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THERMAL STABILITY AND RADIATION RESISTANCE OF SM-CO BASED PERMANENT MAGNETS

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Abstract – *We will review in this paper the recent data on thermal stability and radiation resistance of rare earth permanent magnets. Scanning electron microscopy analysis suggests that the affected surface layer of SmCo magnets is almost undetectable (less than 1 micron) after exposure to a temperature lower than 550^{o}C for 240 hours under vacuum. For SmCo T550 magnet samples with 10mm in diameter and 10mm long, magnetic properties do not change much up to its maximum operating temperature. SmCo based magnets have better neutron radiation resistance as compared to Nd-Fe-B type magnets. It is noted that the radiation resistance and thermal stability are somewhat related because the irradiation damage is most likely caused by a radiation-induced thermal spike. $Sm(Co,Fe,Cu,Zr)_z$ magnets do not show any noticeable changes in magnetic properties while $Nd_{13}Dy_2Fe_{77}B_8$ samples lost almost 100% of its magnetic flux with a neutron flux of 10^{16} n/cm^2. It is also worthwhile to point out that the magnetic properties of irradiated Nd-Fe-B type magnets are recoverable after re-magnetization, which indicates that radiation damage is caused by a thermal spike instead of microstructure changes.*

I. INTRODUCTION

Sintered $SmCo_5$, Sm_2TM_{17} and $Nd_2TM_{14}B$ magnets were developed in 1960s, 1970s and 1980s, respectively (TM: Transition Metals) [1-3]. $SmCo_5$ and Sm_2TM_{17} magnets have good thermal stability and radiation resistance while $Nd_2TM_{14}B$ magnets exhibit higher room-temperature magnetic properties. Rare earth permanent magnets have found applications in a variety of industries due to their superior magnetic properties. NASA applications include high power ion propulsion engines and alternators in high efficiency dynamic power converters.

In the high power ion engines, the electrons collide with Xe atoms, ionizing them. Permanent magnets create an axial magnetic field that extends the electron paths and increases the probability of an ionizing collision. Having a consistent magnetic field is essential for ion engine performance. These high power ion engines would operate at elevated temperatures under vacuum and radiation. In space, existent radiation comes from the trapped particles (electrons and ions) in the radiation (Van Allen) belts, solar flare protons and galactic cosmic rays. Figure 1 shows Xenon ion propulsion engine with high temperature magnet used in Deep Space I.[4]

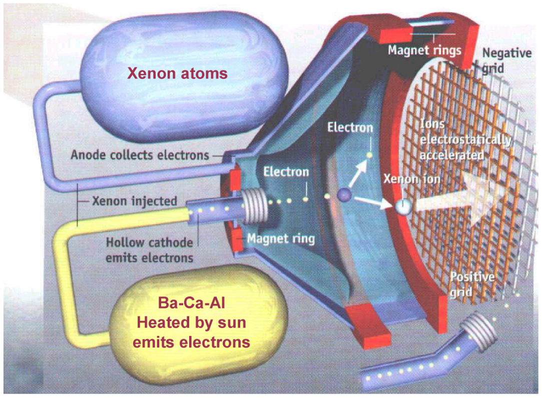

Fig. 1. Xenon ion propulsion engine with high temperature magnet used in Deep Space I [4]

The converters in high efficiency Stirling Radioisotope Generators (SRG) developed for NASA Space Science missions have operating temperatures below 150ºC. The performance of high intrinsic coercivity Nd-Fe-B magnets is acceptable below 150ºC, but their radiation resistance makes it very vulnerable.

The outstanding magnetic properties of SmCo based magnets—particularly, excellent stability over the widest range of environmental conditions—led to an exciting variety of applications, including also traveling wave tubes for communications, accelerometers and gyroscopes for guidance systems, power tools for medical applications, and motors and generators for aircraft engines.

Different applications require different magnet materials to satisfy their requirements. In this paper we will review the recent results on high temperature stability and radiation resistance of rare-earth permanent magnets.

II. MAGNETIC PROPERTIES OF HIGH TEMPERATURE MAGNETS

Prior to 1997, the best high temperature magnets available were limited to applications where temperatures did not exceed 300°C. Serious efforts to improve the high temperature magnetic properties of Sm-Co magnets began in 1995. A series of $Sm(Co_wFe_vCu_xZr_y)_z$ type magnets with linear demagnetization curves up to 550°C was developed in late 1990s.[5-10] Typical magnetic properties of some rare earth permanent magnets are shown in Table 1 for comparison.

