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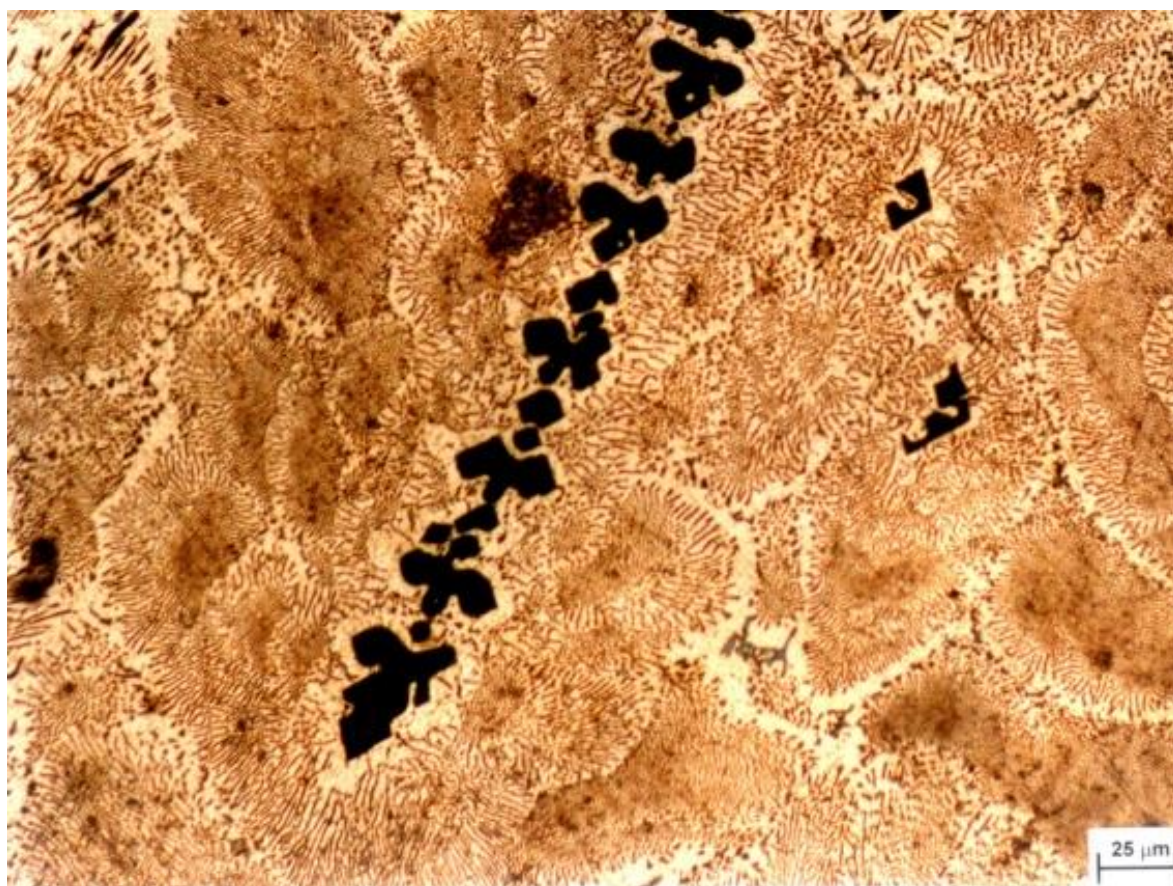
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Editors: Dr. T.P.D. Rajan, Mr. M. Agilan, Dr. M. Sundararajan



“Intermetallic Orchid”

Micrograph of Al–Al₃Ni in situ functionally graded composite processed by centrifugal casting showing Al₃Ni intermetallic phase dispersed in the form of an orchid in aluminum alloy matrix

Editors desk

The editorial committee has great pleasure in informing to its members and readers that the METNEWS is marching successfully into thirty sixth year of its publication. In the present issue we could bring you some special articles on Si-Ge materials for thermoelectric devices, welding and joining of space components, metal oxides for supercapattery and smart anticorrosive coatings. We are grateful to all the contributing authors. We also request the members and readers to contribute articles in their areas of research and expertise. The 3rd International Conference on Advanced Materials and Manufacturing Process (ICAMPS-2018) will be organized by the Indian Institute of Metals, Trivandrum Chapter during October 25-27, 2018. We wish the event a grand success.

Development of Si-Ge materials for Thermoelectric Devices through Mechanical Alloying

S. Steaphen, Dr. A.K. Shukla

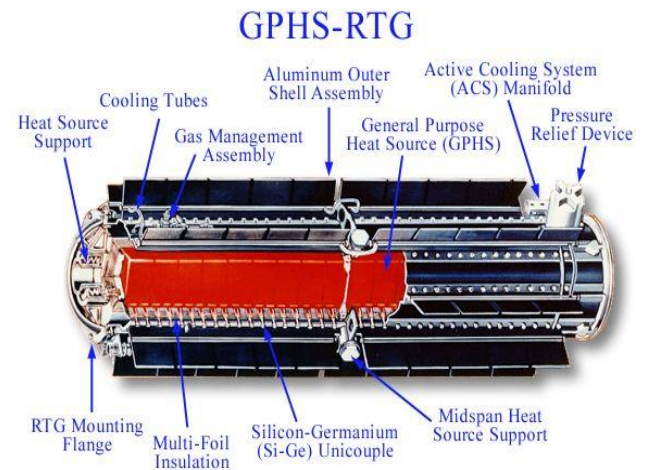
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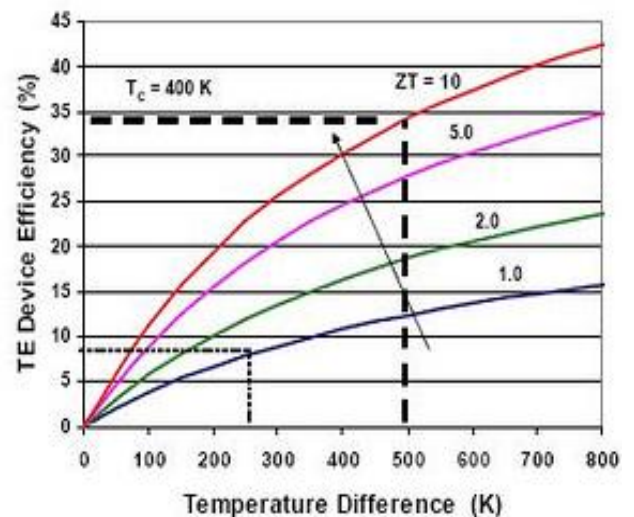
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Thermoelectric devices convert thermal energy into electrical energy using thermoelectric effect (Seebeck effect). Radioisotope Thermoelectric Generator (RTG) uses radio-isotopic decay as source of thermal energy. The efficiency of such devices is directly dependent on the dimensionless figure of merit: $ZT = (S^2 \sigma / k) T$, where S-Seebeck coefficient, σ -electrical conductivity, k-thermal conductivity and T-absolute temperature. Si-Ge thermoelectric alloys have been used in RTG for last few years, for their high efficiency in the operating conditions.

$Si_{80}Ge_{20}$ alloy is generally manufactured by powder metallurgical technique. Mechanical alloying is a process where elemental powders are subjected to high energetic compressive impact forces resulting in formation of composite powder. $Si_{80}Ge_{20}$ alloy powders are prepared by mechanical alloying followed by powder consolidation using hot pressing or spark plasma sintering. Both, Si and Ge powders were kept in a vial and placed inside a planetary ball mill. The grinding media and Ball to Powder Ratio (BPR) were varied while keeping the RPM constant. The milling was carried out using SS & WC balls in the respective SS & WC vials. Samples were collected at different time periods and XRD analysis was carried to study the extent of mechanical alloying.



