Neutron Shielding Material
Applicable for Advanced Transport Packaging

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ABSTRACT

From among the neutron shielding materials of the "*kobesh* " series developed by Kobe Steel, Ltd. for transport and storage packagings, silicon rubber base type material has been tested for several items with a view to practical application and official authorization, and in order to determine its adaptability to actual vessels.

Silicon rubber base type " *kobesh* SR-T01" is a material in which, from among the silicone rubber based neutron shielding materials, the hydrogen content is highest and the boron content is most optimized. Its neutron shielding capability has been already described in the previous report (Taniuchi, 1986). The following tests were carried out to determine suitability for practical application;

1) Long-term thermal stability test
2) Pouring test on an actual-scale model
3) Fire test

The experimental results showed that the silicone rubber based neutron shielding material has good neutron shielding capability and high long-term fire resistance, and that it can be applied to the advanced transport packaging.

INTRODUCTION

The burn-up of nuclear fuels in power reactors is increasing owing to trouble-free operation and the employment of high-performance fuels. Consequently, the intensity of neutron source and decay heat in spent fuels is greatly increasing. On the other hand, greater efficiency of transport / storage packaging, which means a large capacity with a small size, is required to minimize transportation / storage cost and risk. As a result, neutron shielding materials are becoming an increasingly important component in transport / storage packaging.

Neutron shielding materials for transport / storage packaging containing materials generating decay heat, such as spent fuels and high-level waste, are exposed to fairly high temperatures. Many neutron shielding materials are made of polymers, so thermal stability of the material, especially its neutron shielding capability, is one of the most important factors.

The highly effective neutron shield *kobesh* has been developed in order to supersede the conventional type of neutron shield, by providing superior ability in neutron shielding and heat resistance. *kobesh* consist of four kinds of base materials: silicone rubber base, polypropylene base, ethylene-propylene rubber base and titanium hydride base.

Thermal properties of silicone rubber base type *kobesh* are described in this paper.

kobesh SR-T01

kobesh SR-T01 has the highest hydrogen content among silicone rubber base *kobesh*. The base material is a newly developed room vulcanized type silicone rubber. Silicone rubber offers good fabricablity owing to its good fluidity before curing, excellent heat resistance, fire resistance and stability of mechanical properties at a wide temperature range. The silicone rubber of this type has a higher hydrogen content, 5.0×10^{22} atom(H)/cc, than usual types of silicone rubber which generally have $(4.0\sim4.5)\times10^{22}$ atom(H)/cc of hydrogen. The hydrogen content of *kobesh* SR-T01 is increased up to 5.5×10^{22} atom(H)/cc by adding titanium hydride powder. Boron as a form of boron carbide is mixed with the material in order to lower secondary gamma rays emitted by (n,γ) reaction. The amount of boron is optimized from the viewpoint of cost and shielding ability. Aluminum compound is mixed with the material in order to improve fire resistance.

The chemical composition of *kobesh* SR-T01 are shown in Table 1 and the density of it is $1.7\sim1.8$ g/cm^3.

THERMAL STABILITYT

Polymers, widely used as neutron shielding, have a tendency to degradation by heat even if the temperature is lower than its melting point or softening point as well as its decomposition point. We have therefore been measuring the mass reduction and hydrogen reduction of the neutron shielding during prolonged heating.

WEIGHT CHANGE

1) Experiment

Specimens of *kobesh* SR-T01 ($20\times50\times5$mm) were heated in the glass test tube for 360 days at 140, 160 and 170℃ using the oven. Weight measurements and chemical analysis were made at starting and 10 days, 30 days, 90 days, 180 days and 360 days of a heating period. Chemical analyses were made using a C-H-N analyzer.

2) Results

The weight change (reduction) of the specimen after 360 days of a heating test was about 1.5% at 140℃ and 2.1% at 170℃ as shown in Fig. 1. The change of hydrogen content of the specimen at 170℃ heating test was shown in Fig. 2. The error bars in this figure mean the detection accuracy. While the initial hydrogen content was 5.0% and was decreased to 4.7% after 360 days, the hydrogen content was thought to be constant even after 360 days of a heating test taking into account the detection accuracy.