TABLE I
Typical magnetic properties of high temperature rare earth magnets

Magnet Grade	Maximum Energy Product $(BH)_{max}$		Residual Induction B_r (nominal)		Coercive Force H_c (minimum)		Intrinsic Coercive Force H_{ci}		Maximum Operating Temperature
	MGOe	kJ/m^3	kG	mT	kOe	kA/m	kOe	kA/m	ºC
NdFeB N48	48	382	13.9	1390	10.5	836	>12	>955	70
NdFeB N40SH	40	318	12.5	1250	11.6	923	>17	>1353	150
NdFeB N30EH	30	239	11.0	1100	10.2	812	>30	>2388	200
SmCo 2:17-31	31.0	247	11.5	1150	10.5	835	>25	>1990	250
SmCo 2:17-27	27.5	219	10.8	1080	10.1	803	>25	>1990	300
UHT SmCo T400	24.0	191	10.2	1020	9.6	763	>25	>1990	400
UHT SmCo T450	21.5	171	9.6	960	8.9	708	>25	>1990	450
UHT SmCo T500	20.0	159	9.3	930	8.6	685	>25	>1990	500
UHT SmCo T550	16.0	127	8.5	850	7.5	598	>25	>1990	550

High-energy Nd-Fe-B type sintered magnets could not be used at elevated temperatures due to their low Curie temperature (312°C). In order to increase their intrinsic coercivity, which would improve their thermal stability, heavy rare earth elements, such as Dy and Tb, have to be used to replace light rare earth element Nd. However, the residual induction, B_r, and maximum energy product, $(BH)_{max}$, is reduced significantly with heavy rare earth substitution.[11]

Sm-Co based magnets have a high Curie temperature (750^o – 900^oC), and therefore can be used at high temperatures. The reversible temperature coefficient (RTC) of residual induction is only about –0.035%/°C for Sm-Co base magnets as compared to –0.110%/°C for Nd-Fe-B based magnets. Substitution of Sm by other heavy rare earth elements, such as Gd and Er, can further reduce the reversible temperature coefficient of residual induction to almost zero within certain temperature range, which led to many applications, such as inertial devices.

The recently developed ultra high temperature (UHT) Sm-Co magnets (T400, T450, T500, and T550 as shown in Table 1) can be used up to 550°C.

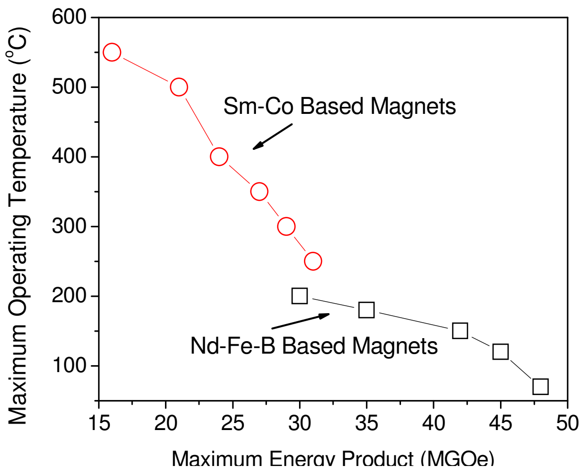

Figure 2. Maximum energy product versus maximum operating temperature for rare earth permanent magnets

Figure 2 shows the maximum energy products versus maximum operating temperature of Nd-Fe-B and Sm-Co magnets. The trade-off between the magnetic performance at room temperature and the maximum operating temperature is very obvious. SmCo magnets exhibit high maximum operating temperatures than Nd-Fe-B magnets.

III. THERMAL STABILITY IN AIR FOR HIGH TEMPERATURE MAGNETS

Magnets samples (ϕ10mm x 10mm discs) were placed in an oven at 300°C in air for over three years. The magnetic flux was monitored and the magnetic irreversible losses plotted in figure 3. All samples were uncoated except one set of T550 magnets, which was coated with aluminum by ion vapor deposition (IVD).