(a)



(b)

Figure 1: (a) Typical Radioisotope thermoelectric generator [1] (b) Efficiency Vs Temperature difference plot for thermoelectric devices [2]

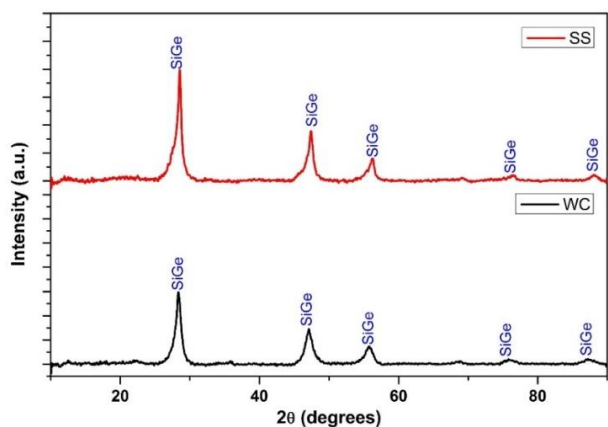


Figure 2: XRD pattern of $\text{Si}_{80}\text{Ge}_{20}$ after 10hrs. of milling time

The $\text{Si}_{80}\text{Ge}_{20}$ got mechanically alloyed after **10 hours in both cases without any impurities** in milled powder.

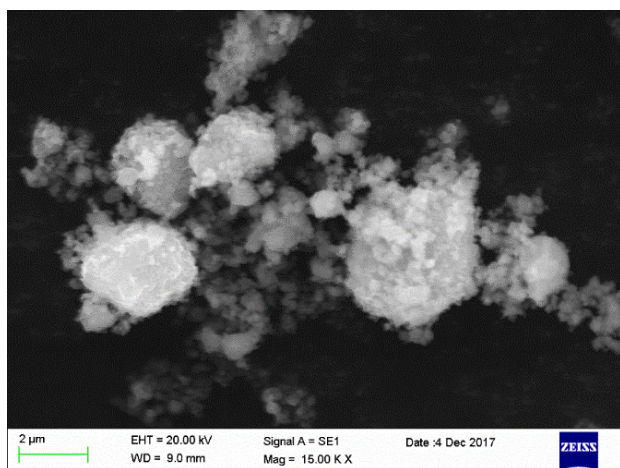


Figure 3: SEM micrograph (Mag.15 KX) of mechanically alloyed $\text{Si}_{80}\text{Ge}_{20}$ powder

These materials can be used in satellite applications, space probes, unmanned remote facilities, power source for robotic situations, places where solar cells are not practical etc.

References

1. <http://solarsystem.nasa.gov/rps/rtg.cfm>
2. <http://solarsystem.nasa.gov/rps/rtg.cfm>

IIM Trivandrum Chapter Awards

Prof. Brahm Prakash Best Thesis Award for the year 2015 of the IIM, Trivandrum Chapter was conferred during the Chapter day celebration on Feb. 3, 2018.

The Prof. Brahm Prakash Best Ph.D. Thesis Award of the IIM, Trivandrum Chapter was conferred to **Dr. Sankar Sasidharan** CSIR-NIIST, Trivandrum for the Ph.D. thesis entitled **“Sol-Gel Lanthanum Phosphate Composites and Coatings for Functional Applications”**. The Ph.D. degree was awarded by the Cochin University of Science and Technology, Cochin. Supervisors are Dr. KGK Warriar and Dr. S. Ananthakumar, CSIR-NIIST, Trivandrum.

The Prof. Brahm Prakash Best Post Graduate Degree Thesis Award of the IIM, Trivandrum Chapter was shared by two members: 1. **Mr. Jithu Jayaraj**, CSIR-NIIST, Trivandrum for the M.E. thesis entitled **“Chemical Conversion Coatings of Lanthanum Phosphate on Magnesium Alloys”**. The M.E. degree was awarded by the National Institute of Technology, Surathkal. Supervisors are Dr A. Srinivasan and Dr. UTS Pillai CSIR-NIIST, Trivandrum. 2. **Mr. Joby V Thomas**, LPSC-VSSC, Trivandrum for the M.E. thesis entitled **“Feasibility Studies on 15-5 PH Stainless Steel as an Alternative Material for Vikas Engine Components”**. The M.E. degree was awarded by Indian Institute of Space Science and Technology, Trivandrum.

Welding and Joining of Space Components

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Abstract

Launch vehicle and spacecraft components demand for highest quality and reliable joints. Also, there are many material combinations that cannot be joined by conventional fusion welding techniques. Wrong choice of welding technique and compromise in quality can result in catastrophic failure. This makes joining of components for space application highly challenging. Also, exotic and difficult to weld materials, dissimilar metal joints, metal-ceramic joints and inaccessible joints add to the complexity. Size of the parts to be jointed varies from few microns to meters. Gas tungsten arc welding (GTAW), electron beam welding (EBW) and friction stir welding (FSW) are major welding processes play significant role in fabrication of launch vehicle structures. Specialised solid state processes such as explosive bonding, diffusion bonding and friction welding are being used to produce critical bi-metallic and non-accessible joints. Further, vacuum brazing is also playing an important role for joining intricate, inaccessible and dissimilar joints in rocket engine and spacecraft components. Selection of process for specific application is made based on various aspects such as weldability of materials, mechanical property requirement, quality of the joint, size/ configuration/ material characteristics of the components to be joined etc. This paper provides an overview of the range of joining processes being applied for Indian space program and highlights the challenges faced.

Keywords: welding in space industry, fusion welding, solid state welding, dissimilar joints

1. INTRODUCTION

Joining of materials is an important and integral part of manufacturing activity for space industries which avoids riveting and fastening to improve structural integrity. Welding can be broadly classified into fusion welding and solid state welding. In a space program, there is requirement to join a range of material combinations. For many components, conventional fusion welding is not possible owing to the material combination/accessibility of the joint involved. Various welding and joining methods employed in space application, the selection of process is based on materials to be joined, properties required, joint configuration, service temperature and service environment. Structures and components used in launch vehicle and spacecraft demand for superior quality and high reliability. Any compromise in quality may lead to catastrophic failure, huge economic loss and at times fatality. The following are major welding and joining process used for manufacturing components for space applications.

- ❖ Fusion welding processes
 - Gas tungsten arc welding
 - Electron beam welding
 - Laser welding
 - Variable polarity plasma arc welding
- ❖ Solid state welding processes
 - Friction stir welding
 - Linear friction welding
 - Explosive bonding
 - Diffusion bonding
- ❖ Vacuum brazing

In the present review paper, the joining processes being utilized for space components are briefly described with associated challenges.

2. FUSION WELDING PROCESSES

2.1 GAS TUNGSTEN ARC WELDING (GTAW) (Maraging steel/Al alloy and SS/ Superalloys)

Gas tungsten arc welding (GTAW) is a major welding process to being utilized to realize launch vehicle structure and components. More than 80% of the space structures are being welded by GTAW. Although GTAW has limitations like less productivity and high production cost, this process stands superior in quality than conventional processes like shielded metal arc welding (SMAW) and gas metal arc welding (GMAW).

In ISRO's launch vehicles, solid motor cases made of maraging steel are fabricated by GTAW process. Various structures are being welded in multiple passes using a specially developed filler wire, as use of parent metal filler wire results in low fracture toughness in the weld. Segregation of major alloying elements like Ni, Ti and Mo produces austenite pool in the weld, leading to lower toughness. This issue has been addressed by developing a new filler wire controlled Co and Al/ Mo and Ti combinations.