THERMAL EXPANSION AND GAS ANALYSIS

In order to verify the gas pressure in the fin cavity where kobesh is poured, the following tests were performed;

① Thermal expansion measurement
② Gas pressure measurement
③ Chemical analysis of released gas

Pressure rising mechanism is complex, especially because of the combination of reduction of void volume due to thermal expansion of *kobesh* material and released gas pressure (see Fig. 3). Because of the small volume of void compared to the volume of *kobesh* material, thermal expansion of *kobesh* material is a large factor for pressure rising in an actual flask condition.

Table 1. Chemical Composition of kobesh SR-T01

Element	Content (minimum)	
	wt%	atoms/cm3
H	5.2	5.3×E22
B	2.0	1.9×E21
B10	0.4	3.8×E20
B11	1.7	1.6×E21
C	11.2	9.6×E21
O	27.2	1.8×E22
Al	11.3	4.3×E21
Si	12.4	4.6×E21
Ti	30.7	6.7×E21

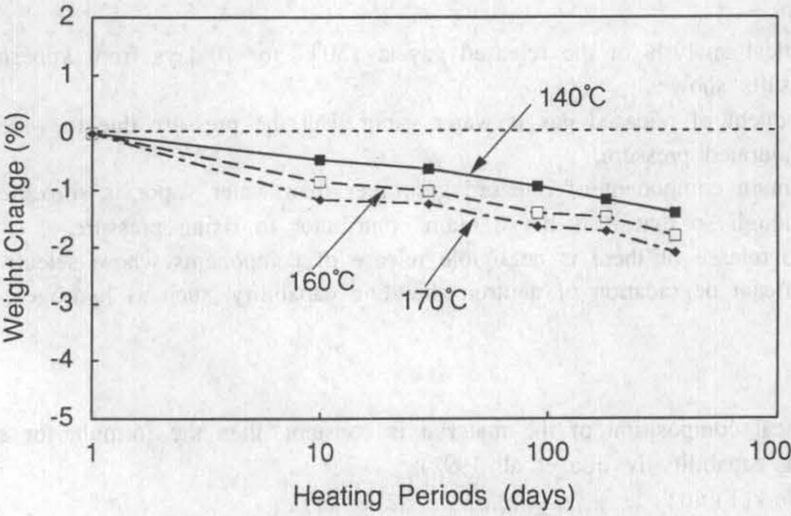

Fig. 1 Weight Change of Silicone Base *kobesh*

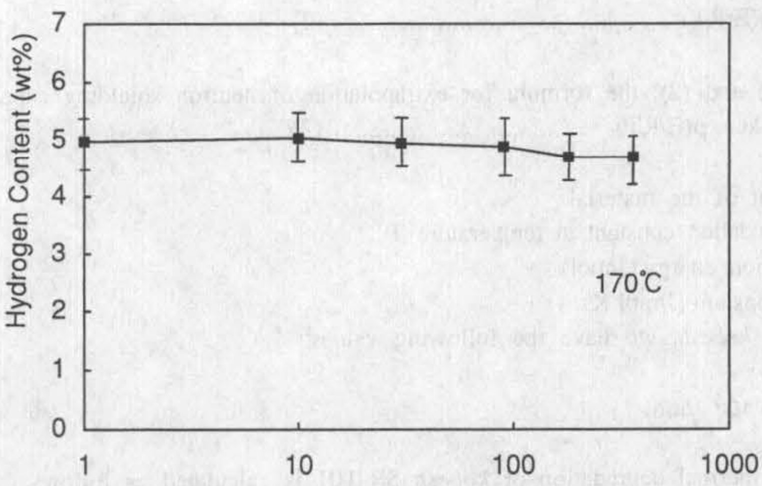

Fig. 2 Hydrogen Content Change of Silicone Base *kobesh*

The objective of this test was to measure the effect of thermal expansion and that of released gas pressure separately.

1) Experiment

Test specimens were heated in the oven for more than one week at 125℃ and 150℃. Thermal expansion of the specimens (ϕ97mm×H132mm) was measured using a ruler. In the gas pressure measurements, the specimens were set in the closed test cylinder. The void space in the cylinder was 10% and 50%. Released gas from the specimens was gathered and analyzed using Karl Fischer's method for vapor and gas chromatography for hydrogen, cyclic siloxane and the other gas component. The test equipment for thermal expansion and gas pressure measurement is shown in Fig. 4.

