Indian J.Sci.Res. 17(2): 53-59, 2017

ISSN: 0976-2876 (Print)
ISSN: 2250-0138(Online)

FORMATION AND APPLICATIONS OF SINGLE CRYSTAL MATERIAL

[1] Ashish R. Prajapati, [2] Shilpesh R. Rajpurohit
[1, 2] Department of Mechanical Engineering, S. V. National Institute of Technology, Surat

Abstract- The single crystal is essentially a single giant grain in which the arrangement of molecules exhibits strict order. Due to this, the crystal lattice is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give monocrystals unique properties to the single crystal materials. The Czochralski process and the Bridgeman technique are most commonly used for formation of single crystal materials. Because of the good physical properties particularly mechanical, optical and electrical, single crystals produced by the Czochralski process are widely used in the semiconductor and solar photovoltaic industries. The other application of single crystal material is to manufacture the turbine blades by the Bridgeman technique using nickel-based alloy because conventionally cast turbine blades are polycrystalline having grain boundaries which lead to creep, and this creep is responsible for turbine failure. Apart from that, single crystalline diamond has extraordinary physical properties and used in abrasives, cutting and polishing tools, CO_2 lasers, and gyrotrons. In spite of having this much good property, due to the lack of large, high quality single crystals prevents its use in many applications. So, the formation of large single crystal at high growth rate can open a new era for applications of the material. This paper reviews several formation techniques of single crystal material and various applications of it.

keywords— Single Crystal, Czochralski process, Single crystal turbine blade, Synthetic Diamond.

I.Introduction

A single crystal or monocrystalline solid is a mixture of metals that can be cast in such a way that the entire object is essentially a single giant "grain," i.e., one continuous crystal. In the single crystal material the crystal structure is near perfect, i.e., the arrangement of the atoms or molecules exhibits strict order. In this entire sample, the crystal lattice is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give monocrystals unique properties, particularly mechanical, optical and electrical, which can also be anisotropic, depending on the type of crystallographic structure. These features, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics. The almost perfect crystal structure yields the highest light-to-electricity conversion efficiency for silicon. The primary application for single crystal superalloys is the manufacturing of jet engine turbine blades.

Single crystals exist in nature, but they may also be produced artificially. They are ordinarily difficult to grow because the environment must be carefully controlled. If the extremities of a single crystal are permitted to grow without any external constraint, the crystal will assume a regular geometric shape having flat faces, as with some of the gemstones; the shape is indicative of the crystal structure. The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. For example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] directions. This directionality of properties is termed anisotropy, and it is associated with the variance of atomic or ionic spacing with crystallographic direction. Substances in which measured properties are independent of the direction of measurement are isotropic. The extent and magnitude of anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure; the degree of anisotropy increases with decreasing structural symmetry. Single-crystal alloy parts have no grain boundaries; however, they are highly resistant to this kind of wear. Here, the absence of grain boundaries actually gives a decrease in yield strength but more importantly decreases the amount of creep which is critical for high temperature, close tolerance part applications [1].

II. Formation Of Single Crystal Material

Specific techniques to produce large single crystals include the Czochralski (CZ) process and the Bridgman technique. Other less exotic methods of crystallization may be used, depending on the physical properties of the substance, including sublimation, simply solvent-based crystallization and hydrothermal.

A. Czochralski Process

This process was invented by polish scientist Jan Czochralski in 1915. The idea of Czochralski method is based on pulling a crystal from the melt against gravity forces. [2]

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[1]Corresponding Author

photovoltaic industries. The Czochralski process is a well-established method for growing large-scale single crystals of semiconductors, metals, salts, and gemstones. The most important use of the method is the growth of semiconductors, particularly that of monocrystalline silicon, which cannot easily or inexpensively be grown using other methods. Silicon is a particularly important material because it has many desirable properties; it is abundant and cheap, reliable and its semiconducting properties are excellent. [3]