Liquid propellant tanks and cryogenic propellant tanks of launch vehicles are made of AA2219 alloy and welded by GTAW process. Hot cracking and porosities formation are major concerns in welding of aluminum alloys. Hot cracking in welds are influenced by various factors such as weld metal composition, amount and distribution of eutectic constituents, weld metal grain size, etc. Higher Cu Containing filler wire is developed to prevent hot cracking in AA2219. It produces more amount of eutectic and acts as reservoir to fill the cracks during welding. Also, grain refiners like Ti and Zr are added to prevent hot cracking.

In rocket engine, parts of subsystems such as turbo pump, gas generator, thrust chamber and control components are welded by GTAW. These

components are made of various stainless steels and superalloys. GTA welding of similar and dissimilar materials joining are carried out. Also, engine integration and assemblies are done by GTAW.

Inconel 718 is a nickel based superalloy used in various parts of engines and hot structures. Weldability issues like microfissuring, laves phase formation are important concerns in welding of Inconel 718 which affect the mechanical properties and joint integrity. These problems are controlled by heat input and welding process modification.

In addition to regular welding of components, GTAW process is used for repair welding of castings. Stainless steel and superalloy cast components are widely used in cryogenic and semi-cryogenic engine. Major casting defects which are removed by GTAW are shrinkage defects, gas porosities, inclusions, cold shut and cracks.

2.2 ELECTRON BEAM WELDING (EBW) (Ti alloys, Superalloy, and Columbium alloy)

Electron beam welding is high energy beam welding process which produces highest quality and deep narrow welds with small HAZ. Heat input of EBW is about ten times lesser than GTAW. In space applications, EBW is suitable to weld highly reactive materials like titanium, refractory materials like niobium and materials which are difficult to weld like copper. EBW can produce welds with 100% weld efficiency.

Launch vehicle and satellite propellant tanks, high pressure gas bottles are of titanium alloys (Ti-6Al-4V, Ti-5Al-2.5Sn etc) are being welded by EBW. Titanium is a material of interest at upper stages of rockets due to less density, high strength and chemical compatibility with fuel.

Oxygen storage containers for human space programme can be made of Inconel-718 superalloy. EBW is chosen because of high weld efficiency, repeatability, and high quality welds. However, microfissuring and spatter are main

issues in EB welding of Inconel 718. Spatter is not allowed in this application as the spatter may have the tendency to ignite and inhalation of loose metal particles may be life threatening for crew.

Satellite engine thrusters of columbium refractory alloy (C-103) and bimetallic joints of columbium to titanium are welded by EBW. Dissimilar metal joints of Copper to Nickel are welded for cryogenic engine thrust chamber. Various dimension critical and distortion-less components are welded by EBW. Eg: propellant acquisition system (PAS) parts made of aluminum alloy, structures made of Inconel 718 for air breathing propulsion rockets.

2.3 LASER BEAM WELDING (LBW) (Al alloy and SS to Nichrome)

Laser beam welding (LBW) is another high energy beam process which uses high power density light to weld the parts. Unlike EBW, LBW is operated in air or argon atmosphere. Due to low heat input, laser welding is used to join very small parts of millimeter and micron size. LBW ensures least damage to the adjacent parts of weld.

Battery cell cases are made of aluminum alloy AA3003, LBW is used to weld 1 mm thick cell cases to lid and lid to terminal seals. LBW is selected as joining process to avoid heat damage on polymer separator which is located very close to weld joint.

In cryogenic engine initiators, dissimilar joint between 1 mm stainless steel and 80 micron Nichrome wire is welded by LBW process. LBW is an only welding process to join such miniature parts.

2.4. VARIABLE POLARITY PLASMA ARC WELDING (VPPAW) (Al alloys)

Variable Polarity Plasma arc welding (VPPAW) is an advancement of plasma welding process, used to weld thick sections of aluminum alloys in space application. It is a direct current plasma arc

welding process operated with change in polarity, to produce high quality and deep penetration weld. The basic difference between alternate current (AC) and variable polarity is the wave form shape. In variable polarity the ratio of polarities can be varied independent control of current amplitude and duration.

VPPAW has many advantages over GTAW like 100% joint penetration, better quality welds, less joint preparation, reduction in number of weld passes (Single pass up to 12.7 mm for aluminum) and significantly lesser distortion.

3. SOLID STATE WELDING PROCESSES

3.1 (a) FRICTION STIR WELDING (FSW) (Al-Li alloy)

Friction stir welding (FSW) is a solid state joining process where a non-consumable rotating tool is inserted into the joining edges of sheets/ plates and traversed along the line of joint. Heat is generated by friction between tool and work-piece and the plastic deformation of the work piece. The tool performs three major roles, i.e., heating the work piece, stirs the material around the pin and pushes to the back leading edge, restrict the material underneath the tool shoulder.

FSW was originally developed for welding of aluminum alloys since fusion welding produces weldability issues like hot cracking, porosities in welds, weakening of HAZ etc. In FSW, aforesaid defects are eliminated and high weld efficiency joints are produced. In space industries, FSW is currently used for welding propellant tanks made of AA2219 and AA2195 alloys. Adoption of FSW technology can reduce the weld repair significantly and increases the productivity.

FSW technology has been extended to welding of various metallic materials like stainless steels, superalloys and titanium alloys.

3.1 (b) FRICTION WELDING (FW) (Ti alloy-SS)

Similar and dissimilar tubular joints are realized by friction welding process. In this process, joint

is achieved by frictional heat combined with pressure. The friction is induced by mechanical rubbing between the two surfaces, by rotation of one-part relative to the other. It is a rapid and economic process. In launch vehicles, transition joints between titanium propellant tank and stainless steel plumbing lines and seamless joining of turbine blade are made by this process.

3.2 EXPLOSIVE BONDING/WELDING (EXW) (Al alloy to SS)

In explosive bonding, joining occurs due to high velocity impact of the work piece as result of controlled detonation. The explosion accelerates the metal to a very high speed & high stress (>10 times yield strength) leading to jet formation and bonding. EXW produces sound metallurgical bonding with mechanical interlocking.

In space applications, stainless steel to aluminum alloy bimetallic adaptor is made by explosive bonding technique. These adaptors connect propellant tank (Aluminum alloy) and plumbing lines (Stainless steel). Joining of stainless steel to aluminum alloy is not possible by conventional fusion welding process or diffusion bonding. This is due to wide difference in melting point and physical properties of stainless steel and aluminum.

Magnetic pulse welding (MPW) is another process which can produce stainless steel to aluminum joints. In both EXW and MPW, joining mechanism is similar with difference in source of energy.

3.4 DIFFUSION BONDING (DB) (Ti alloy-Ti alloy and Ti alloy to SS)

In diffusion bonding, joint produces a weld by application of pressure at elevated temperature with or without macroscopic deformation or relative motion of the work pieces. The primary mechanism of joining is solid-state diffusion involving atomic movement across the interface. DB is suitable to join dissimilar materials, reactive materials (eg: Titanium, Beryllium) and metal matrix composites. In DB, Joints can be

produced with properties and microstructures very similar to base metal.

In launch vehicle, turbo pump impeller is made of titanium (Ti5Al2.5Sn) alloy which has intricate shapes and inaccessible joints. Diffusion bonding is adopted to realize the component. Transition joint between stainless steel to titanium is also made by this process.

3.5 ULTRASONIC WELDING (USW) (Cu to Al)

In Ultrasonic welding (USW,) oscillatory shear stresses of ultrasonic frequency are applied to the interface to produce sound joint. Oscillatory motion breaks down any surface films to allow intimate contact and strong metallurgical bonding between surfaces.

