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Nuclear Graphite Inhomogeneity as Revealed by Nonuniformity of Oxidation Rates and New Billet Qualification Requirements

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1. Introduction

The effects of oxidation are specially considered, along with irradiation, abrasion and erosion, fatigue, and buckling for the design of graphite core components in high temperature gas-cooled reactors (HTGR). The design code ASME Section III, Div. 5, HHA-3140, HHA-3141 requires data on the relative changes in strength, elastic modulus (dynamic), and thermal conductivity as a function of oxidative weight loss (2%, 4%, 6%, 8%, 10%) [1].

On the other hand, with the new interest in advanced nuclear graphite grades for HTGR, a large number of oxidation rate (OR) measurements of various nuclear graphite grades became available from various sources. Comparison of these data results in frequent observation of a large scatter in OR, not different from the large variability of mechanical and physical properties.

However the variability observed in OR for a given grade graphite, likewise the mechanical strength for example, has not been thoroughly evaluated for the design and operation of graphite core components (GCC) in HTGR. Selection of samples (coupons) with similar OR for oxidation design data (ASME HHA-II-2000 **MDS**) will be the first challenge for GCC designers.

In this study, a limited number of OR data on some nuclear graphite grades for HTGR are compared, and the significance of results is evaluated in view of ASME HHA-II-2000 Materials Data Sheet Form for oxidation.

2. Graphite manufacture and microstructure inhomogeneity.

Graphite shows a large scatter in the physical and mechanical properties owing to its ingredients and manufacturing process (Fig. 1, Fig. 2). Considering this characteristics of graphite, namely its heterogeneity or inhomogeneity in microstructure, a probabilistic design method based on the Weibull distribution of strength was adopted in the 2011 edition of ASME graphite code (Section III, Div. 5, HAB, HHA) (Fig. 2). During the design of graphite core components (GCC) having fracture probability, characterization of the variability (scatter) of physical, mechanical properties between different lots, different billets, and different positions from within a single billet affecting the integrity or safety of GCC is important [2].

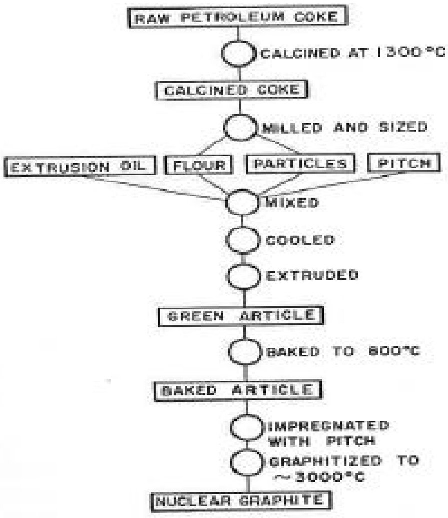
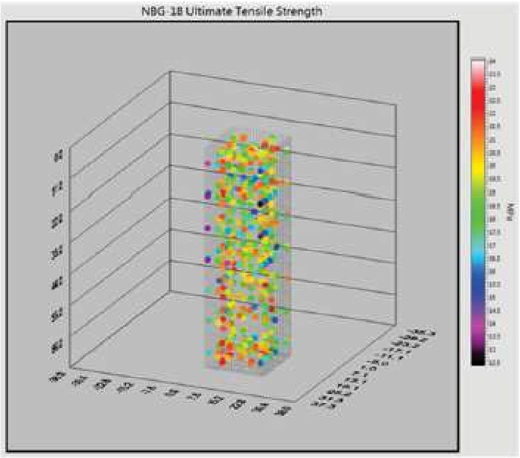
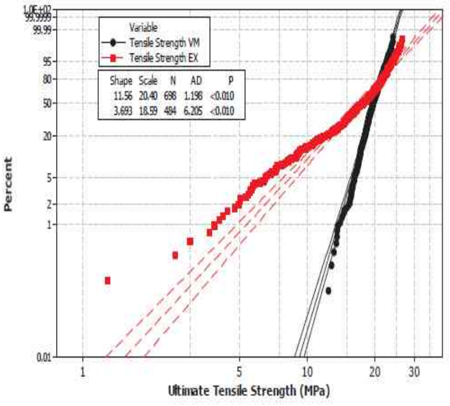


Fig.1 Graphite manufacturing process.



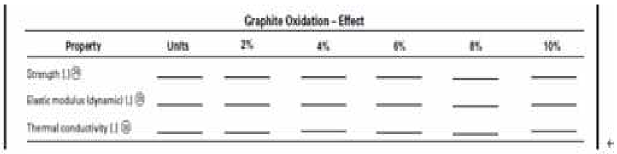
(a)



(b)

Fig. 2 3-D ultimate tensile strength (UTS) distribution of NBG-18 (**a**) and Weibull distributions of the tensile strengths of NBG-18 (Black) and PCEA (**b**) [2]..

It is noticeable that most of Gen. IV GWG (graphite working group) member institutes have been involved in characterizing the variability (inhomogeneity) of physical and mechanical properties, but not of oxidation, in their graphite grades selected for study. This includes the variability between different lots, different billets, and different positions from within a single billet. Fig. 3 shows the graphite design data form necessary for GCC design considering oxidation effects [1].