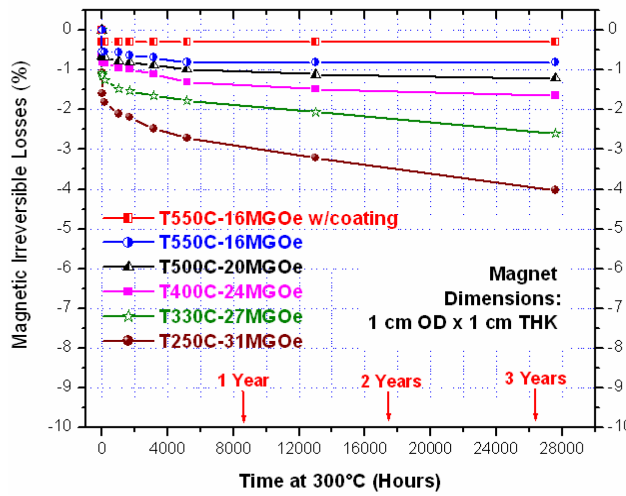

Figure 3. Thermal stability of various Sm-Co magnets at 300°C in air for more than three years

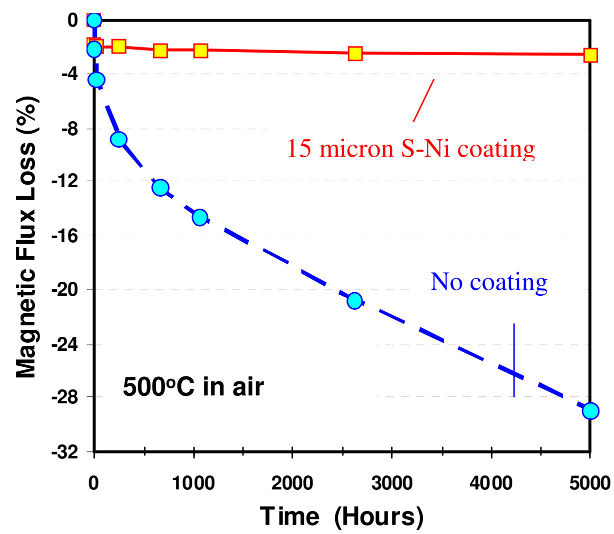

Figure 4. Magnetic flux loss for SmCo T500 magnets at 500°C in air for 5000 hours

Following initial thermal stabilization for two hours, these uncoated high temperature magnets, held at 300°C in air for more than three years, had losses of only about 0.3%. No detectable loss was measured for the magnets coated with aluminum IVD.[12-13] Magnetic losses are significant for non-coated T500 magnets[14] at 500°C in air, as is shown in Figure 4. The magnetic flux is reduced by about 30% for T500 magnets after 5000 hours at 500°C in air. A 15-micron surface S-Ni coating can effectively reduce the magnetic flux degradation at 500°C. Only about 2.5% flux reduction is observed for the coated sample, as shown in Figure 4. Coating is not necessary for SmCo magnets under 300^{o}C although coating could offer further surface protection from gradual oxidation. Magnets are handled extensively in many applications. Coating on the surface could also prevent chipping, which would be an added benefit. High temperature magnets are metallurgically stable at temperatures up to 550°C based on the experiments conducted recently (See Figure 4, 7, 8 and 9). More work is required to understand the thermal stability of these magnets beyond 5000 hours between 300 to 550^{o}C.

IV. THERMAL STABILITY AT ELEVATED TEMPERATURES UNDER VACUUM

The major challenge for magnets in space applications is the degradation caused by Sm depletion at high temperature under high vacuum.

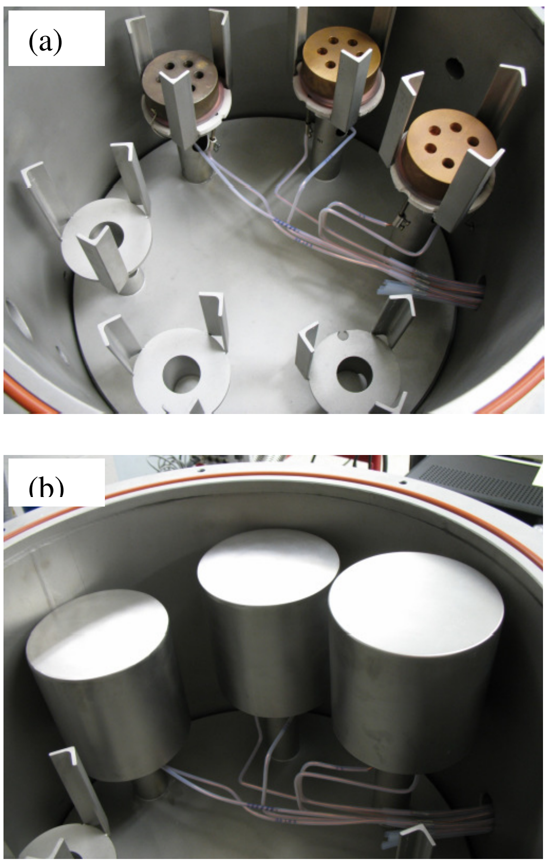

Figure 5: Top view of heater assembly inside the vacuum chamber (a), and final heaters assembly showing oxygen-free copper plates with lids inside the vacuum chamber (b). The lids protect the magnets and collect out-gassed material so that it does not coat the chamber wall.