In advanced batteries, 20 micron foils of copper and aluminum are stacked together and welded by USW. Further, it is welded with tab of batteries.

4. VACUUM BRAZING

Vacuum brazing is one of the most important joining techniques for space application which joins dissimilar metals and intricate shapes that cannot be joined by conventional processes. In vacuum brazing, base metals do not melt but filler metal melts and wets the surface of base metal, thereby sound joints are produced. Capillary action and wetting of filler metal are important phenomenon in brazing. Vacuum brazing possesses several advantages over fusion welding process like joining of inaccessible areas, many joints can be made in single operation, less distortion and precision dimensional tolerance, minimum residual stresses etc. This process has ability to join dissimilar metals, ceramic to metals, different thicknesses, porous metal components etc without destroying the metallurgical characteristic of base metal.

In cryogenic engine and semi-cryogenic engine, vacuum brazing plays a critical role in functioning of various parts such as turbo pump, combustion chamber, gas generator, injector head and igniters. Dissimilar joints between copper to

stainless steel, stainless steel to superalloys and similar material joints of stainless steels, superalloys and titanium alloys are made.

A typical example for the importance of vacuum brazing in cryogenic engine is brazing of thrust chamber. Thrust chamber is made of inner shell (high conductivity copper) and outer shell (stainless steel AISI 321). Inner shell contains channel milled ribs through which coolant passes through. Specialized rotary vacuum brazing is carried out to join ribs and inner surface of outer shell.

In reusable launch vehicles, hot structures of Inconel 718 and Inconel 617 panels are brazed with superalloy braze foils.

In satellite applications, thrusters and pressure transducers made of stainless steel is brazed using Au-Ni braze alloy

Metal-ceramic joints in critical parts of launch vehicles and satellites are done by vacuum brazing. Brazing of ceramics especially alumina is quite complex as compared to metals, since the wettability of alumina is poor due to covalent bonding. The joints require hermetic sealing and leak tightness of 10^{-8} m.bar-lit/s or better. Few applications are listed below

Kovar to alumina joint in travelling wave tube (TWT) of communication satellites. Since the parts are tiny (about 100 microns to 5 mm), handling, positioning, fixturing are very difficult during brazing

In advanced batteries, terminal seals are realized by vacuum brazing technique. In negative terminal, joint is made between OFHC copper to Alumina. In positive terminal joint is made between Aluminum AA3003 alloy to Alumina. Brazing of aluminium is not easy as other metals since it has inherent tenacious oxide layer. Oxide layer restricts the wetting of braze alloy over metallic surface. This issue is addressed by use of magnesium metal inside the furnace chamber during vacuum brazing. At brazing temperature and vacuum level, Mg vaporizes and catches the

oxygen present in aluminium surface. Thus, surface of aluminium is cleaned and wettability is improved. Kovar to Alumina ceramic joint in electric propulsion system utilizes Ti-Cu-Sil braze alloy.

In outer space, solar panels in satellites are deployed using thermal cutters. These cutters have Kovar to Alumina ceramic joints, the alumina gets heated up and aids the deployment mechanism.

5. CONCLUSIONS

From conventional fusion welding to highly specialized solid state joining processes are being utilized in space applications due to wide range of materials and functional criticality. Challenges encountered in joining of various space components are presented in this paper. Highest quality and leak tightness in welds are achieved to perform in extreme environments.

6. REFERENCES

[1] AWS Welding Handbook, American Welding Society, Volume 1 to 5, Edition 9, Miami, USA
[2] M.C.Chaturvedi, Welding and Joining of Aerospace Materials, Woodhead Publishing, 2011

Metal Oxides for Supercapattery- An Emerging Electrochemical Energy Storage Technology

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The rising power and energy demand in applications ranging from ubiquitous portable electronics to hybrid electric vehicles to power grid point up the need for developing new electrode materials for rechargeable batteries and/or supercapacitors. However, the charge storage of rechargeable lithium batteries mainly depends on the ion intercalation/de-intercalation within the crystalline structure of electrode materials, and therefore controlled by the diffusion of ions within the crystalline framework, which significantly limits the charge-discharge rate (i.e., power density) of batteries. On the other hand, supercapacitors can deliver much higher power density than batteries as their charge storage is based on surface reactions of electrode materials, without ion diffusion within the bulk of materials. Even though Li-ion batteries are desired for various practical applications, it is apparent that supercapacitors can complement or replace batteries because of their ability to store and release energy at a high rate (in seconds) with a high power density and long cycle life.^{1,2} Supercapacitors are one of the crucial power devices as they have potential applications in regenerative braking, frequency regulation in smart grids and storing the alternating energy profiles of renewable energy sources. But, it should be noted that the limitation of charge storage to the surface (or near surface) of supercapacitors makes their energy density much lesser than that of batteries. This situation urge ground-breaking changes in the design and development of materials for electrochemical energy storage technologies, leading to the smart integration of rechargeable battery and

supercapacitor characteristics into one device, namely *supercapattery* whose behavior is more like a supercapacitor in power capability and cycle life and like a battery in energy density.³

Based on the principle of energy storage, supercapacitors can be categorized into electric double layer capacitors (EDLCs) and pseudocapacitors. EDLCs store charges using the thin electric double layer structure formed at the electrode-electrolyte interface through reversible ion adsorption-desorption process, which consist of carbon electrodes. While, pseudocapacitors with transition metal oxide or conducting polymer electrodes use fast and reversible faradaic redox reactions, and display much higher specific capacitance than EDLCs. Pseudocapacitance can be accomplished through several faradaic mechanisms: (1) under potential deposition (UPD), (2) redox pseudocapacitance and (3) intercalation pseudocapacitance. These processes are demonstrated in fig.1. UPD involves the faradaic absorption/desorption of metal ions on the surface of a different metal to form an adsorbed monolayer above their redox potential. Redox pseudocapacitance occurs when ions electrochemically adsorb on the surface/near surface of electrode material along with faradaic charge transfer process. Intercalation pseudocapacitance arises when ions intercalate into the tunnel/layer structure of a redox active material accompanied by a faradaic charge-transfer without any crystallographic phase change.^{1,4}

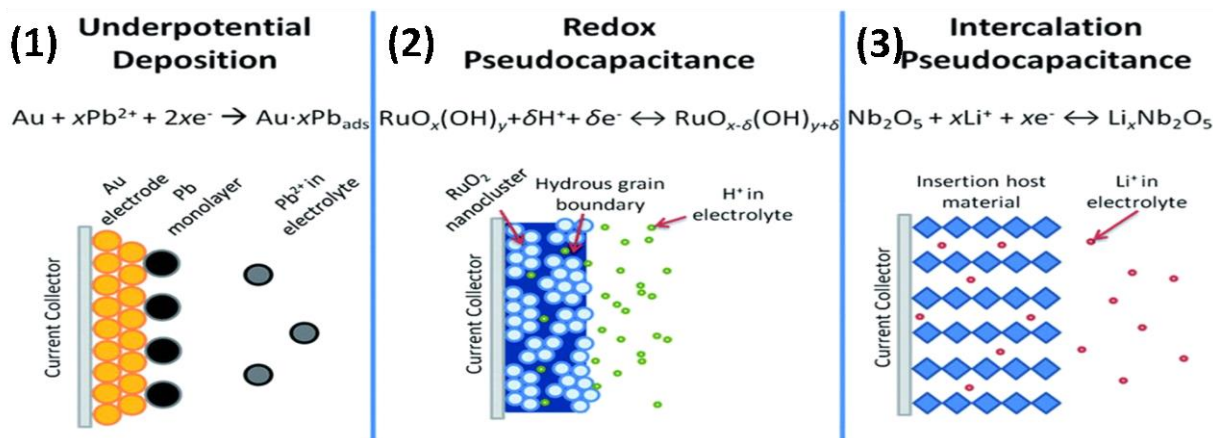


Fig. 1: Different types of pseudocapacitive mechanisms.¹

Electrode materials are considered as the vital soul of the energy storage devices, which play a crucial role in determining device performance. It is widely identified that the energy density of a supercapacitor relies upon both the specific capacitance of the electrode materials and the cell voltage, i.e., electrode kinetics of the charging and discharging processes. Electrode kinetics studies concentrate the transfer of charges (electrons and/or ions) at the interface between the electrode and electrolyte. Manipulation of charge transfer kinetics can be accomplished by selecting suitable electrode materials. Subsequently, controlling the architecture and interfacial property of electrode materials is inevitable to improve the capacitive performances.^{3,5}

