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Moisture-resistant sealing materials for downhole HPHT electrical feedthrough packages

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Abstract

A bismuth oxide based multi-component glass system, $x\mathrm{H_3BO_3}$-$y\mathrm{Bi_2O_3}$-$(1\text{-}x\text{-}y\text{-}\delta)MO$-$\delta\cdot$REO with MO=$\mathrm{TiO_2}$, BaO, ZnO, $\mathrm{Fe_2O_3}$, etc., and lanthanum series based rare earth oxides (REO), for making downhole high-pressure and high-temperature (HPHT) electrical feedthrough package, has been developed using high-temperature melt-quenching and sintering technologies. By properly controlling phase structures in the material manufacturing processes, the obtained sealing materials have shown moisture-resistant properties in their monoclinic and tetragonal mixed phase structures, but strongly hydrophobic properties in their covalent bond tetragonal phase. The sealed electrical feedthrough packages have been evaluated under boiling water immersion and 200^{o}C/30,000PSI water-fluid simulated downhole harsh environments. The post measurement has demonstrated to be greater than $1.0\times10^{14}\,\Omega$ electrical resistance. This paper will show that such a high-bonding-strength and high-insulation-strength sealing material could be used to seal electrical feedthroughs and connectors for 300^{o}C/30,000PSI downhole and subsea wireline, logging while drilling (LWD), and measurement while drilling (MWD) tools' signal, data, and electrical power transmissions.

Key words
Electrical feedthrough, hydrophobicity, HPHT, insulation resistance, moisture-resistant, sealing material

I. Introduction

Downhole logging tools and electrical circuits are packaged in a hermetically-sealed metal enclosure, which is either sealed and pressurized, or filled with fluid, to protect the circuits from downhole corrosive environment and humidity. The sealed tool enclosure uses an electrical feedthrough that transmits the electrical power to internal electronics, or sends the measured downhole data to surface instruments. For permanent installations in the downhole environment, it is important that these electrical feedthroughs are reliable. In particular, it is critical that the downhole fluid is prevented from penetrating the electrical feedthroughs because the presence of a conductive fluid, such as seawater, in the electrical feedthroughs can cause a short circuit in the system. An electrical feedthrough package generally comprises electrically-conductive pin(s), an outer metal shell, and an electrically insulating material, hermetically sealed to the center conductive pin(s) and the outer metal shell. Here a high insulating sealing material with high mechanical and electrical insulation strengths is critical for making a downhole electrical feedthrough for reliable operation in water-based or moisture-rich oil-based wellbores. Several failure modes from the electrical feedthrough packages may be found specifically from harsh environmental operation. In one case, a sealing material may be of high electrical insulation strength but lack of the mechanical strength and appropriate coefficient of thermal expansion that may lead to sealing material cracks by high pressure. In another case, a sealing material may be of high mechanical strength and a matched coefficient of thermal expansion to the metal shell but lack sufficient electrical insulation strength to survive downhole temperature without electrical failure. In a further case, a sealing material may have high dielectric and mechanical strength and also a matched coefficient of thermal expansion to the metal shell but may lack moisture resistance that could also lead to electrical breakdown by the deteriorated resistivity.

Aromatic polyether ketone-based (PEEK, PEK, PAEK, and PEKK) organic polymers are the first type of dielectric sealing materials that are widely used in an electrical feedthrough seal for subsea and downhole logging tools. Typically, in low temperature installations, aromatic polyether ketones based polymer materials are used as the pressure barrier and insulating component. However, the structural integrity, as well as the dielectric strength of aromatic polyether ketones can be compromised at higher temperatures because of a low glass transition temperature of less than 150°C. On the other hand, such thermoplastic sealing materials have water absorption of ~ 0.5% even under ambient conditions. Under long-term exposure to high pressure, and high temperature, and corrosive fluids, the polymer seals will eventually fail, allowing fluid to enter the pressure bulkhead and reach the contact pins. If the invading fluid is conductive (a usually the case in downhole and subsea environments), a short circuit may occur in the system, resulting in power and data loss.