Today, solar cells made from crystalline silicon (Si) substrates have a share more than 90% of the global solar cell market, and they are likely to continue to dominate this market for many years to come. The efficiency of a solar cell is to a large extent dependent on the structure of the wafer, which, in turn, depends on the crystallization of the grown crystal ingot. The solidification process is, therefore, an important step in reducing PV energy costs and increasing cell efficiency. [4]

1)Experimental Setup

In the CZ process, the solid silicon is placed in a crucible. Electrical heaters are used both to melt the silicon and to maintain an appropriate temperature trajectory throughout the crystallization process. Here, the furnace is heated above 1500º C, since Si melting point is 1412º C. A single crystal seed is put in contact with the molten silicon. The seed is then slowly withdrawn from the melt, and surface tension causes the formation of a meniscus which connects the crystal to the melt. Both crucible and seed crystal are rotating in the opposite direction. As the crystal is withdrawn, the melt solidifies along the top of the meniscus, causing the crystal to grow. After a brief period producing a thin crystal, the crystal diameter is increased quite quickly, whereas for most of the duration of the process it is desirable to keep the crystal diameter constant. In the case of solar cell production, the ingot is sliced into very thin wafers when the crystallization process is over. Each wafer is polished and cut into a particular shape, depending on the final application. A sketch of the Czochralski process is shown in Fig.1. During growth, the radius of the crystal is typically measured by a CCD (charged couple device) camera aimed at the meniscus, which can be identified as a glowing ring due to rejections from the glowing environment. Pulling speed and heater power are the two primary actuator inputs for the CZ crystal growth process, but they influence the material solidification process at the interface in different ways. The heater power affects the energy balance at the interface region, while the pulling rate acts on the crystal radius through manipulation of meniscus shape and growth angle [4].

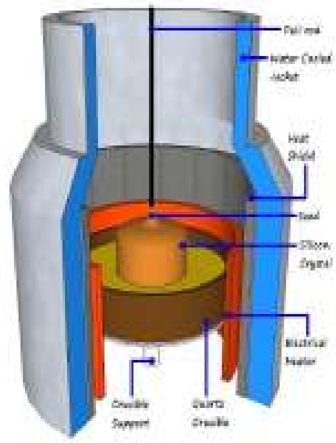

Fig.1. Czochralski crystallization process [4].

B. Continuous-Feeding Czochralski (Ccz) Method

Single silicon crystals produced by the Czochralski (CZ) method are used widely in the semiconductor and solar photovoltaic industries. However, the cost of single crystalline silicon solar cells is about 20% higher than multi-crystalline silicon solar cells. The continuous-feeding Czochralski (CCZ) method is an effective way to reduce the cost, and it has been applied to produce various kinds of crystals. However, CCZ-grown crystals exhibit special defects, i.e., the cavity problem, which does not meet the requirements of most electronic devices. This issue restricted the development of CCZ method. Fortunately, concerning the solar application, defects that are generated during the CCZ process show little impact on the solar cell performance, and so the CCZ method has become popular again in producing high-efficiency solar cells. A modified design of CCZ-Si furnace with the water-cooled jacket was proposed to produce high-quality silicon crystals under a high crystal growth rate. The continuous-feeding Czochralski method is an effective way to reduce the cost of single crystal silicon. By promoting the crystal growth rate, the cost can be reduced further. In this process, a water-cooled jacket was applied to enhance the heat transfer at the melt-crystal interface with a modified heat shield design; heat transfer at the melt-crystal interface is well controlled. The crystal growth rate can be increased by 20%. [3]

III. Machining Of Single Crystal Materials

Machining of single-crystal materials is of interest due to the demand from various applications for single crystal parts due to their uniformity and reduced level of defects (e.g., turbine blades, precision mirrors). Recent interest in ultra-precision machining and micromachining also motivated single-crystal machining analysis, since those processes include chip-thicknesses commensurate with the grain size of many engineering materials, making crystallographic anisotropy critical in machining response [5].