This article intends to offer an overview of various materials explored for pseudocapacitance through Li^+ intercalation mechanism. Transition metal oxides with layered/tunnel crystalline structures are the most investigated group of pseudocapacitive materials owing to their intrinsic ability to intercalate/de-intercalate Li^+ ions in a wide range of lattice sites. This mechanism has the ability to surmount the slow Li^+ solid-state diffusion limited battery kinetics with the surface controlled processes. However, Li^+ storage through intercalation pseudocapacitance is hardly inspected in most metal oxides. To date,

only a few transition metal oxides are reported to exhibit this pseudocapacitive behaviour. Dunn *et al.* demonstrated Li^+ insertion into microfibrillar TiO_2 crystalline framework governed by a pseudocapacitive faradaic process. This extraordinary behaviour of TiO_2 was discussed in terms of their crystal structure which possesses numerous freely accessible parallel channels for Li^+ transport, perpendicular to the (010) plane.⁶ The layered $\text{H}_2\text{Ti}_6\text{O}_{13}$ nanowires were investigated by Xia *et al.*, and exhibited pseudocapacitive characteristics of Li^+ storage because of the nanosize and expanded interlayer space.⁷ Dunn *et al.* reported orthorhombic Nb_2O_5 (T- Nb_2O_5) with Li^+ accessible (001) plane for pseudocapacitive Li^+ storage. T- Nb_2O_5 is identified as a material possessing intrinsic intercalation pseudocapacitance.⁸ Brezesinski *et al.* observed Li^+ intercalation pseudocapacitance in $\alpha\text{-MoO}_3$ benefited from its mesoporous morphology, iso-oriented crystalline domains and alternately stacked layers held together by weak van der Waals forces along (010).⁹

Among a variety of intercalation host materials for rechargeable Li^+ ion battery, layered, spinel and inverse spinel type structures received a special interest. The presence of three dimensional Li^+ diffusion pathways associated with a low energy barrier in spinel or inverse spinel type crystalline frameworks render them

fast Li^+ transfer kinetics. The nanoscale architecture of materials further improves the pseudocapacitance contribution by providing increased accessible surface area towards the electrolytes. To be precise, nanosized materials are capable of accommodating Li^+ with extended solid-solution limits. The spinel/inverse spinel crystal structure offer reversible Li^+ intercalation/de-intercalation reaction on the surface and bulk crystalline framework of the material and nanoscale architecture present a minor amount of electrical double layer formation, thus high energy and power densities can be expected in the same material.

In particular, lithium transition metal oxides got significant consideration as electrode materials for capacitive Li^+ storage due to their intrinsic Li^+ intercalation/extraction ability. Detailed examination of those materials indicate that an element having a low oxidation state plays foremost role in the generation of pseudocapacitance, while an element having a high oxidation state has an insignificant influence on pseudocapacitance. So far, only a few lithium transition metal oxides are reported to exhibit capacitive Li^+ storage. Chen *et al.* reported nanoscale spinel LiFeTiO_4 for intercalation Li^+ storage with partial $\text{Fe}^{3+}/\text{Fe}^{2+}$ oxidation in the tunnel structure with minor lattice changes.¹⁰ Recently our group prepared nanocrystalline inverse spinel LiMVO_4 (M = Ni, Co), and investigated their Li^+ storage behaviour in aqueous electrolyte. LiMVO_4 possess a cubic crystal structure in which Li^+ and M^{2+} ions equally exist in the octahedral sites and V^{5+} ions reside in the tetrahedral sites. The Li^+ ions present in the octahedral site take part in the intercalation/de-intercalation process with negligible crystallographic phase change. In particular, nanocrystalline LiMVO_4 displayed better Li^+ intercalation property benefited from its small crystallite size and open Li^+ selective crystallographic channels towards electrolyte.¹¹

Subsequently, supercapattery (hybrid capacitors) were developed as attractive high energy devices combining the battery-type intercalation transition metal electrode with an

EDLC type carbon electrode. The positive electrode offers the required power density depending on the reversible non faradaic charge storage mechanism. The negative electrode undergoes a faradaic Li^+ insertion/extraction reaction. As a result, hybrid capacitors typically exhibit energy densities larger than that of EDLCs, and power densities comparable with lithium ion batteries. In addition, hybrid capacitors with transition metal oxide negative electrode exhibit excellent cycling stability owing to the intercalation behaviour without any crystallographic phase change. Thereby, integration of energy and power requirements in the same material offer a guaranteed move towards advanced energy storage technologies for both industrial as well as consumer applications.

References

1. Augustyn, V.; Simon, P.; Dunn, B. Pseudocapacitive Oxide Materials for High-rate Electrochemical Energy Storage. *Energy Environ. Sci.* **2014**, *7*, 1597.
2. Wang, G.; Zhang, L.; Zhang, J. A Review of Electrode Materials for Electrochemical Supercapacitors. *Chem. Soc. Rev.* **2012**, *41*, 797–828.
3. Wu, Z.; Li, L.; Yan, J.; Zhang, Z. Materials Design and System Construction for Conventional and New-Concept Supercapacitors. *Adv. Sci.* **2017**, *4*, 1600382.
4. Wang, Y.; Song, Y.; Xia, Y. Electrochemical Capacitors: Mechanism, Materials, Systems, Characterization and Applications. *Chem. Soc. Rev.* **2016**, *45*, 5925–5950.
5. Sun, J.; Wu, C.; Sun, X.; Hu, H.; Zhi, C.; Hou, L.; Yuan, C. Recent Progresses in High-Energy-Density all Pseudocapacitive-Electrode-Materials Based Asymmetric Supercapacitors, *J. Mater. Chem. A* **2017**, *5*, 9443-9464.
6. Brezesinski, T.; Wang, J.; Tolbert, S. H.; Dunn, B. Next Generation Pseudocapacitor Materials from Sol-Gel Derived Transition

- Metal Oxides. *J. Sol-Gel Sci. Technol.* **2011**, 57, 330–335.
7. Wang, Y.; Hong, Z.; Wei, M.; Xia, Y. Layered $H_2Ti_6O_{13}$ -Nanowires: A New Promising Pseudocapacitive Material in Non-Aqueous Electrolyte. *Adv. Funct. Mater.* **2012**, 22, 5185–5193.
 8. Kim, J. W.; Augustyn, V.; Dunn, B. The Effect of Crystallinity on the Rapid Pseudocapacitive Response of Nb_2O_5 . *Adv. Energy Mater.* **2012**, 2, 141–148.
 9. Brezesinski, T.; Wang, J.; Tolbert, S. H.; Dunn, B. Ordered Mesoporous α - MoO_3 with Iso-Oriented Nanocrystalline Walls for Thin-Film Pseudocapacitors. *Nat. Mater.* **2010**, 9, 146–151.
 10. Chen, R.; Knapp, M.; Yavuz, M.; Ren, S.; Witte, R.; Heinzmann, R.; Hahn, H.; Ehrenberg, H.; Indris, S. Nanoscale Spinel $LiFeTiO_4$ for Intercalation Pseudocapacitive Li^+ Storage. *Phys. Chem. Chem. Phys.* **2015**, 17, 1482–1488.
 11. Hareendrakrishnakumar, H.; Chulliyote, R.; Joseph, M. G. Effect of Crystallite Size on the Intercalation Pseudocapacitance of Lithium Nickel Vanadate in Aqueous Electrolyte. *J. Solid State Electrochem.* **2017**, 22, 1–9.