Figure 6: Front view of the vacuum system for thermal stability studies

The magnetic degradation is a function of the temperature reached, time at temperature, vacuum level, the surface conditions of the magnets, and the composition of the permanent magnet material itself.

EEC designed and built a multi-platform high vacuum system for thermal stability studies at elevated temperatures under vacuum. This vacuum system consists of a VHS-6 Varian diffusion pump and two Duo-seal 1402 roughing pumps. The heater platforms fitted with oxygen-free copper sample holders were made to achieve high vacuum. The heater platforms, as shown in Figure 5, are of varying height in order to prevent out-gassed Sm from cross-contaminating magnet samples on surrounding heater plates. Each heater has independent temperature controller, therefore, experiments at a few different temperatures can be conducted in the same vacuum chamber at the same time. Figure 6 is a picture of the vacuum system.

Figures 7-9 show magnetic flux change with time at various temperatures under vacuum (10^{-5} Torr) in the chamber shown in figure 6 for different UHT Sm-Co based magnets. It is noted that the magnetic flux change is limited if magnets are only exposed to a temperature below its maximum operating temperature. It can be clearly seen that T550 magnets have the best thermal stability.

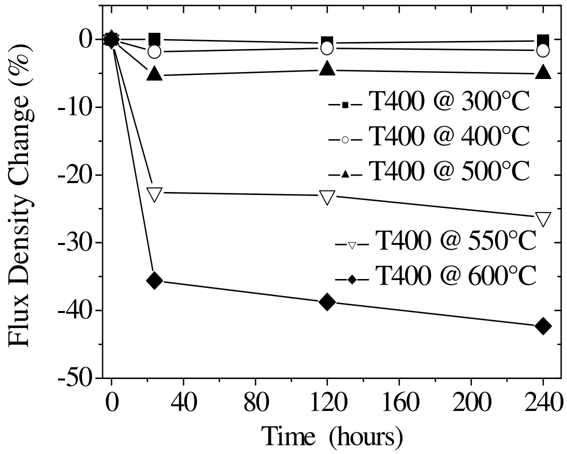

Figure 7. Magnetic flux change versus time at various temperatures under vacuum (10^{-5} Torr) for T400 UHT Sm-Co magnets.

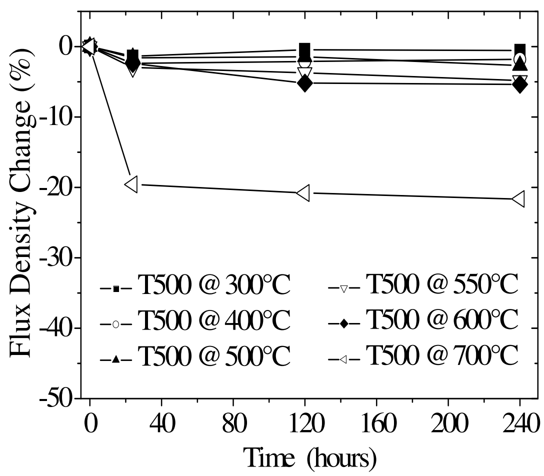

Figure 8. Magnetic flux change versus time at various temperatures under vacuum (10^{-5} Torr) for T500 UHT Sm-Co magnets.

Sm depletion is proved to be a problem at very high temperatures. Figure 10 shows the scanning electron microscopy image and local compositional analysis by energy-dispersive X-ray spectroscopy of a magnet sample after exposure to 700°C for 240 hours. The Sm-depleted surface layer is 30 microns in thickness. Of course the Sm vaporization will be a lot slower at lower temperatures, but the long-term stability would be affected when the operating temperature is above 300°C.

Experiments suggest that surface coating would act as a diffusion barrier, which would help improve thermal stability. As seen in figure 11, uncoated samples exhibits more flux loss than all coated samples. There are quite a few choices for surface diffusion barriers to prevent Sm depletion.