Inorganic glasses and glass-ceramics, such as Corning 7070, S8061, EG2927, Li_2O-Al_2O_3-SiO_2, MgO-Al_2O_3-SiO_2, and ZnO-Al_2O_3-SiO_2, are a second type of dielectric sealing materials that have high dielectric strength, high electric resistivity, good mechanical strength, and high break-down voltage. Despite the great success in many glass-to-metal seal or glass/ceramic-to-metal systems these glass and glass-ceramic sealed electrical feedthroughs often fail not due to mechanical stress but due to the deterioration of the electric insulation. One failure mode is that the sealing material is of a hydrophilic nature (due to its porosity) that leads to absorption of moisture and eventual electrical strength deterioration. Existing sealing materials are generally hydrophilic and require thermoplastic materials (PEEK, PEK, PAEK, and PEKK) for providing a fluid barrier against moisture ingress into the downhole tools, unfortunately, these polymer barriers are deteriorated under harsh conditions and provide limited reliability for long-term operation.

To solve sealing material challenges for making reliable downhole or subsea electrical feedthroughs and connectors, it is desirable for having a high moisture resistant sealing material that has to have not only high mechanical strength but also electrical insulation and dielectric strength. It is more desirable that the sealed electrical feedthrough or connectors can be used in high-voltage, high-current, high-radiation, high-pressure, high-moisture, and high-temperature (6H) harsh environments, such as downhole, geothermal wells, and nuclear reactor. This paper presents a novel sealing material that has shown not only desirable moisture-resistant or hydrophobic properties but also demonstrated sufficient bonding strength and electrical insulation and dielectric strength to enable an electrical feedthrough or connector for being used in the downhole and subsea logging tools, LWD and MWD tools, where the temperature and pressure could vary from -55°C to 300°C and 0 PSI to 30,000 PSI. On the other hand, the high metal oxide nature of the bismuth oxide based sealing material may also enable the electrical feedthroughs and connectors to be used in nuclear and high-energy radiative instruments and environments.

II. Experimental

A. Material preparation

The dielectric sealing material utilized in the electrical feedthrough package is a B_2O_3-Bi_2O_3-MO-REO based multi-component glass system, where MO=ZnO, BaO, and Fe_2O_3, and REO represents the lanthanide series rare-earth oxides. The first three elements are basic moisture-resistant ternary glass system, while REO is used to enhance moisture resistance by its unique electronic structure of the rare-earth metal atom that inhibits hydrogen bonding with interfacial water molecules resulting in a hydrophobic hydration structure where the surface oxygen atoms are the only hydrogen bonding sites [1]-[2].

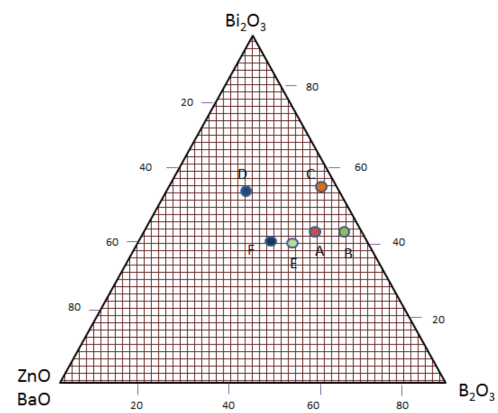

Figure 1 Triangulation phase diagram for making moisture-resistant dielectric sealing material composition selections.

Initial powders were mixed and melted in a crucible, such as made from Pt, Al_2O_3, and silica, by a conventional melting and quenching method, which first heats the initial glass mixtures up to 1000-1400°C for an hour, then, they are quenched in a de-ionized water bath to form glass frit. The second step is to grind the glass frits to powder with a desired mesh size of 100-400, then mix with polymeric binders. The third step is to compress the bonded powder as a glass green bead with a typical hollow cylindrical shape. The fourth step is to sinter the compressed glass beads, where the polymer binder will be burned off at the elevated temperature. The sintered glass beads have a glassy like structure with its dimensions shrunk by ~10%, compared with its green bead's dimensions.