New Members

We have great pleasure in welcoming the following members to our Chapter...

Life Members

- Dr. Subrata Das, CSIR-NIIST
- Dr. J. Mary Gladis, IIST
- Mr. T.T. Saravanan, VSSC
- Mr. Paul Murugan, VSSC
- Mrs. Aishwarya, VSSC
- Dr. V.M. Sreekumar, RSET, Kochi

Associate Members

- Mr. R.G. Rejith, CSIR-NIIST
- Ms. P. Suja, CSIR-NIIST
- Ms. P. Anju, CSIR-NIIST

The Executive Committee of The Indian Institute of Metals, Trivandrum Chapter.

Chairman	-	Dr. K. Harikrishna Bhat Chief Scientist, MSTD, CSIR-NIIST, Trivandrum
Vice Chairman	-	Dr. S.V.S. Narayana Murty Scientist MCD, VSSC, Trivandrum
Hon. Secretary	-	Dr. A. Srinivasan Senior Scientist, MSTD, CSIR-NIIST, Trivandrum
Hon. Joint Secretary	-	Shri. S. Dinesh Raj Scientist, VSSC, Trivandrum
Hon. Treasurer	-	Dr. K. Jayasankar Sr. Scientist, MSTD, CSIR-NIIST, Trivandrum

Executive Committee Members:

1. Dr. P. Ramesh Narayanan
2. Dr. T.P. D. Rajan
3. Dr. U.S. Hareesh
4. Dr. M. Sundararajan
5. Mr. Sushant K Manwatkar
6. Mr. M. Agilan

Smart Anti-corrosive Coatings

Sarah B. Ulaeto, Jerin K. Pancreicious, P. Suja, T.P.D. Rajan and B. C. Pai

Materials Science and Technology Division,

CSIR-National Institute for Interdisciplinary Science and Technology,

Trivandrum, Kerala, India

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Anti-corrosive coatings are barrier coatings utilized in various environments which include continuous immersion in water, buried in soils, exposed in industrial areas and faced with ultraviolet radiation, air polluted environments, and hot corrosive liquids depending on its functionality. Precisely, coatings in industrial areas are constantly exposed to chemicals and acid rain while coatings on soil buried structures or in water bodies encounter foulant, micro-organisms, and humidity. The categories of coatings in regular use are metallic, inorganic, organic and hybrid coatings consisting of several layers such as pre-treatment, primer, and topcoat etc. However, failure is inevitable if inappropriately formulated and coated on the substrate of choice. Coatings primarily provide barrier protection to materials amongst other functions based on its formulation and unavoidably experience several atmospheric elements, wide temperature ranges, and even electromagnetic radiations. These eventually degrade coating matrices of industrial facilities and products on exposure giving rise to initially unseen micro cracks which degenerate with time into actual fractures which can be seen and subsequent coating failure. Severe corrosion reactions occur on the metallic substrate and cost-intensive damages are incurred. Good coatings should be cost-effective alongside low moisture penetration, impact resistance, durability, chemical resistance, good substrate adhesion, defect-free surface morphology, eco-friendly, flexible and easy to apply. For corrosion protection of the metal substrate, utilization of corrosion inhibitors that can provide a resistive film on the substrate during application is required as well as a coating that can provide an impermeable barrier to moisture and corrosive species.

Smart coatings are seen as coatings of value in the coatings industry. Loaded with inhibitors alongside other additives and modifiers, they reflect the advancements in corrosion inhibition of metallic materials. Smart coatings can be multifunctional in their response to corrosion triggers. Smart coatings with corrosion sensing, self-healing, anti-fouling, superhydrophobic and self-cleaning functionalities have contributed to corrosion protection of metals and alloys. These chemically active smart coatings can be functional either on film-substrate interfaces, air-film interfaces or within the bulk of the film. Smart anticorrosive coatings provide feedback responses during corrosion processes, depending on their formulation, which enhances durability. Aggressive changes caused as a result of pH changes, temperature, pressure, surface tension, ionic strength, electrical or magnetic fields, acoustics, light, mechanical forces including abrasions etc. resulting in certain photochemical, acid-base, complexation, bond formation/ breakage, electrochemical reactions etc. are triggers for the responses exhibited by smart coatings.

Corrosion sensing coatings contain dyes and/or compounds within the film matrix that fluoresce or change color due to oxidation reactions at high pH values, other pH sensitive reactions or formation of complexes with metal cations during possible mechanical damage. Self-healing coatings are formulated to ensure that the polymer matrix is constructively repaired after damage occurs to deter the onset of corrosion and maintain its mechanical properties. The evolution of an ideal damage-repair cycle in polymeric materials is illustrated in Figure 1. When a mechanical damage occurs, the cleavage of macromolecular chains in the polymer matrix

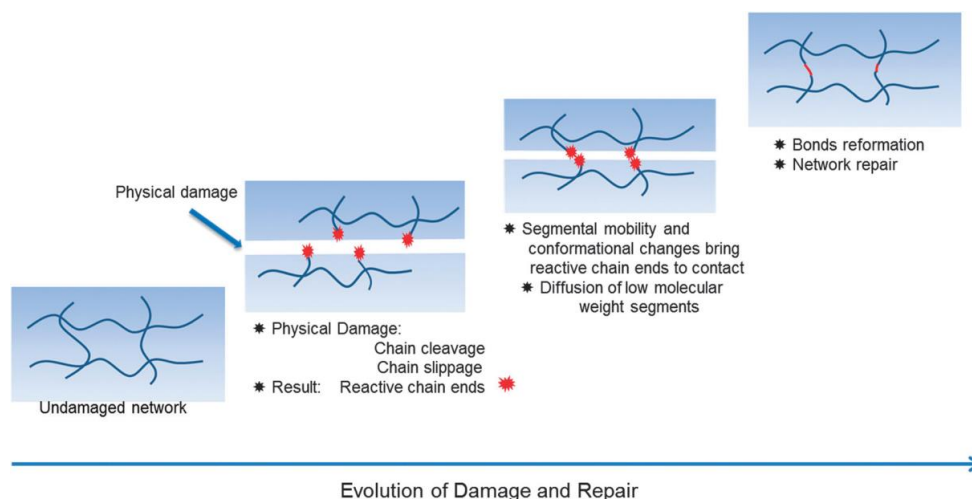


Figure 1. The illustrative evolution of an ideal damage-repair cycle in polymeric materials [Yang and Urban 2013].

leads to the formation of reactive end groups which may be free radicals or functional groups consisting of heteroatoms, double bonds etc. and when in contact with each other bond reformation and physical network repair occurs.