A. Effect of the crystallographic orientations on machining

A number of experimental studies have confirmed that machining response including machining forces, chip lamellae, dynamic shear stress, and surface roughness strongly depends on the crystallographic orientation in fcc metals. Some investigations also considered the effect of crystallographic anisotropy on the built-up edge (BUE) and material side-flow [6].

Plunge turning and planing of single crystal aluminum provide equivalent force data at different crystallographic orientation for large rake angles, while forces alter between two distinct levels while cutting single crystals with small rake angles. To test the possibility of subsurface deformation being the cause for such alternations, measurements were made using OIM (Orientation image microscopy) [5].

Clarebrough and Ogilivie, who microtomed large crystals of lead and observed a strong correlation between the crystallographic orientation and lamellae spacing. Subsequent studies of Black and von Turkovich shed light on various aspects of microscale chip formation in single-crystal cutting. They performed a quantitative study of chip formation mechanisms in single-crystal copper and aluminum via an ultra-microtomy process. The lamellae thickness was seen to be affected by the crystallographic orientation and uncut chip thickness (below 2 μm) [7].

The results from the planning studies showed that the anisotropy of fcc crystals strongly affects the machining forces, inducing up to 312% variation in machining forces at different crystallographic orientations for a given zone axis [8]. The magnitude of variation in machining forces must be contrasted with results from nanoindentation, where the dependence of hardness on orientation is observed to be minimal. For example, the observed variation in hardness in copper, between {1 1 0} and other surfaces was 6% [9].

In turning aluminium crystals, the best surface finish is obtained in machining crystals with the {100} planes as the cutting planes, whereas the {110} planes would result in the highest surface roughness [10].

IV. Single Crystal Turbine Blade

A turbine blade in a jet engine operates continuously in an environment where the gas flow from the combustion system may reach a velocity of more than 500 m/s. Each turbine blade extracts 750 HP from the high-energy gas stream. Rotating at about 10,000 rpm each blade exerts an outward pull of some 20 tons per square inch. Also, turbine blades are required to operate for 10,000 hours or five million miles of flying. So, the turbine blade has the most demanding role in the function of the engine. In jet engines, maximum energy can be extracted from their fuel if the turbine blade can sustain very high temperature [11]. So, ultimately the thermal efficiency of the turbine increases when the temperature of the gas flow at the exit of the compressor and at the entry of turbine is very high. In today's modern jet engines, the temperature of this gas can exceed 1,650º C. Non-aviation gas turbines operate at 1,500º C or lower, whereas military jet engines can reach 2,000º C. Here, the shaft rotates around speed range of 12,000 rpm. The melting temperature of turbine blade material is several hundreds of degrees lower than this operating environment of a jet engine. Earlier, these turbine blades were made from wrought steel which can be operated in the temperature range of 1000º C. Since the 1950s, blades are made from superalloy which is a combination of metals based on high melting point nickel. In this superalloy, nickel has a face-centered cubic crystal structure where one atom is at the center of each corner and one atom at each corner. They are made from conventional casting methods. These conventionally cast turbine blades are polycrystalline having grain boundaries which lead to creep, and this creep is responsible for turbine failure. Their melting temperature is in between 1250º C to 1400º C [12].

A. Types Of Turbine Blade

Until now, there are total three types of turbine blades are being used, which is,

Conventionally cast turbine blade

Directionally solidified (DS) turbine blade

Single crystal (SX) turbine blade.

Blades produced by conventional casting process proved very durable but microscopic grain boundaries present in these castings were a potential source of weakness. So, for eliminating this problem, the concept of directional solidification has been developed. In spite of the fact that, grain boundaries are present in this type of blades but only in longitudinal direction various defects can be minimized and this process doubled creep life of the blade. But still grain boundaries are present in the material so, it has to prevent grow to get a maximum outcome from the engine. These all defects are overcome by single crystal turbine blades which do not have any grain boundaries. The breakthrough in single crystal technology was achieved at the end of the 1970s using an extension of directional solidification technology. This can be obtained by growing only one grain into the main body of casting. Figure 2 shows the types of turbine blade. Over recent decades Rolls-Royce has developed many of the advanced casting and machining processes now standard across the world and established comprehensive facilities to produce cast aerofoil in near-laboratory conditions [13].