Figure 1 has detailed the method to determine appropriate composition in mole percentage, and six samples have been

Table 1 Down selected six sealing materials for making initial electrical feedthrough packages

Sample#	ZnO/BaO (mol%)	Bi2O3 (Mol%)	B2O3 (Mol%)	REO (CeO, Mol%)
A	12	42	40	6
B	5	42	46	7
C	5	55	36	4
D	24	54	20	2
E	24	40	32	4
F	20	40	40	0

designed for research purposes. The selected sealing material composition has composed of water insoluble glass former(s) and network modifier(s) with varied compositions from each glass material. Bi_2O_3 acts as both glass-network former with [BiO_3] pyramidal units and as modifier with [BiO_6] octahedral units. As shown in Table 1, six synthesized sealing materials (A, B, C, D, E, and F) are composed of 5-24 mol% MO, 20-46 mol% B_2O_3, 40-55 mol% Bi_2O_3, and 0-7mol% Rare earth oxide (REO, such as cerium oxide). The triangulation diagram with primary Bi_2O_3, B_2O_3, ZnO or BaO, can be used to find approximate composition for the synthesized dielectric sealing material performance in both mechanical and dielectric properties. In fact, the down selection of a moisture-resistant sealing material could be a binary glass system (for example, Bi_2O_3-B_2O_3), a ternary system (for example, Bi_2O_3-B_2O_3-MO, MO=ZnO, BaO, Fe_2O_3, TiO_2 etc.), and quaternary system (for example, Bi_2O_3-B_2O_3-ZnO-REO). The material analyses have shown that the quaternary B_2O_3-Bi_2O_3-MO-REO based dielectric sealing materials have their glass transition temperatures of 400-480°C, but decreasing with the increasing of Bi_2O_3/B_2O_3 ratio, and increasing with the increasing of ZnO/B_2O_3 ratio and BaO/B_2O_3 ratio. [3]

To obtain appropriate mechanical and thermal properties from a synthesized sealing material the mass density of such a quaternary glass system depends upon ratio of each composition in the synthesized material system. The effective density can be approximately written by

$$\rho = \sum_{n=1}^{k} a_n \cdot \rho_n \quad and \quad \sum_{n=1}^{k} a_n = 1 \tag{1}$$

where a_n and ρ_n are mole fraction and mass density of each glass composition, and k represents the number of compositions in the synthesized material system. If starting from an initial density, ρ_o, of the simple glass system, such as only Bi_2O_3, the incorporation of different glass compositions, such as B_2O_3, ZnO, BaO, and CeO, the density variation in the dielectric sealing material could lead to a corresponding variation in the effective coefficient of thermal expansion (CTE) by

$$CTE = \frac{\Delta V}{(T_g - T)V_o} = -\frac{\rho - \rho_o}{(T_g - T_o)\rho} \tag{2}$$

where T_g is glass transition temperature and ΔV is volume change of the material. It is clear that the incorporation of low density glass compositions will increase CTE of the synthesized material system. The initial density of Bi_2O_3, B_2O_3, and ZnO glasses is 8.90, 2.55, and 5.61 g/cm^3, respectively. The coefficient of thermal expansion could be from 6.0 to 12.0× 10^{-6} m/m·°C, with values increasing with increasing Bi_2O_3/B_2O_3, ZnO/B_2O_3 ratio or BaO/B_2O_3 ratio. On the other hand, the increase of the B_2O_3 composition could effectively reduce effective mass density, but inversely increase CTE.

B. Electrical feedthrough prototype fabrication

Fabricating an electrical feedthrough package is to bond an electrical conductive pin(s) with a metal shell with sintered beads under a temperature of $T_1 \approx 600^oC$ for τ_1=0.5-1.0 h, namely a one-stage (T_1, τ_1) electrical feedthrough package fabrication process. For large-size electrical feedthrough assembly it normally requires a two-stage fabrication process. The metal shell may be preheated at T_1 for a certain amount of time τ_1, then, fire the metal shell with pin(s) and glass sealing beads at T_2 with duration of τ_2. Also the pre-oxidation of the metal shell surface may be required to enhance the sealing material and metal shell bonding strength. To control the phase structure in the sealing material, the first control parameter is the setting of T_2 and τ_2, then, a second control parameter is cooling rate (η). A higher firing temperature (T_2) and a longer duration (τ_2) will prompt a covalent bonded tetrahedral phase formation, but a low firing temperature may favor the formation of monoclinic phase. Conversely, a fast cooling of the fired electrical feedthrough from an elevated temperature to ambient may favor the formation of the amorphous glass phase, and a slowly cooling may prompt a monoclinic structure formation. By appropriately controlling these parameters, the obtained sealing material may show light yellowish color from monoclinic phase, but gray or white color at covalent bonded tetrahedral phase.