For the purpose of industrialization, the “passive hosts and active guests” is generally acceptable and appears to be the most promising formulation strategy in use. The active guests are usually encapsulated and embedded within the matrix with the main tasks of detecting defects and self-healing automatically. While the passive barrier coating prevents aggressive species from reaching the surface of underlying substrates. Figure 2 (A & B) is an epoxy coating containing a polymeric nanocontainer loaded with benzotriazole for corrosion protection on steel surfaces via self-healing process. In response to the aggressive environment Figure 2C illustrates the electrochemical reactions during the corrosion induced inhibitor release from the pH-responsive nanocontainers leading to a new protective layer on steel surface [Li et al. 2014].

Anti-fouling coatings are based on biocide-release and the non-biocide-release antifouling coatings. These coatings are especially relevant for Microbial Influenced Corrosion (MIC) of metals and alloys in water bodies where marine

organisms form colonies on surfaces of vessels and equipment in the water bodies. The colonies give rise to biological growth attached to the surface of the coatings and result in increased weight on the coatings, loss of hydrodynamic properties in addition to loss of machine efficiency. The ensuing effect includes decreased speed and maneuverability, rapid fuel consumption, cross-contamination of bio-entities, and eventual damage to coatings on ocean/sea vessels and ships. While the corrosion protection displayed by self-cleaning and superhydrophobic coatings is due to surface contact angles of liquid drops. The self-cleaning action of hydrophobic or superhydrophobic coatings leaves the surface dry and clean. Self-cleaning coatings can also be hydrophilic with lower surface contact angles of liquid drops thus wettability is high. Hydrophilic coatings clean via the photocatalysis process and usually consist of metal oxides, such as titanium oxide, TiO_2 .

The current motivation in coatings technology focuses on controlling the composition of coating formulations to the molecular level and the morphology to the nanoscale. The application of smart anti-corrosive coatings is directed at reducing inspection times, maintenance costs and equipment downtime in

the industrial sector besides improving coating efficiency.

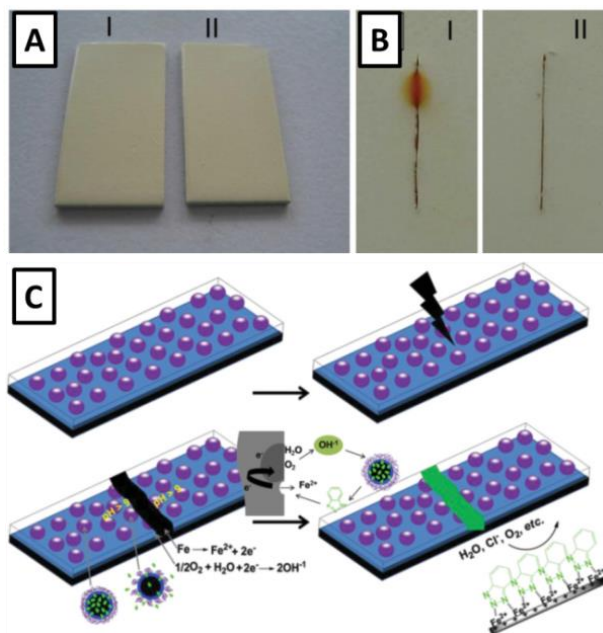


Figure 2. Self-healing illustration of inhibitor loaded polymeric nanocontainers embedded in epoxy coatings for corrosion protection of steel surfaces [Li et al. 2014].

References

1. D.G. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M.G.S. Ferreira & H. Moehwald, Layer-by-layer assembled nanocontainers for self-healing corrosion protection, *Adv. Mater.* 18 (13) (2006) 1672–1678.
2. A.S.H. Makhlof, Techniques for synthesizing and applying smart coatings for material protection, in: A.S.H. Makhlof (Ed.), *Handbook of Smart Coatings for Materials Protection*, Woodhead Publishing Limited, Oxford, United Kingdom, 2014, pp. 56–74.
3. J. Baghdachi, Smart coatings, in: T. Provder, J. Baghdachi (Eds.), *Smart Coatings II*, vol. 1002, ACS Symposium Series, American Chemical Society, Washington DC, 2009, <http://dx.doi.org/10.1021/bk-2009-1002.ch001> (Ch. 1).
4. Y.C. Yuan, T. Yin, M.Z. Rong & M.Q. Zhang, Self-healing in polymers and polymer composites.

Concepts, realization and outlook: a review, *Polym. Lett.* 2 (4) (2008) 238–250.

5. A. Tiwari & L. Hihara, J. Rawlins, *Intelligent Coatings for Corrosion Control*, Butterworth-Heinemann, 2015.

6. M. Wang, M. Liu & J. Fu. An intelligent anticorrosion coating based on pH-responsive smart nanocontainers fabricated via a facile method for protection of carbon steel, *J. Mater. Chem. A*, 3 (2015) 6423-6431.

7. S.B. Ulaeto, R. Rajan, J.K. Pancrecius, T.P.D. Rajan & B.C. Pai. Developments in smart anticorrosive coatings with multifunctional characteristics. *Prog. Org. Coat.* 111 (2017) 294-314.

8. Y. Yang & M.W. Urban. Self-healing polymeric materials, *Chem. Soc. Rev.*, 42, (2013), 7446-7467.

9. G.L. Li, M. Schenderlein, Y. Men, H. Möhwald, & D.G. Shchukin. Monodisperse polymeric core-shell nanocontainers for organic self-healing anticorrosion coatings. *Adv. Mater. Interfaces*, 1, (2014), 1300019.

Members News

	Name	Achievements
1.	Dr. P.V. Venkitakrihshnan, VSSC	Distinguished Alumni Award IIT Chennai 2017 ISRO Performance excellence award 2016
2.	Dr. S.C. Sharma, VSSC	INAE fellowship awarded on Dec. 15, 2017 in Induction Ceremony, Annual Convention of INAE in Chennai
3.	Dr Bhanu pant, VSSC	IIM Fellow
4.	Dr. U.T.S. Pillai, CSIR-NIIST	IIM Fellow
5.	Dr. M.T. Sebastian, CSIR-NIIST	1. Outstanding reviewer of American Ceramic Society 2. Publons peer review award in Materials Science 3. Publons Peer review award in Physics and Astrophysics 4. Awarded Korean Govt Brain Pool Fellowship 5. Published the book Microwave materials and applications. Two volumes. Wiley 2017.
6.	Dr. S.V.S. Naraya Murty, VSSC	Fellow, A.P. Academy of Sciences, Andhra Pradesh
7.	Dr. S. Chenna Krishna, VSSC	Young Metallurgist of the Year- Non Ferrous category instituted by the Ministry of Steel, Government of India for the year 2017
8.	Dr. A. Shunmugavel , VSSC	ISRO young scientist merit award - 2015 on 18.12.17.
9.	Dr. Bhoje E Gowd, CSIR-NIIST	Raman Research Fellowship (2017-2018) to Dr. E. Bhoje Gowd by CSIR, India. Best poster award for the paper entitled "Influence of Additives on the Formation of Block Copolymer- based Supramolecules in Bulk and Thin Films" by Deepthi Krishnan and E. Bhoje Gowd in the Indo-Japan Joint Symposium on Polymeric materials held during January 31- February 1, 2017 at Trivandrum.
10.	Dr. A K Asraf, LPSC	PhD awarded from University of Kerala –Civil Engineering department. "Investigations on ductile fracture of high conductivity and high ductility copper alloys through micro mechanical modeling"
11.	Dr. Sudarshan Rao, VSSC	PhD award from IITM, Chennai for the thesis title" Tensile isothermal fatigue behavior of annealed Cu-Cr-Zr-Ti alloy in argon atmosphere. Supervisors, Prof. Ganesh Sundara Raman, and Dr. VMJ Sharma
12.	Dr. K.M. Sree Manu, CSIR-NIIST	Doctor of Philosophy (Faculty of Engineering Sciences), July 2017 Academy of Scientific and Innovative Research (AcSIR), New Delhi, Thesis on 'Fabrication and Characterization of Aluminum Composites by Squeeze Infiltration and Compocasting Techniques' supervisor: Dr. TPD Rajan Best Poster Award (First Prize) – Area: Ceramics, composites and functional materials International Conference on Advanced Materials and Processes (ADMAT 2017 Sky Mat), December 14-16, Trivandrum, India.