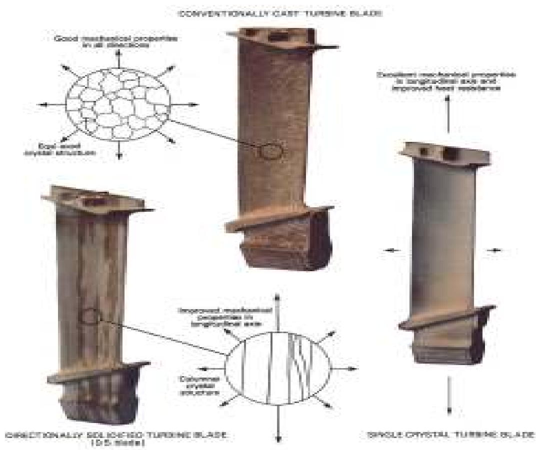

Fig. 2. Different types of the blade with a cross-section [13].

B. Common Failures In Gas Turbine Blades

In aviation application, the failure rates of the modern gas turbine are considered low because of its high level of reliability. This is due to the fact that high level of inspection is carried out for different parts of the jet. The most commonly rejected parts of the jet engine are compressor blades and turbine blades. The failure in compressor blades is because of mechanical damage specifically foreign object damage as they exposed to ingested debris. Here, the turbine blades are operated at a very high temperature and pressure; these bring mechanical damage like creep, fatigue and high-temperature corrosion [14].

C. Failures Due To Grain Boundaries

The presence of grain boundaries in polycrystalline blades leads to various effects like intergranular cavitations, void formation and stress loading due to which defects like creep generated in blades. Creep is the tendency of blade material to deform at a temperature-dependent rate under stresses well below the yield strength of the material. Apart from creep it shortens cyclic strain life and decreases overall ductility. Creaks and corrosion also start at grain boundaries [12].

D. Recent Breakthrough In Blade Manufacturing

Single crystal technology is being further developed for other turbine aerofoil products such as nozzle guide vanes in aerospace applications and the turbine blades of large electrical turbo-generating machinery.

The blades that Rolls-Royce currently manufactures can withstand a temperature of about 1550º C, rotate at 10,000 rpm, remove 560 kW each from the gas stream and last up to 5,000,000 km of flying. The key advances have been the manufacture of single-crystal blades, with internal cooling channels, and, latterly, thermal barrier coatings. Derby's precision casting facility, for instance, was purpose-built in 1970 to meet the demand for complex air-cooled aerofoils. With a floor space of 100,000 square meters, it is one of the largest precision casting facilities in the world [15].

V. Single crystal synthetic diamond growth

Diamond is a unique material in every possible way. Single crystalline diamond has extraordinary physical properties which make diamond the material of choice for many applications. Diamond is not only the hardest material but its other properties like high thermal conductivity, singular strength, chemical inertness, low thermal expansion, excellent optical, infrared, and X-ray transparency, and semiconductor properties of the material offers many applications. In spite of having this much good property, due to the lack of large, high-quality single crystals of diamonds prevents its use in many applications. The synthesis of large single-crystal at high growth rate has opened a new era for applications of the material. In this process, large and thick single crystals can be produced at very high growth rates. The mechanical, chemical, optical and electronic properties of the material can be changed over a wide range [16].