For preparing such a bismuth oxide contained glass, both the firing temperature and isothermal heating time are critical for obtaining a stable dielectric sealing material with the preferred dielectric and mechanical strengths. Figure 2 illustrates the quaternary B_2O_3-Bi_2O_3-MO-REO based dielectric sealing material which may also have similar several polymorphs as Bi_2O_3 glass. The room temperature phase, α-Bi_2O_3 has a monoclinic crystal structure. δ- Bi_2O_3 is principally an ionic conductor with a defective fluorite-type crystal structure. During the growth of crystallites both α and δ phases are two stable polymorphs of bismuth oxides. During the glass firing process the monoclinic α-phase transforms to the cubic δ-Bi_2O_3 if it is heated above 730°C, until melting at 820-860°C. The behavior of Bi_2O_3 on cooling from the δ-phase may transform to tetragonal β-phase or γ-phase, then to α-phase. The γ-phase can exist at

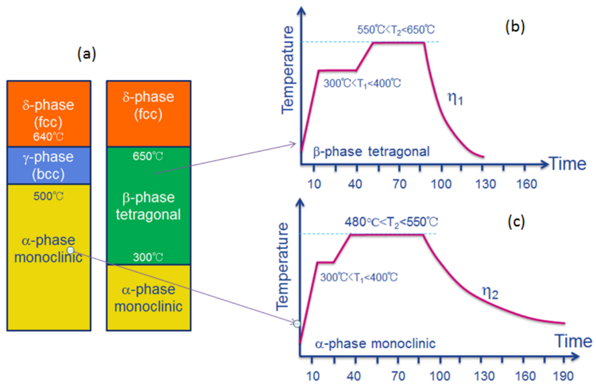

Figure 2 Fabrication processes for making electrical feedthrough packages under elevated temperature and duration with different phase sealing materials.

room temperature with very slow cooling rate, but α-Bi_2O_3 always forms on cooling the β-phase. The α-phase exhibits p-type electronic conductivity at ambient which transforms to n-type conductivity between 550°C and 650°C, depending on the oxygen partial pressure. The conductivity in the β, γ and δ-phases is predominantly ionic with oxide ions being the main charge carrier (Fig. 2(a)). The conductivity of δ- Bi_2O_3 is about three orders of magnitude greater than monoclinic phase.

Figure 2(b) and (c) have illustrated a two-stage fabrication process for making an electrical feedthrough package by using different metal shell materials (SS304L, Inconel alloy, 17-4PH, and Ti-alloy etc.) and pin materials (Kovar, BeCu, CrCu, X750, PtIr etc.). [4] Accordingly, the material phase formation is determined by firing temperature, duration, and cooling rate. Specifically, the high-temperature firing at T>550°C is more likely to form

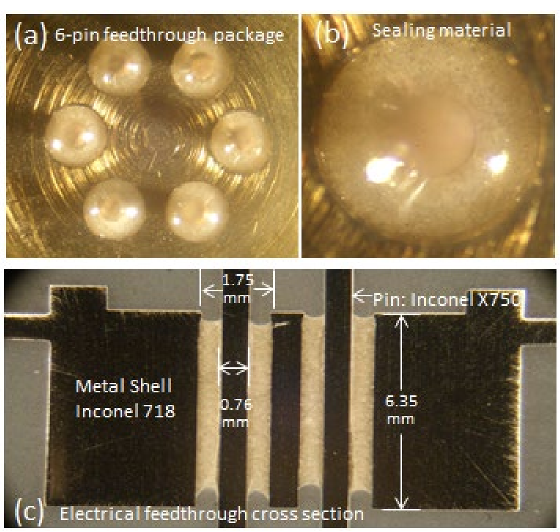

Figure 3 A typical electrical feedthrough package made from Inconel alloy with a quaternary B_2O_3-Bi_2O_3-MO-REO based dielectric sealing material.