13.	Dr. E. Jayakumar	Received PhD from CUSAT on the thesis title "Processing and Characterization of Functionally Graded Metal and Polymer Composites" Supervisor: Dr. TPD Rajan
14.	Mr. S. Dineshraj , VSSC	Received the SAME Ankit-Umesh Patel Best Paper Award for the paper titled 'Quality Improvement of Aerospace Components by Hot Isostatic Pressing (HIPing)' presented in the National Aerospace Manufacturing Seminar (NAMS-2017) Won a Best Poster Award for the paper titled 'Joining of materials through Hot Isostatic Pressing (HIPing)' presented in the international Conference on Advanced materials and processes (ADMAT 2017-SkyMat) held at Kovalam during Dec 14-16, 2017. The award carries a cash prize and citation.
15.	Mr. P. Manikandan, VSSC	1. Received award for Best Poster, titled "Uniaxial and Biaxial Tensile Behavior of Aluminium Alloy AA2219-T852" presented in the international conference on Advanced Materials and Processes (ADMAT 2017-SkyMat). (Co-authors are Dr.G.Sudarshana Rao, Dr.SVS.Narayana Murty and Dr.P.Ramesh Narayanan) 2. Received Dr. Vikram Sarabhai Memorial Award (10-08-2017) from VSSC-Staff Benevolent Fund for topper in B-Tech degree examination (mechanical engineering - evening course) conducted by University of Kerala, 2012-2016 batch. 3. Received CET-PTA award (08-04-2017) from College of Engineering Trivandrum (CET) - Parent Teachers Association (PTA) for topper in B-Tech degree examination (mechanical engineering - evening course) conducted by University of Kerala, 2012-2016 batch
16.	Dr. M.K. Karthikeyan, VSSC	Received SAME Ankit Best Paper Award" in National Aerospace Manufacturing Seminar (NAMS-2017), for the paper titled, Effect of Quench Media on Mechanical Properties of 0.3%C-Cr-Mo-V(ESR)Steel" Co-Authors are F. Gino Prakash, Balvinder Singh Bhatia, S. Mohan, P. Ramkumar
17.	Mr. Agilan M, VSSC	Received best paper award in International Welding Congress, IC-2017 for the paper titled "Mechanical properties and microstructural evolution in Al-Cu-Li 2195 alloy GTA and FSW welds. organized by The International Institute of Welding, December 7-9th 2017, Chennai - Co authors are Agilan M, G.Phanikumar, D.Sivakumar Received Best Poster Award in ADMAT 2017 International Conference on Advanced Materials and Processes (ADMAT-2017), SkyMat for the paper titled ", Effect of Friction Stir Welding Parameters on Mechanical Properties of 2195 Al-Cu-Li alloy Welds". Co authors are Agilan M, G.Phanikumar, D.Sivakumar
18.	Dr.. Naresh kumar K	Received Yuva Anweshak Award from Society of Aerospace Manufacturing Engineers (SAME) awards 2016 during Technical

		Colloquium on Aerospace Fastening Systems at Trivandrum on 20 th Feb 2017.
19.	Mr. V. Anilkumar	<p>Two 'Best Poster Awards' in International Conference on Advanced materials and processes (ADMAT-2017 Skymat), Trivandrum held during 14th-16th December-2017 for the papers titled</p> <ul style="list-style-type: none"> • Mechanical Behavior of 0.3%C-CrMoV (ESR) Steel at Elevated Temperature'. Co-Authors- Dr. R.K.Gupta, Dr.S.V.S.N.Murty. • Microstructure Evolution of Advanced Titanium Aluminide alloy during Hot Compression. 'Co-Authors- Dr.R.K.Gupta <p>"SAME Ankit Best Paper Award" in National Aerospace Manufacturing Seminar (NAMS-2017), Trivandrum held during 17th-18th November-2017 for the paper titled, 'Variation of Microstructure, Texture and Mechanical Properties in β-Titanium Alloy Ti-15V-3Cr-3Sn-3Al Sheets with Cold Rolling and Heat Treatment'. Co-Authors Dr. R.K. Gupta, Shri. P. Ramkumar, Dr.S.V.S.N. Murty.</p>
20.	Shri. C. Venkateswaran, VSSC	<p>Received Best Poster Award during International Conference on Advances in Glass Science & Technology (ICAGST-2017) for the work entitled 'Development of near-zero expansion transparent Glass-Ceramic through microwave hybrid heat-treatment', which was co-authored by Dr. S.C. Sharma, Deputy Director, VSSC (PCM).</p> <p>Also Received first prize for his tutorial project work 'Novel glasses from Inorganic wastes' convened by International Commission on Glass (ICG).</p>
21.	Ms. Jerin K. Pancrecious	Best Paper Award for the paper on "Studies on wear and corrosion behavior of electroless Ni-B-CeO ₂ nanocomposite coatings on A356 alloy" Jerin K. Pancrecious, Sarah. B. Ulaeto, R. Ramya, T.P.D. Rajan, E. BhojeGowd and B.C. Pai, National Conference on Critical and Strategical Materials for Advanced Technologies, Munnar, Kerala, March 9-11, 2017.
22.	Ms. Sarah Bill Ulaeto	Best Poster Award for the paper "Extract-mediated Fabrication and Characterization of Silver Nano Crystals Initiated from A. Indica Leaves for Anticorrosive Coatings, Sarah Bill Ulaeto, JerinK. Pancrecious, Ramya Rajan, T.P.D. Rajan, and B. C. Pai, National Conference on Critical and Strategical Materials for Advanced Technologies, Munnar, Kerala, March 9-11, 2017.
23.	Dr. M. Sundararajan, CSIR-NIIST	<p>1) Awarded for the best contribution in the field of Geochemistry Applied to Mineral Resources during 2017 by Indian Society of Applied Geochemists (ISGA).</p> <p>2) Become Fellow in Mineralogical Society of India. (FMS-2017)</p>
24.	Dr. Subodh. G Asst. Professor, Dept of Physics University of Kerala, Trivandrum	Selected as one of the 40 most inspiring faculties under forty years of age from South India by the New Indian express group

Events

National Workshop on Advanced Materials Characterization Techniques was organized by the Indian Institute of Metals, Trivandrum Chapter during August 9-10, 2017 in CSIR-National Institute of Interdisciplinary science and Technology, Trivandrum. The meeting was attended by more than 100 participants from various organizations. The felicitation function to Dr. U.T.S. Pillai and Mr. M.C. Shaji on the occasion of their superannuation was also arranged.





IIM, Trivandrum Chapter Day Celebrations was organized at Hotel Apollo Dimora, Thampanoor, Thiruvananthapuram on February 3, 2018 at 6.00 PM. Dr. R. Velayudhan, GM of Media City Channel and Media City e-Paper delivered a lecture on the topic: “Numerology and its influence in Human Life”.



The **Foundation day lecture** of The Indian Institute of Metals, Trivandrum was organized on **February 27, 2018** in CSIR-NIIST, Trivandrum. **Dr. P.R. Harikrishna Varma**, Head, Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences and Technology, Poojappura, Trivandrum delivered the foundation day lecture in the topic “Bioactive materials for clinical Applications- Scope and new challenges”.