2) Results

Thermal expansion was about 0.04~0.05% both at 125℃ and 150℃ as shown in Fig. 5 and Fig. 6. These values are smaller than calculated values as free expansion. The gas pressures after 1000 hr heating test were 5.4bar and 7.9bar at 125℃ and 150℃,respectively, in the case of 50% void space as shown in Fig. 7 As to 10% void space, the gas pressures were 25bar at 125℃ and 42bar at 150 ℃ (see Fig. 8).

Results of chemical analysis of the released gas at 150℃ for 10 days from *kobesh* are shown in Table 2. The results show ;

- Main component of released gas is water vapor. But the pressure due to water vapor is limited up to its saturated pressure.
- The other main component of released gas other than water vapor is siloxane, but its amount is small enough so that it is not a main contributor to rising pressure.
- There is no release or there is negligible release of components whose selective release would cause significant degradation of neutron shielding capability, such as hydrogen, methane or ethylene.

3) Discussion

Assuming chemical composition of the material is constant, then the formula for extrapolation of neutron shielding capability is (Iida, et al., 1991);

$$W(T,t)=W_0-k(T)\ln(t) \quad \text{.....} \quad (1)$$

Generally, degradation of polymers by heat is represented by Arrhenius' equation;

$$k(T)=k_0 \exp(E/RT) \quad \text{.....} \quad (2)$$

From equation (1) and (2), the formula for extrapolation of neutron shielding capability is;

$$W(T,t)=W_0-k_0\exp(E/RT) \quad \text{.....} \quad (3)$$

where,

W=weight of the material

k(t)=degradation constant at temperature T

E=activation energy (J/mol)

R=gas constant (J/mol K)

From the data of *kobesh*, we have the following values,

$k_0=46$

$E=-1.82\times10^4$ J/mol

Using these data, thermal degradation of *kobesh* SR-T01 is calculated as follows;

(For transport use, 200 days a year for 20years)

Weight loss of the material is 1.6% at 125℃ and 2.4% at 150℃.