Graphite Oxidation – Effect

Property	Units	2%	4%	6%	8%	10%
Strength [ ]	____	____	____	____	____	____
Elastic modulus (dynamic) [ ]	____	____	____	____	____	____
Thermal conductivity [ ]	____	____	____	____	____	____

Fig. 3. ASME Section III Division 5, ARTICLE HHA-II-2000 Material Data Sheet Form on graphite oxidation.

3. Observation of OR data scattering (inhomogeneity) in nuclear graphite grades for HTR.

3.1 KAERI Observation [3].

KAERI obtained OR data from 3-zone furnace (600-1100℃, specimen: cylinder, 25.4(dia) x 25.4(h) mm, air flow rate: 10 L/min) based on ASTM D 7542-15 [4]. The results showed large differences in ORs for the same billet of NBG-18, but not for the same billet of NBG-25 as seen in **Fig. 4**. Thus, while the ORs reported in 2008 and 2017 are the same for NBG-25 both at 700℃ and 800℃, the ORs of NBG-18 reported in 2017 are far higher than those of 2008, and even higher than ORs of NBG-25 at both 700℃ and 800℃.

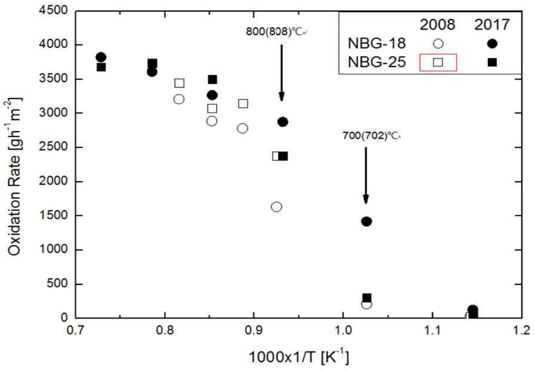


Figure 4. Oxidation Rate (OR) – Temperature Relationship for NBG-18 and NBG-25 obtained in 2008 and 2017 [3].

3.2 University of Missouri Observation [5].

J. Lee et al. reported OR data (Fig. 5) for nuclear graphite grades for HTGR. They obtained OR data by TGA (600-1600°C, 0.05 L/min of dry medical-grade air, 12.5 mm cubes). It is seen in Fig. 5 that all the OR data are quite comparable (similar) with those reported by other studies, except the OR of NBG-18 at 1200°C. To confirm the odd OR behavior of NBG-18 at 1200°C, they repeated the TGA experiment at the same condition for NBG-18 and confirmed good repeatability of the data, and thus ensured that there were no outliers including the OR at 1200°C (Fig. 6).

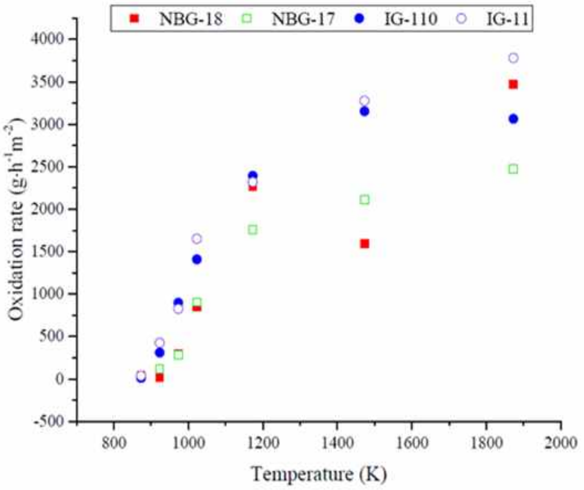


Fig. 5 Comparison of oxidation rate behaviors of nuclear graphite grades for HTGR in air.

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* ASTM D 7542-09: Standard Test Method for Air Oxidation of Carbon and Graphite in the Kinetic Regime

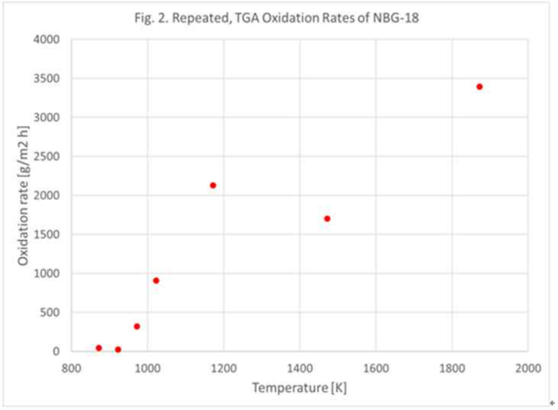

Fig. 6. Repeated TGA results for the OR of NBG-18 at Univ. of Missouri.

3.3 EU Raphael Project Observation (K. Kuhn, et al, 2006) [6].

Within the RAPHAEL (**Re**Actor for **P**rocess heat, **Hy**drogen **A**nd **EL**ectricy generation) framework, oxidation experiments were performed on graphites selected for the irradiation tests in the HFR in Petten.

