plate of the specimen after cooling (Fig. 2). It was placed onto the goniometer head, which allowed examining both immobile specimens and those rotating around the axis perpendicular to the radiation beam.

It is evident in Fig. 2*b* that the reflections are somewhat scattered over the layer lines. This indicates that a large crystal subjected to stresses has fractured into a number of smaller crystallites having bicrystalline structure. Their misorientation angle is found to be about 10°.

INVESTIGATION OF STRUCTURE AND MORPHOLOGY IN THE COURSE OF CHEMICAL REACTIONS

Composite materials are also produced via chemical reactions. Let us demonstrate the potential of the above approach using the interaction of liquid gallium with copper and its alloys, which are used as bases for metal alloys, as an example. If we mix copper powder with liquid gallium, a chemical interaction begins resulting in the formation of

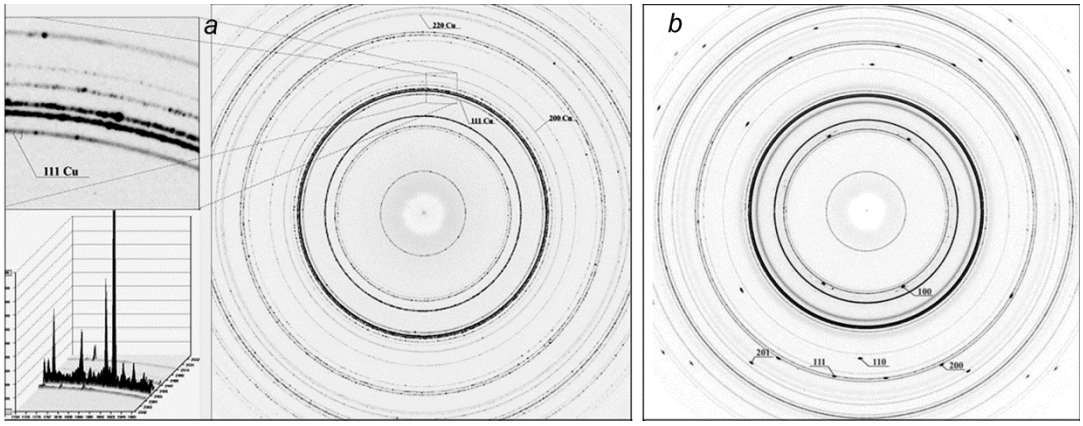

Fig. 3. Diffraction pattern from the reaction product: copper with liquid gallium and magnified fragments in two- and three-dimensional representation (*a*), Solid solution of indium in copper with a gallium-stannum melt of eutectic composition (*b*) [8]. Reflections from $InSn_4$ are indexed.

an intermetallic compound, $CuGa_2$. It is clear from the diffraction pattern (Fig. 3) that the reflections from copper are considerably less intensive than those from intermetallic $CuGa_2$.

Copper can be assumed to dissolve in liquid gallium. During investigation of the interaction between the solid solution of indium in copper with the eutectic gallium-stannum melt a $CuGa_2$ phase was observed and traces of one more phase. In order to obtain additional information during imaging the specimen was rotated by the angle 60° around the axis perpendicular to the primary radiation beam. Even, concentric rings from the $CuGa_2$phase are observed in Fig. 4 and single, symmetrically located reflections belonging to the phase of $InSn_4$. These reflections indicate that the $InSn_4$-phase has crystallized as a single-crystal network containing grains of intermetallic $CuGa_2$ inside.

The reaction of iron recovery from its oxide using aluminum is followed by a substantial heat release. In massive specimens the recovery process, once activated, proceeds until complete heating of the components. In a mechanical activator, the process of recovery occurs at the moment of collision of the milling bodies with each other and with the activator housing. In order to decrease the relative heat release, we performed the recovery reaction from iron oxide using a solid solution of aluminum in iron to form a Fe/Al_2O_3 composite. The X-ray diffraction studies demonstrated the presence of reflections from iron and weak reflections from iron oxides six minutes after mechanoactivation, while in 12 minutes there were only reflections from iron and herzinite ($FeAl_2O_4$) left. Note the absence of aluminum oxides. Tempering at 720°C for 6 hours results in recrystallization of iron or its solid solution. Figure 4 presents some fragments of the diffraction patterns obtained from the reaction products of interaction between the iron oxide with the solid solution of aluminum in iron. It is evident from the diffraction patterns that the initial product consists of α-iron with small impurities of herzinite. Under the conditions of heating iron is annealed. At the temperature above 620°C α-iron is transformed into γ-iron. Tempering of the specimen for 6 hours at 720°C results in a complete transformation of α-iron into γ-iron. Classically, this phase transition occurs at the temperatures higher than 912°C. It is well known that even a small amount of aluminum (1.285 at.%) solved in iron prevents an α–γ phase transition. It should also be noted that the crystallites of α- and γ-iron after tempering for 6 h at 720°C remained (from the shape of diffraction rings) submicron in their size, though in the products of iron interaction with aluminum iron was recrystallized. During heating there is a larger number of diffraction peaks from wustite (FeO) in the diffraction patterns. Presumably, there is a large amount of oxygen adsorbed on the surface of nanosized iron particles; moreover a certain amount of air remains in the capillaries – altogether this gives rise to additional oxidation of iron. During heating no aluminum oxide phases were observed. Presumably, strongly deformed or amorphous aluminum is on the surface of nanosized iron crystallies in the layers of a few nanometers in thickness. Thus no reflections from aluminum oxides are observed in the diffraction patterns. The above-mentioned layers prevent iron from recrystallization. The use