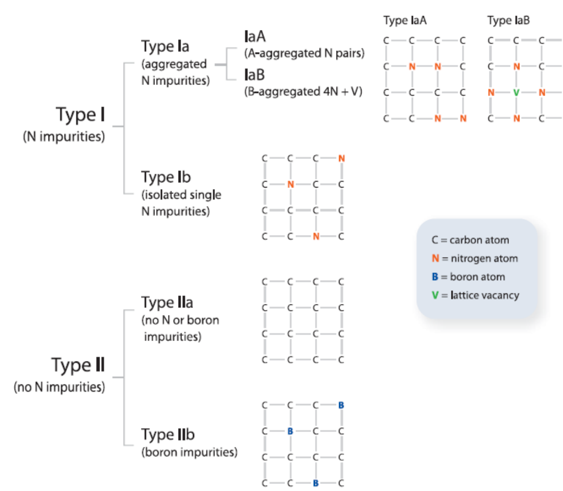

Fig. 3. Classification of Diamonds [18].

Diamond has better semiconducting properties than silicon for many electronic applications. Diamond is used in many applications from Jewelry to surgical blades, grinding and polishing to wire drawing dies, and electronic heat sinks to infrared windows. The demand for producing man-made diamonds with tailored properties has been increasing throughout the years. The primary challenge in wider production, however, remains the high cost of manufacturing, particularly for large monocrystals [17].

A. Classification Of Diamond Types

Based on the presence or absence of nitrogen and boron impurities and their configuration, diamond is classified. Type Ia diamonds contain aggregated N purities – including A-aggregates (IaA), which consists of pairs of N atoms, and B-aggregates (IaB), which are made of four N atoms around a vacancy. Type Ib diamonds have isolated N atoms. Type IIa contains no measurable impurities, and type IIb diamonds has boron impurities. Synthetic diamonds are generally type Ib in which the majority of nitrogen atoms occupy isolated substitutional sites as shown in Fig.3. Most of the natural diamonds are type Ia diamonds [18].

B. High Pressure High Temperature Method

The high pressure high temperature technology is first developed by Bundy et al. at GE in 1955. This process has been widely used to produce type Ib, IIa and IIb single crystals. In this process, the pressure and temperature required are around 5–6.5 GPa and 1300º–1700º C, depending on desired crystal geometry. To increase growth rate, different catalysts are used which involve alloys of Fe, Ni and Co, with other elements such as Ti, Al, B and Ge added to getter nitrogen impurities for producing colorless or blue diamonds. However, the growth rates using metallic catalysts are in the range of 2–15 mg/h, with the largest single crystal grown reported as 34.80 carats [19].

Fig. 4. The HPHT apparatus [17].

In most HPHT processes split sphere growth apparatus (BARS) is used as shown in Fig. 4. These apparatus consisted of two spherical halves held together with steel clamps. In the cavity between the inner surface of the spherical chamber and a rubber membrane, pressurized oil is pumped. This cavity is surrounded by eight anvils which have truncated octet shape. This anvil transfers the pressure into the tetragonal growth cell via six pyramid shaped WC-Co anvils. The spilt sphere apparatus is capable of maintaining pressure for required days by using the small mechanical pump. Here in this process for generating 5.0-6.5 GPa pressure approximately 2.5 Kbar of oil pressure is needed in the growth chamber. Diamonds seeds are placed at the bottom of the press. The internal part of the press is heated above 1400º C and melts the solvent metal. This molten metal dissolves the high purity carbon source, which is then transported to the small diamond seeds and precipitates forming a large synthetic diamond [17].