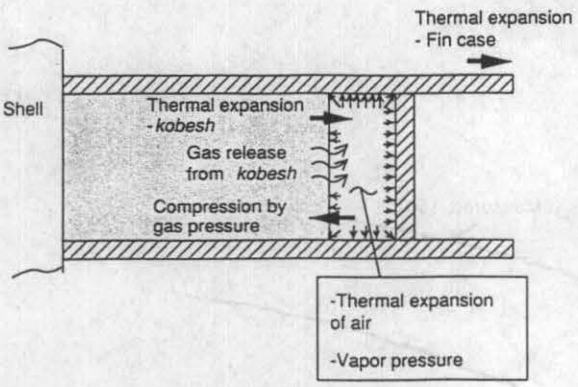

Fig.3 Pressure Rising Mechanism

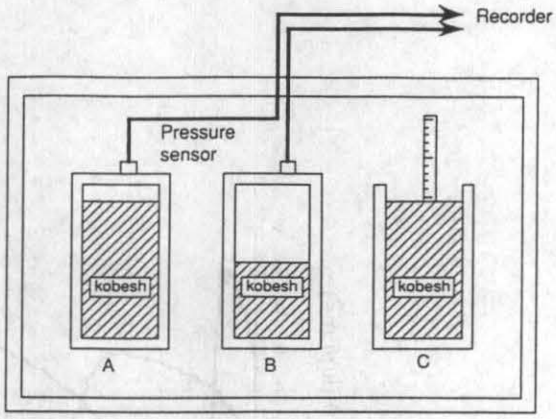

Fig.4 Test Equipment of Thermal Expansion and Gas Pressure Measurement

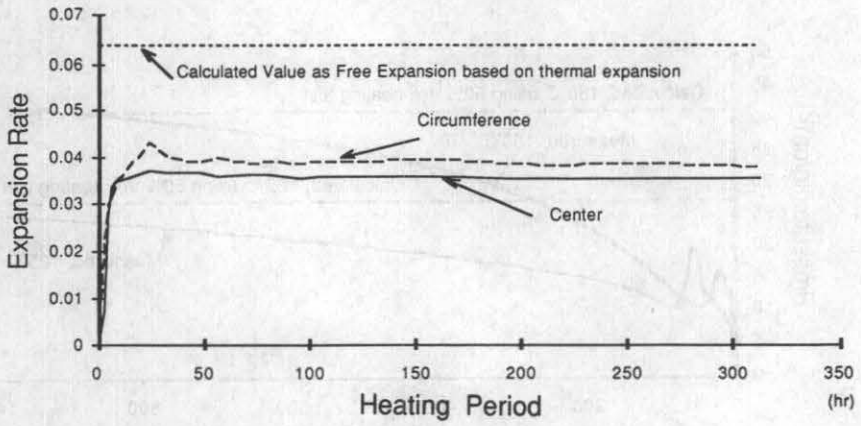

Fig.5 Thermal Expansion Test at 125℃

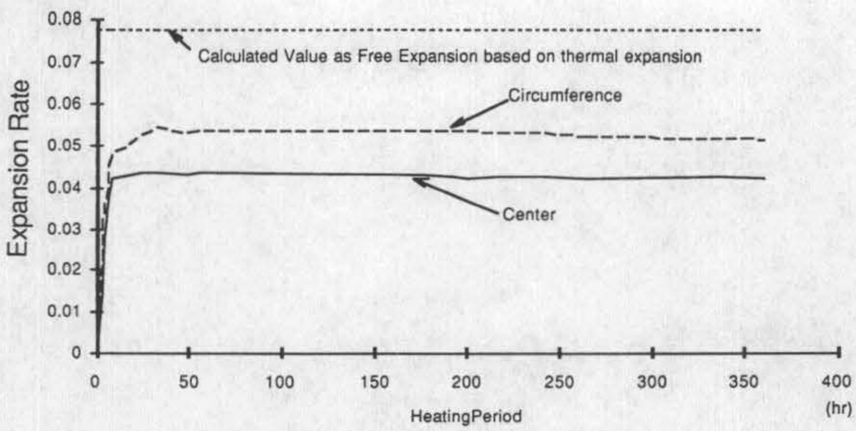

Fig.6 Thermal Expansion Test at 150℃

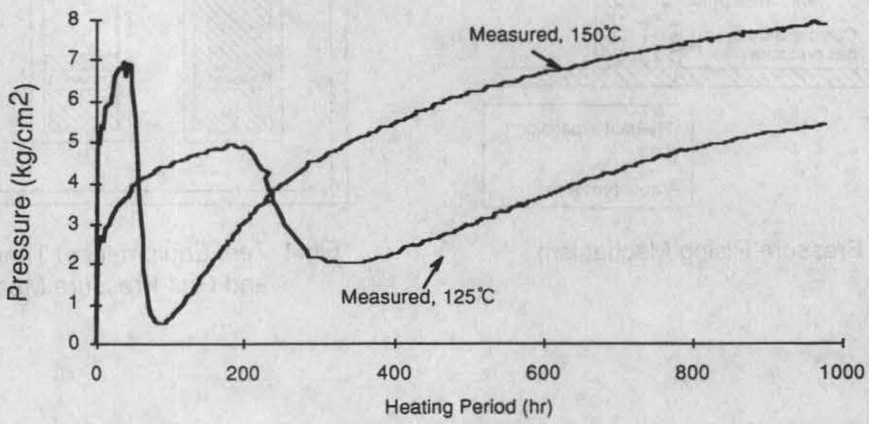

Fig.7 Measured Gas Pressure (50% void space)

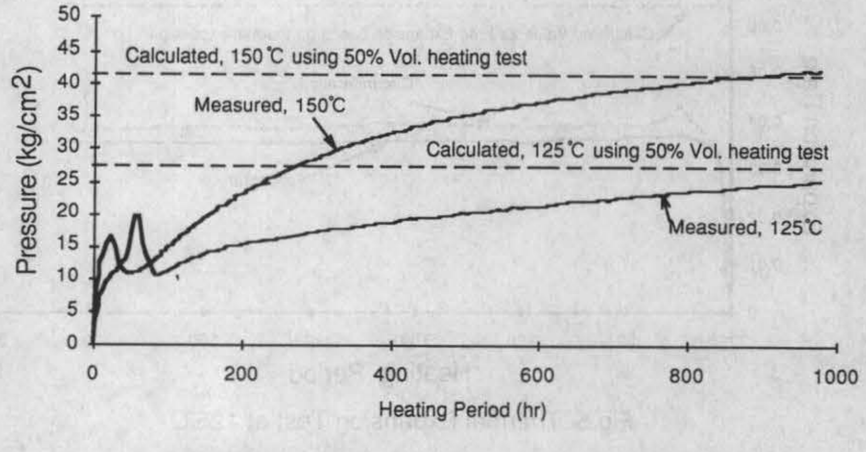

Fig.8 Measured Gas Pressure (10% void space)