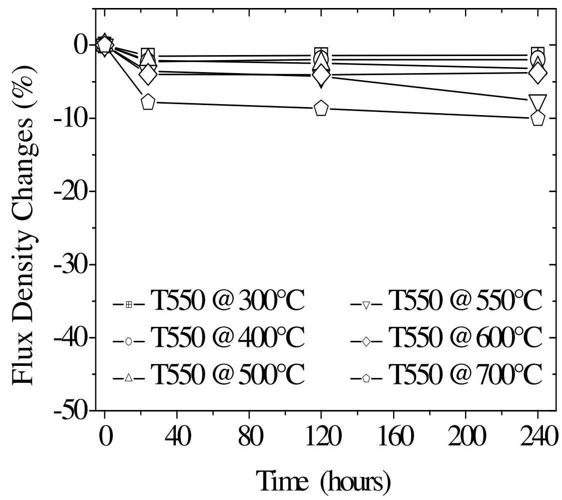

Figure 9. Magnetic flux change versus time at various temperatures under vacuum (10^{-5} Torr) for T550 UHT Sm-Co magnets.

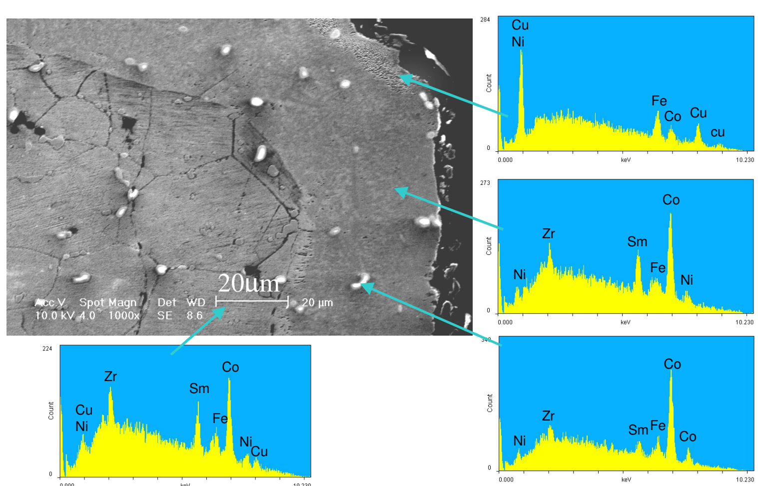

Figure 10. Microstructure and compositional analysis of the cross-section of T550 magnet after exposure to 700°C for 240 hours under a vacuum of 10^{-5} Torr

The saturation vapor pressure of Sm in high-temperature magnets is in the order of 10^{-10}, 10^{-7}, 10^{-5} and 10^{-4} Torr at 300, 400, 500 and 600°C, respectively. It should be noted that the saturation vapor pressure is very low (about 10^{-10} Torr) at 300°C, and therefore SmCo magnets can be used in vacuum at 300°C. At 400°C, the saturation vapor pressure is up to 10^{-7} Torr, which is still reasonably low if it is going to be used in a vacuum of only 10^{-5} Torr, but extensive testing may be required to verify their lifetime. At temperatures above 400°C, the saturation vapor pressure of Sm is getting closer to the vacuum level of the environment in space, and therefore surface treatment is required for applications at temperatures above 400°C. Surface diffusion barrier can be applied by eletroless/electrolytical plating, ion vapor deposition (IVD), and ion beam assisted deposition (IBAD). The bonding strength between surface diffusion barrier and the magnet matrix is a critical factor to guarantee 10-years service life at a temperature of at least 400°C and in a vacuum of 10^{-5} Torr or higher.