Fig. 7 shows the NBG-10 block (billet) cut for sample preparation, and Fig. 8 shows burn off (%)-time(h) behavior for samples extracted from different locations at 750°C (R, M, F). NBG-18 is a vibro-moulded grade of graphite manufactured from similar ingredients as NBG-10 (which is made by extrusion).

Fig. 7. NBG-10 Block with parts of extracted samples (R, M, F) [6].

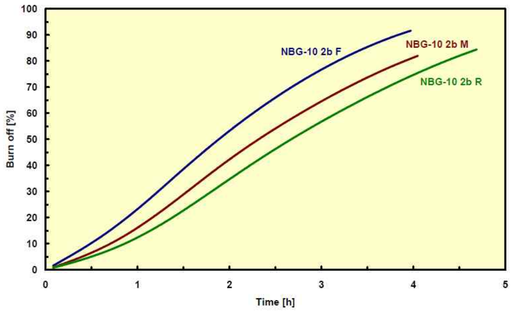

Fig. 8. Burn off vs. time of NBG-10 samples extracted from different locations (750°C) [6].

While no OR – temperature data are presented in the report, Fig. 8 implies that the differences in burn off (%)–time (h) behavior should be attributed to the inhomogeneity in OR among samples from a NBG-10 block (Fig. 7).

In a more detailed report [7] Hinsen et al. compared the OR vs. weight loss curves at three temperatures (650, 700, and 750 °C) for three cylinders of, respectively, NBG-10 and NBG-18 (Fig. 9). While there was some variation between the three NBG-10 specimens, the scatter of NBG-18 rates was stronger in identical conditions. The same authors noted however that this “inconveniently high” variability may have been caused by microstructure inhomogeneity of the billets produced on a small scale.

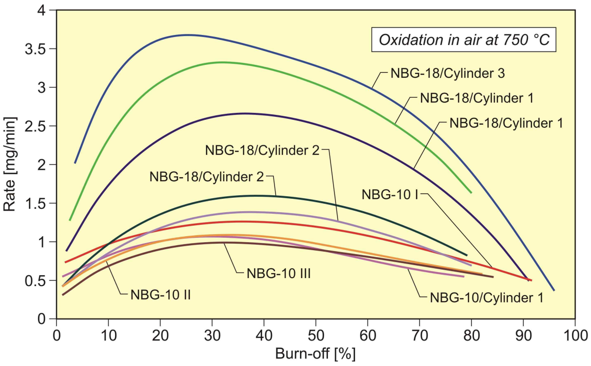

Fig. 9. Comparison of OR vs. burn off curves for oxidation in air of NBG-10 and NBG-18 specimens [7].

In addition to the two examples discussed above, similar observations showing inhomogeneities in ORs of nuclear graphite (or billets) have also been reported by Wei-Hao Huang, et al [8] and by a nuclear graphite manufacturer in a private communication at INGSM-18, Baltimore, USA, Sept. 17-21, 2017.

4. Technical Requirements for Reliable OR Data

All the observations above strongly suggest that several graphite grades also have distributions (scatter, inhomogeneity) in OR as they have for mechanical properties (for example, tensile strength). This observation is not surprising in that both the observation of scatter or inhomogeneity in strength and OR are attributed to the common ground, i.e., inhomogeneity of the microstructure of nuclear graphite grades. Graphite shows a highly inhomogeneous microstructure caused by its ingredients and the manufacturing process without melting.

Present observations of the scatter in OR in a grade (billet) or between grades (billets) may lead to sample (coupon) selection issue in view of GCC design data preparation for oxidation tests. ASME code HHA-II-2000 **MDS** Forms (Fig. 3) requires selection of coupons homogeneously oxidized at 2-10 % weight loss and the same OR for their subsequent strength, elastic modulus, and thermal conductivity measurements. It is important to stress that the design issue related to the scatter in mechanical properties (strength) of nuclear graphite has been resolved by the probabilistic design approach based on the Weibull modulus during preparation of the ASME Section III, Div. 5 HHA. Detailed implication of the present observation (i.e., OR distribution in a graphite grade) on the design and operation of GCC may need further study.

Here, the authors suggest introduction of some requirements that can help screening out billets of unusual oxidation behavior from the blocks used for GCC manufacture. That would require modification of the relevant ASTM graphite materials specification (ASTM D-7219 [9] or ASTM D-7301 [10]) or ASME HHA design rule as an easy technical solution to account for OR distribution.

5. Summary

This study shows that several nuclear graphite grades developed for HTGR exhibit scatter in OR (oxidation rate) much like the physical and mechanical properties of the same grades. The implication of OR scatter on the design and safe operation of GCC may need further investigation. As an example, regarding the HHA-II-2000 MDS on oxidation, if the OR distribution in a grade is confirmed, then it should be determined whether the specimens used for MDS are of same OR or not. For a safe design and operation of GCC, the inclusion of new requirements in the relevant ASTM graphite materials specification (ASTM D-7219 or D 7301) or ASME GCC design rule (Section III, Div. 5 HHA-3141) is suggested in order to help screening out billets of unusual oxidation behavior (OR) from blocks used for GCC manufacture.

Acknowledgements

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