C. Chemical Vapour Deposition (Cvd)

A series of gas phase then surface chemical reactions, and finally, the deposition of reaction products are involved in the CVD process. Generally in most CVD processes, for diamond nucleation and growth, a carbon containing precursor is used. Methane is most used gas phase carbon source. In 1984, Spitsyn et al. added atomic hydrogen to the CVD process and found that it stabilized the metastable diamond surfaces and promoted diamond growth and this growth rate is around one µm h^{-1} [20]. But, in the mid-2000s millimeter sized single crystal diamonds were developed. The CVD setup consists of a vacuum chamber, a holder for the diamond, and a heating source to superheat the chamber. Here, input materials are hydrocarbon gas and a seed of diamond. The seed is a thin sliver of single crystal diamond that acts as an atomic template for the ensuing crystal growth. This is necessary as the starting point for all single crystal diamond at this point. This diamond seed crystal (natural, HPHT, or CVD in origin) is introduced into the gas mixture, at an elevated temperature of 900º to 1200º C. The activated carbon-hydrogen species travels across the surface of the diamond seed until it finds an available carbon atom, and then attaches itself to this seed atom. The seeded growth is now one carbon atom thicker. The plasma assisted CVD setup is shown in Fig. 5. This process repeats itself endlessly to replicate the crystal structure of the diamond seed crystal in three dimensions [16] [21].

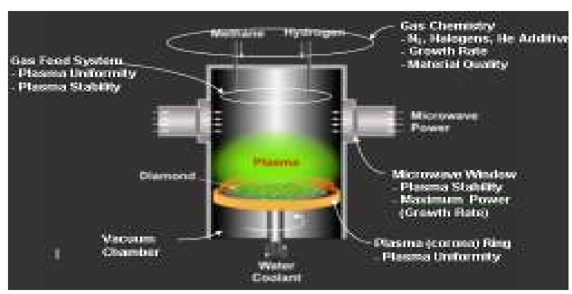

Fig. 5. Plasma assisted CVD setup [16].

By managing the growth process the shape of the diamond and its crystal features can be maintained to a certain degree. To further tailor the diamond properties, impurities can be selectively and controllably added to the growing diamond by adding gases that contain elements such as boron, nitrogen or phosphorous [22].

The discovery that single crystals of diamond can be produced by microwave plasma chemical vapor deposition (CVD) has opened a vast range of new possible applications of the material. With high gas pressures of 150 torr, methane concentrations up to 20% in the CH_4/H_2 gas mixture, and the addition of a small amount of nitrogen gas, diamond growth rates of up to 150 µm h^{-1} were achieved much faster than the typical CVD diamond growth rate of 1 μm h^{-1}. The growth-rate enhancement with the addition of nitrogen single-crystal CVD diamond annealed at 2000°C and 5–7 GPa results in color change. In addition, the hardness of the material can be significantly enhanced, beyond that of conventional natural and as-grown synthetic diamonds. The high fracture toughness of the material prior to annealing and the enhancement of the hardness correlate with changes in the mosaic character of the crystals and transformation of residual carbon defects present in the as-grown crystals. The microwave plasma CVD method can routinely produce one 3 mm-thick, twin-free, a diamond in approximately one day and single crystals produced in this way exhibit very high toughness [23] [24].

V. Conclusion

Through comparison, the new CCZ system shows much less convection under the crystal, which is favorable for high-quality crystal growth. The crystal growth rate can be increased by 20% with this modified design which ultimately reduce the cost.

Rolls-Royce has made turbine blades that run at the highest gas temperature ever attempted by turbine engine; after the stringent test they were found to be in better condition than any previously examined. Single crystal blade technology is a key element in Rolls-Royce's strategy for the future. The single crystal casting business in that decade will be worth a potential £l billion, with 70 per cent of sales achieved overseas.

In CVD process, until today, the deposition rate has risen further as a result of the increasing power and gas flow, without a physical limitation. The only known limitation is the increase to the atmosphere pressure. Hence the growth rate is technically limited by the energy supply, which also limits the temperature and the maximum gas flow. Finally, there have to be more investigation on the technical and physical growth rate in the future.

The global rough diamonds market is expected to witness a huge demand-supply gap in future due to the low supply of mined diamonds which take hundreds of years to form. Synthetic diamonds on the other hand can be produced within ~200 hours and cost ~30% lesser than natural diamonds. India can explore this new market for synthetic diamonds by developing manufacturing facilities to support the growing demand for rough diamonds.

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