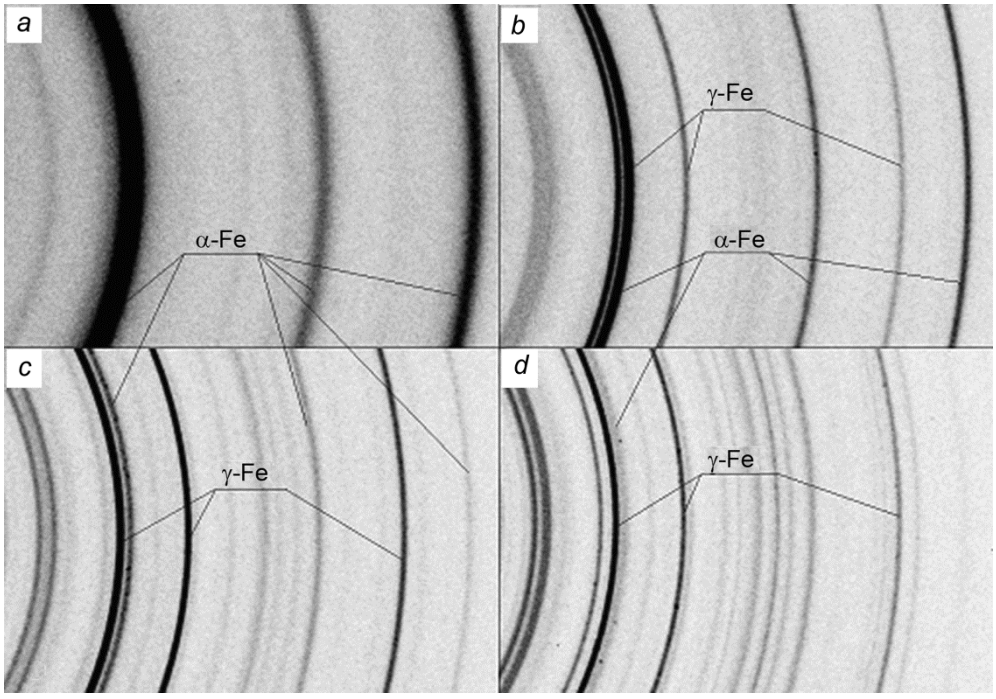

Fig. 4. Fragments of diffraction patterns obtained from the products of interaction between iron oxide with solid solution of aluminum in iron at 720°C: initial product (*a*), product tempered for 1 (*b*), 3 (*c*), and 6 (*d*) hours. All unmarked reflections belong to iron oxides.

of mechanochemical recovery of iron oxides by aluminum and its solid solutions offers a possibility of designing a wide class of composite materials with different morphological features.

SIMULTANEOUS EXAMINATION OF PHASE AND ELEMENTAL COMPOSITIONS OF THE SPECIMEN

Hard synchrotron radiation causes fluorescent emission from the specimen atoms. This allows determining the presence of nearly all elements from their *K*- or *L*-lines, except for the lightest elements (H–Al). If we place an energy-dispersive detector on the side of the specimen, it would register its fluorescent spectrum, while a two-coordinate detector placed perpendicular to the primary beam would register diffracted radiation. Thus both phase and elemental compositions of this specimen would be registered in the same volume of matter. This is especially useful for examination of composite materials. By aiming a thin radiation beam onto certain zones of a specimen under examination we can obtain the information on the elemental and phase composition of these regions simultaneously.

SUMMARY

It follows from the above discussion that the use of hard synchrotron radiation for diffraction studies not only alleviates a number of experimental investigations but also allows obtaining new structural information unavailable with the X-ray tubes. Worldwide, the number of experimental stations using hard synchrotron radiation is increasing. Novel devices are being designed (multi-pole wigglers, undulators, free-electron lasers) capable of generating high-power fluxes of high-energy photons with the energies 150 keV and higher, which would make it possible to obtain structural information within a few micro- and femtoseconds.

This study has been performed within the TOR of ISSCM SB RAS (Project 0301-2016-0016).

REFERENCES

1. G. N. Kulipanov and A. N. Skrinitskii, Usp. Fiz. Nauk, 122, Issue 3, 309 (1977).
2. A. I. Ancharov, A.Yu. Manakov, N. A. Mezentsev, *et al.*, Nucl. Instrum. Methods A, **470**, 80 (2001).
3. J. Böhm, A. Wanner, R. Kampmann, *et al*., Nucl. Instrum. Methods Phys. Res. B, **200**, 315–322 (2003).
4. J. N. Wagner *et al.* , Mater. Sci. Eng. A, **618**, 271–279 (2014).
5. T. P. Tolmachev, V. P. Pilyuggin, A. I. Ancharov, *et al*., The Phys. Met. Metallogr., **117**, No. 2, 155 (2016).
6. A. I. Ancharov andK. V. Zolotarev, Zh. Strukt. Khim., **57**, No. 7, 1438–1444 (2016).
7. T. F. Grigoryeva, A. I. Ancharov, A. P. Barinova, *et al*., Zh. Prikl. Khim., **82**, No. 5, 727–730 (2009).
8. A. I. Ancharov, T. F. Grigoryeva, and V. V. Boldyrev, Dokl. Akad. Nauk, **408**, No. 1, 115–118 (2006).