monoclinic triangular phase (Fig. 2(c)). However, under high cooling rate (η_1>300°C/sec), the sealing material may only have amorphous glass phase or with limited nanocrystalline grids or particles. [5]

Figure 3 shows a typical 6-pin HPHT electrical feedthrough package made from an Inconel 718 shell and an Inconel X750 pin, sealed with the B_2O_3-Bi_2O_3-MO-REO based sealing material, where the feedthrough package has a sealing length of ~ 6.0 mm, 1.75 mm seal diameter, and 0.76mm pin diameter, designed for 200°C and 30,000 PSI downhole application. Fig. 3(a) and (b) show the desired sealing capability with a yellowish color, half transparent, composed of crystalline structures. The cross sectional image in Fig. 3(c) displays the cross-sectional view, showing the bonding and wetting angle along the Inconel 718 shell, sealing material, and Inconel X750 pin surfaces.

III. Results and discussion

A. Moisture-resistant sealing material

The electric insulation resistance (IR) has been measured with a Sefelec M1501P Megohmmeter system that has a 1000 Teraohm (TΩ) upper limit. The IR value is measured before and after 100°C boiling water immersion process for typically 1h. The insulation resistance is tested as a function of the elapsed time, typical 0-600s. This method is fairly independent of temperature up to 50°C range and often can give some conclusive information on moisture

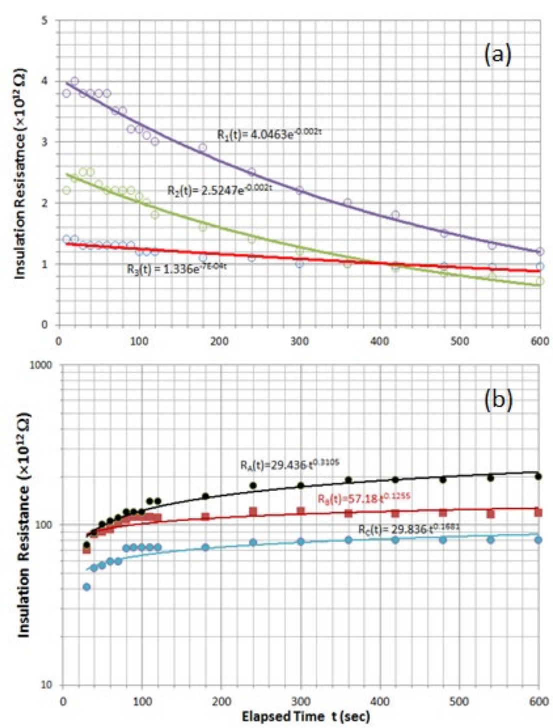

Figure 4 Electrical insulation resistances measured from (a) hydrophilic sealing materials and from (b) moisture-resistant sealing materials.

effect on sealing material electric properties, which is sometimes referred to as absorption tests.

Figure 4 shows the sealing materials with a negative response in Fig. 4(a), and the sealing materials with a positive response in Fig. 4(b) under 500VDC, subsequent to immersion in boiling water for typical 1h duration. Initial ambient insulation resistances from the B_2O_3-Bi_2O_3-MO-REO sealed single-pin feedthrough packages show a typical value of a few hundred TΩ, which indicates excellent electrical insulation resistance. In contrast, most of the existing sealing materials may also have 100TΩ electrical insulation resistance but they are varied by absorbed moisture contents, which are disclosed by a negative exponential function of the time, as seen in Fig. 4(a). The fitted data can be described by $A_o.e^{-\chi}$, where $\chi \approx 0.002$-0.004. Such an IR response character is more or less related to the conductive polar –OH- bond induced surface conductivity increase as a function of time. Since the feedthrough package is immersed in the boiling water under atmospheric pressure, it is more likely that the surface of the sealing material has become conductive due to OH hydroxyl ions by dipole interaction with poled material surface.