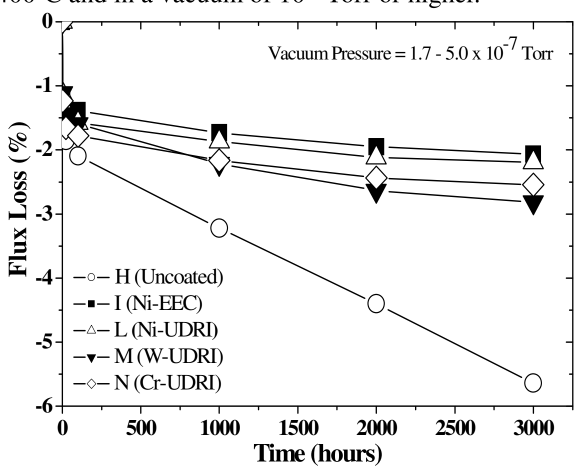

Figure 11. Average flux loss for T500C magnets at 400°C in vacuum

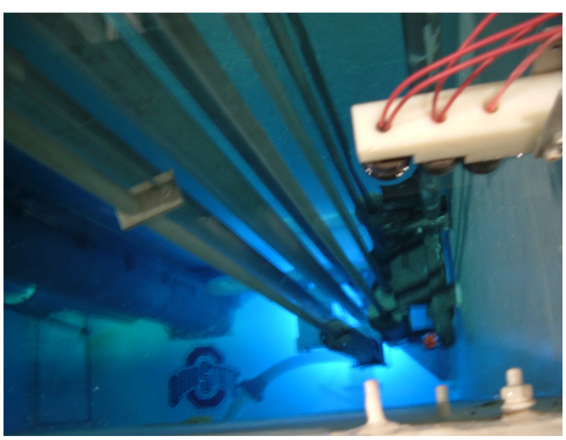

Figure 12: OSU Research Reactor at full power (450 kW) during the radiation experiment.

V. RADIATION RESISTANCE OF RARE EARTH MAGNETS

The irradiation experiments were conducted using the nuclear reactor facility at Ohio State University (OSU) in a cooperative effort between EEC, UDRI and OSU. Figure 12 shows the OSU research reactor at full power (450 kW) during this experiment.

Magnet samples were exposed to total neutron flux of 10^{16}, 10^{17}, 10^{18}, and 10^{13} n/cm^2, respectively. Thermocouples were used to monitor the temperature change during the irradiation experiments, as shown in Figure 13. The magnetic flux of Nd-Fe-B based magnets is reduced by about 1% with 10^{13} n/cm^2 irradiation. Once the radiation level exceeds 10^{16} n/cm^2, Nd-Fe-B magnets would lose 100% of its magnetic strength.

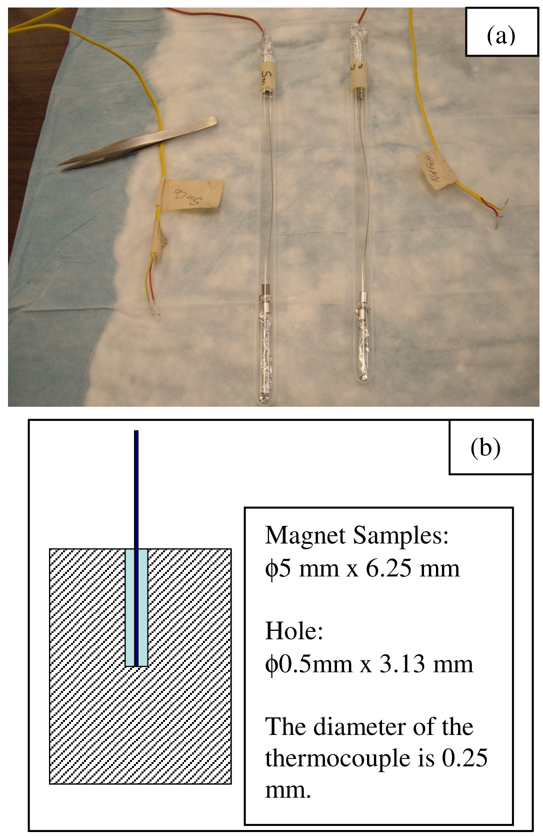

Figure 13: Magnet samples, thermocouples and quartz tubes for the irradiation experiments
(a) Picture showing sample and thermocouple assembly and (b) sketch showing the position of thermocouple inside the sample.

The magnetic properties of Sm-Co samples were not affected with irradiations up to 10^{18} n/cm^2. The normalized magnetic flux data is plotted against neutron irradiation doses in Figure 14, which included data from other groups for comparison. As can be seen, Sm-Co based magnets have superior radiation resistance as compared to Nd-Fe-B based magnets. Our observation is consistent with some earlier reports.[15-17]