Table 2. Released Gas Analysis from *kobesh*
(Heating Condition : 150℃ × 10 days)

Treatment Conditions	Unit	Test Cylinder		Detection Limit
		Glass Cylinder	Carbon Steel Cylinder	
Siloxane	(mg/g)	0.62	0.65	—
Water Vapor	(mg/g)	7.86	7.81	—
Hydrogen	(mg/g)	N.D.	N.D.	0.05
Carbon Monoxide (CO)	(mg/g)	N.D.	N.D.	0.05
Carbon Dioxide (CO_2)	(mg/g)	0.048	0.042	—
Methane (CH_4)	(mg/g)	0.011	0.009	—
Ethylene (C_2H_6)	(mg/g)	0.00004	0.00003	—
Hydrogen Chloride (HCl)	(mg/g)	0.0022	0.0016	—
Fluorine Ion (F^-)	(mg/g)	N.D.	N.D.	0.001
Nitrous Acid Ion (NO_2^-)	(mg/g)	N.D.	N.D.	0.001
Nitric Acid Ion (NO_3^-)	(mg/g)	N.D.	N.D.	0.001
Oxalic Acid Ion (Br^-)	(mg/g)	N.D.	N.D.	0.001
Sulfuric Acid Ion (SO_4^{2-})	(mg/g)	N.D.	N.D.	0.001

Note;
1. Unit ; mg/ g(material). Heated specimens are four pieces of 10×10×50mm(40g).
2. N.D. means 'not detected'.
3. Vapor was measured by Karl Fischer's method.
4. Siloxane was measured by weight measurement method after extraction using n-hexan from gas and surface of cylinders.
5. Hydrogen and other organic components were measured by gas chromatography.
6. Other inorganic components were measured by ion chromatography.
7. Testing Place ; Chemicals Inspection & Testing Institute, Japan, Osaka
8. Testing date ; May 28, 1992

POURING TESTS

Pouring tests were made with full-scale model in order to establish the pouring method that can pour *kobesh* material into fin cavities of assumed packaging without voids which might be harmful for shielding.

In order to fabricate *kobesh* (ID1580mm,OD1790mm,t40mm), *kobesh* material was poured into the acrylic cylinder which simulates the fin cavity, in four installments by rotating the cylinder by 90, 180 and 270 degrees. After *kobesh* material was vulcanized, it was cut into 45 pieces and visual inspection was performed.

There were only three voids in the *kobesh.* The size of these voids were 6.5×2mm, 8.0×1mm and 21.5×1mm. As the number and the size of voids were small, the voids generated in *kobesh* during the pouring process will not be harmful for shielding.

FIRE TESTS

kobesh (thickness: 15cm) was heated by LNG burner for 40 minutes (30 minutes after ambient temperature reached 800℃) in order to observe the behavior of *kobesh* at fire condition. Fire went out at 15 minutes after the burner was off. About 2 cm from the surface of the *kobesh* was transformed or decomposed and white silica (SiO_2) was found on the top.

CONCLUSIONS

When *kobesh* SR-T01 is used in the closed compartment, the pressure in the compartment will increase fairly high level. Therefore it is recommended that such a compartment should have some pressure relief device. *kobesh* SR-T01 has good thermal stability that could keep its neutron shielding capability for more than 20 years transport use below 150℃ with less than 5% weight and hydrogen loss.

It was confirmed that the silicone rubber-based neutron shielding material (*kobesh* SR-T01) has good neutron shielding capability and high long-term thermal stability.

REFERNCES

Taniuchi, H. et al., "Development of Rubber Type Neutron Shields for Transport/Storage Packaging", PATRAM'86, IAEA, 1986

Iida, T. et al., "Highly Effective Neutron Shielding for Transport/Storage Packaging", Nuclear Technology, Vol.2, No.1/3, pp.79-85, 1991