However, the measured IR data, as seen in Fig.4(b), from the moisture-resistant sealing materials can be described as a power function of the elapsed time, namely, $R(t) = R_o t^{\nu}$ ($\nu \approx 0.1$-0.3). Such an IR response is more related to a capacitor discharge effect, where dark current is negligible. The observed IR value of >50TΩ at 300sec indicates moisture-resistance of the B_2O_3-Bi_2O_3-MO-REO sealing material.

The insulation resistance measured from ambient to elevated temperature, as shown in Fig. 5, indicates that the sealed electrical feedthrough package has an initial 1000TΩ ambient insulation resistances, corresponding to 1.45×10^{19} Ω-cm resistivity at 0°C, but it starts to drop at 70°C and 125°C from two typical developed sealing materials, labeled by Kryoflex® HTS and XTS, respectively. The measured "hot IR" data can be fitted to a negative

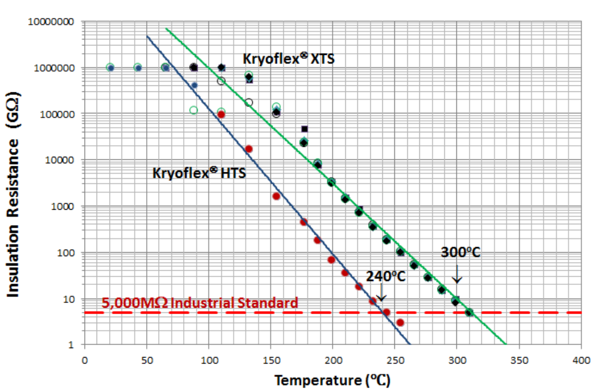

Figure 5 Insulation resistance measurements from two developed sealing materials at elevated temperatures.

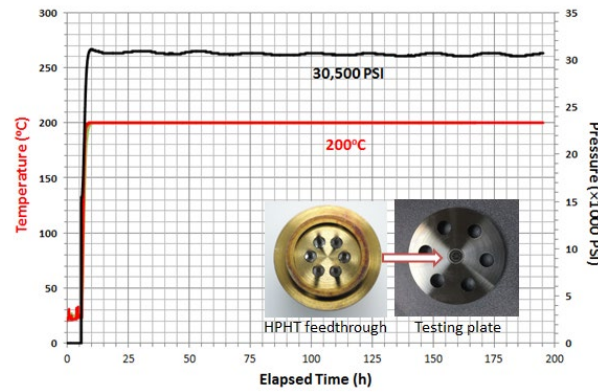

Figure 6 HPHT electrical feedthrough package test under 200°C/30,000 PSI simulated downhole water-fluid condition.

exponential function of temperature. For downhole or subsea electrical feedthrough package reliable operation at 200°C and 30,000 PSI condition, ~5,000MΩ resistances are normally regarded as HPHT industrial standard for product specification reference. Figure 5 has demonstrated that an electrical feedthrough package, sealed with Kryoflex® XTS material, could have about 10,000MΩ electrical insulation resistances even at 300°C, 2× industrial accepted 5,000MΩ standard requirement.

To further prove the moisture-resistance of the sealing material for making a downhole or subsea electrical feedthrough package, the electrical feedthrough prototypes have been exposed to a simulated water-fluid-based downhole harsh condition. Figure 6 has shown a typical electrical feedthrough package test under 200°C and 30,000 PSI water-fluid-based conditions with a testing duration from a few hours to a few hundred hours. To test each feedthrough package under HPHT conditions, a testing fixture has been designed to maintain hydraulic pressure on

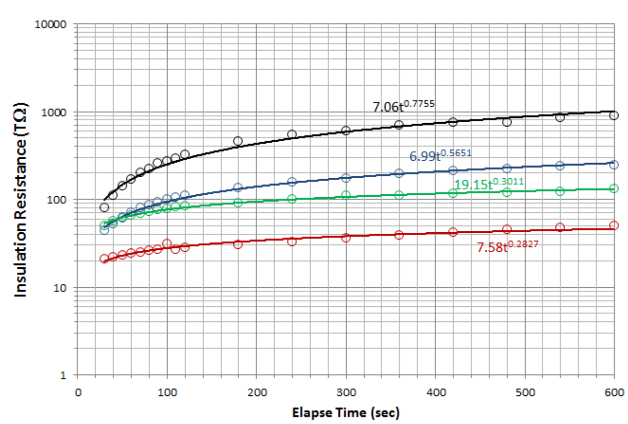

Figure 7 Insulation resistance measurements from four samples, after 24h test under 200°C/30,000 PSI simulated downhole water-fluid condition.