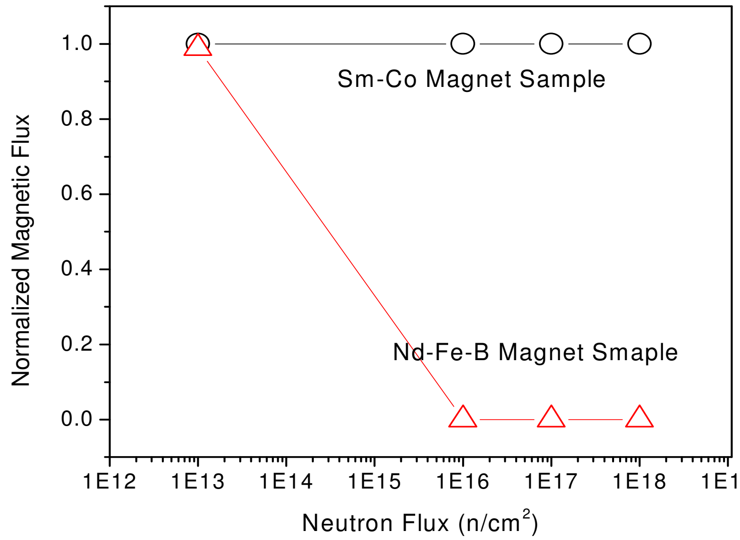

Figure 14. Normalized magnetic flux of permanent magnets versus neutron flux

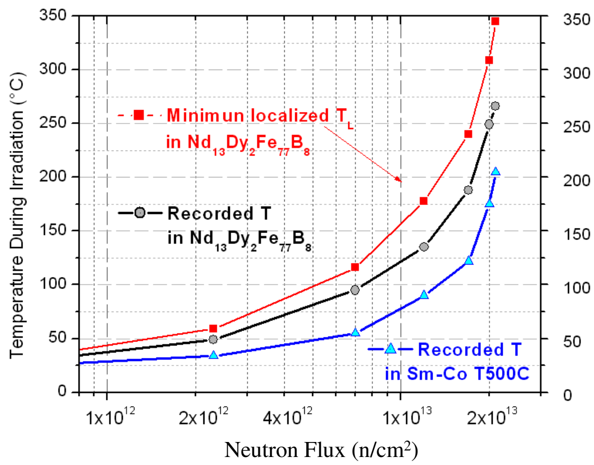

Figure 15. Recorded temperatures caused by thermal effect of radiation vs. neutron flux.
(The minimum localized temperature T_L in $Nd_{13}Dy_2Fe_{77}B_8$ magnets was deduced from magnet flux loss.)

The irradiated Nd-Fe-B samples were re-magnetized and re-tested. It was found that the magnetic recovery was 100% for the samples irradiated with 10^{16} n/cm^2, which indicates that irradiation caused no microstructure changes. The recovery rates were 97.5% and 95% for the samples irradiated with 10^{17} and 10^{18} n/cm^2, which indicates some microstructure damage to the Nd-Fe-B magnets. The magnetic recovery after re-magnetization suggests that the radiation damage is largely due to thermal effect rather than metallurgical degradation.

Figure 15 shows the recorded temperatures inside magnet samples during irradiation experiments caused by thermal effect of radiation at various neutron irradiation levels. The minimum localized temperature in $Nd_{13}Dy_2Fe_{77}B_8$ magnets was deduced from magnet flux loss.

As can be seen that the sample temperature exceeds the maximum operating temperature (about 150^{o}C) and approaches the Curie temperature (310^{o}C) of these $Nd_{13}Dy_2Fe_{77}B_8$ magnets, which explains why they lost all of their magnetic flux after exposure to high level of neutron dosage and why they can be re-magnetized afterwards.

On the other hand, the Curie temperature of most SmCo based 2:17 magnets is around 820^{o}C, which is much higher than the temperature measured inside the sample during the irradiation experiments. This explains why Sm-Co based magnets do not show degradation in radiation environment.[18] Good radiation resistance of Sm-Co magnets proved to be an advantage in space applications.

VI. CONCLUSIONS

Sm-Co based magnets have superior thermal stability and radiation resistance as compared to Nd-Fe-B based magnets. Nd-Fe-B based magnets are not recommended for applications above 150^{o}C. Sm-Co based magnets can normally be used up to 300^{o}C without significant magnetic degradation over a long period of time.

Magnetic flux is barely changed after thermal exposure to 300^{o}C in air for three years for SmCo magnets. The newly developed ultra high temperature magnets can be used up to 550^{o}C, but surface diffusion barrier is needed to prevent Sm depletion when the application temperature is above 400^{o}C.

$Sm(Co,Fe,Cu,Zr)_z$ magnets do not show any noticeable changes in magnetic properties while $Nd_{13}Dy_2Fe_{77}B_8$ samples lost almost 100% of their magnetic flux with a neutron flux of 10^{16} n/cm^2. It is noted that the radiation resistance and thermal stability are somewhat related because the irradiation damage is most likely caused by a radiation-induced thermal effect for Nd-Fe-B magnets. The metallurgical damage from neutron irradiation up to 10^{16} n/cm^2 is very limited. An accelerated testing methodology may be required to estimate the service life of permanent magnets in space environment.

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REFERENCES

1. G. Hoffer and K. Strnat, "Magnetocrystalline Anisotropy of YCO_5 and $Y2Co_{17}$", IEEE Trans. **Mag-2**, 487, (1966)

2. Nagel, Perry and Menth, "Permanent magnets based on $Sm(Co, Cu, Fe)_z$", IEEE Trans. Mag-**11**, 1423, (1975)

3. M. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura and K. Hiraga, "Permanent magnet materials based on the rare earth-iron-boron tetragonal compounds (invited)", IEEE Trans. Magn., **MAG-20**, 1584 (1984)

4. M. DiChristina, "Deep Space Traveler – Ion Propulsion Takes off for Deep Space", Popular Science, page 64, July 1998

5. J. F. Liu, Y. Ding, Y. Zhang, D. Dimitrar, F. Zhang and G. C. Hadjipanayis, "New rare-earth permanent magnets with an intrinsic coercivity of 10 kOe at 500^{o}C", Journal of Applied Physics, **85**, 5660 (1999)

6. J. F. Liu, Y. Zhang, D. Dimitrov and G. C. Hadjipanayis, "Microstructure and high temperature magnetic properties of $Sm(Co,Fe,Cu,Zr)_z$ (z=6.7-9.1) permanent magnets", Journal of Applied Physics, **85,** 2800 (1999)

7. J. F. Liu, Y. Ding, and G. C. Hadjipanayis, "Effect of iron on the high temperature magnetic properties and microstructure of $Sm(Co,Fe,Cu,Zr)_z$ permanent magnets", Journal of Applied Physics, **85,** 1670 (1999)

8. J. F. Liu, T. Chui, D. Dimitrov and G. C. Hadjipanayis, "Abnormal temperature dependence of intrinsic coercivity in $Sm(Co,Fe,Cu,Zr)_z$ powder materials", Applied Physics Letters, **73**, 3007 (1998)

9. G. C. Hadjipanayis, W. Tang, Y. Zhang, S. T. Chui, J. F. Liu, C. Chen, and H. Kronmuller, "High temperature 2:17 magnets: relationship of magnetic properties to microstructure and processing", IEEE Trans. On Magn., **36**, 3382 (2000)

10. Y. Zhang, M. Corte-Real, G. C. Hadjipanayis, J. F. Liu, M. S. Walmer and K. M. Krishnan, "Magnetic hardening studies in sintered Sm(Co,Fe,Cu,Zr)z 2:17 high temperature magnets", Journal of Applied Physics, **87**, 6722 (2000)

11. M. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura, and K. Hiraga, "Permanent magnet materials based on the rare earth-iron-boron tetragonal compounds (invited)", IEEE Trans. Magn. **MAG-20**, 1584 (1984)

12. C. Chen, M. H. Walmer and S. Liu, "Thermal stability and the effectiveness of coatings for Sm-Co 2:17 high temperature magnets at temperatures up to 550oC", IEEE Trans. Magn., **40**, 2928 (2004)

13. J. F. Liu and M. H. Walmer, "Thermal stability and performance data for Sm-Co 2:17 high

temperature magnets on PPM focusing structures", IEEE Trans. On Electron Devices, **52**, 899 (2005)

14. C. H. Chen, M. Huang, A. Higgins, D. Lee, and S. Liu, "Improved mechanical properties and thermal stability of Sm-Co high temperature magnets resulting from surface modifications", Proc. of 19th Int'l Workshop on Rare earth Permanent Magnets and Their Applications, Beijing, China, pp.112-118, (2006)

15. J. R. Cost, R.D. Brown, A.L. Giorgi, and J.T. Stanley, " Effects of neutron irradiation on Nd-Fe-B magnetic properties", IEEE Trans. **Mag. 24**, 2016 (1988).

16. D. Barlow, R. Kraus, and M. Borden, Los Alamos National Lab. Report LA-UR-97-3370 (1997).

17. J. Alderman, P. Job, R.C. Martin, C. Simmons, G.D. Owen, and J. Paul, Research report, LS-290 (2000).

18. C. H. Chen, J. Talnagi, J. F. Liu, P. Vora, A. Higgins, and S. Liu, "The effect of neutron irradiation on Nd-Fe-B nad Sm_2Co_{17}-based high temperature magnets", IEEE Trans. On Magnetics, **41**, 3832 (2005).