one side of the seal while the opposite seal has no pressure. A feedthrough package has to be welded onto a testing plate as shown in Fig.6, then, this testing plate is installed in the middle of two halve cylindrical-like body with six bolts andO-ring seal [6]. The fixture is installed in a temperature controlled oven with external pressure and fluid communication via high-strength stainless steel tubes. Data logging software has been designed to acquire testing data.

Figure 7 displays the measured insulation resistance from Bi_2O_3-B_2O_3-MO-REO material sealed feedthrough package prototypes, after 24 hours at 200°C and 30,000 PSI water-fluid-based pressurized immersion process. First, all four sealing materials have shown positive response as a power function of time, namely, $R(t) = R_o t^{\nu}$ (ν is constant), which is consistent with the IR data shown in Fig.4. By comparing with ambient insulation resistance values of a few hundred TΩ, the measured insulation resistances from the Bi_2O_3-B_2O_3-MO-REO material, at least, indicate negligible electrical deterioration even after HPHT water-fluid-based testing process.

To prove the mechanical bonding strength of the sealing material for making reliable HPHT downhole or subsea electrical feedthrough package, the prototyped electrical feedthrough packages have been further experienced transient pressure shock tests at both 18°C and 200°C, respectively.

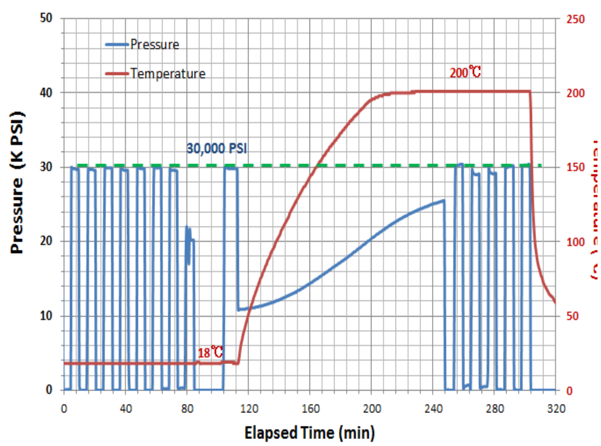

Figure 8 0-30,000PSI pressure shock cycle based sealing material bonding strength test at ambient and 200°C.

Figure 8 has shown a typical pressure shock testing procedure, where the hydraulic pressure is acted onto the front feedthrough package, then, quickly ramped up to 30,000 PSI via a mechanical hydraulic pumping system, with water as pressure transmission fluid. Each pressure cycle is about 10min, with 5 min at ambient and 5min at elevated pressure status, such as 30,000PSI. The transient pressure variation is just in the seconds from ambient to 30,000 PSI, and back to ambient also in seconds. Figure 8 shows first 9 cycles are conducted at ambient, then, turning on the oven to 200°C, with additional 5 pressure shock cycles at 200°C. After these 0 PSI-30,000 PSI pressure shock cycle tests the hermeticity of the feedthrough package is still better than 1.0×10^{-9} atm sccm, measured by Helium Leak Detection technique.

III. Conclusion

A bismuth oxide based multi-component glass system has been developed, evaluated and characterized for making an electrical feedthrough package that could be used in water-fluid-based or moisture-rich downhole and subsea like 300°C and 30,000 PSI harsh environment for signal, data, and electrical power transmissions. The novel moisture-resistance of this ceramic-like sealing material provides significant advantage over the existing hydrophilic dielectric sealing materials for being used in any moisture-rich environments. Due to its high-mechanical strength, high electrical insulation resistance, high-pressure and high-temperature, high-radiation absorption, and hydrophobic nature it is also applicable for solving various moisture related electrical failure modes in oil/gas, subsea, petrochemical, aerospace, power generation, nuclear and defense industries.

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