https://doi.org/10.46813/2024-152-079

SiC-BASED CERAMICS AS A CONTAINER MATERIAL FOR DEEP GEOLOGICAL DISPOSAL OF RADIOACTIVE WASTE*

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In this work the research of Cr-doped SiC ceramics as a promising material for containers for the deep geological disposal of radioactive waste was carried out. Samples were investigated using XRD, Raman spectroscopy, microhardness measurements, nanoindentation and corrosion resistance tests. Obtained results showed that addition of 0.3…0.7 wt.% of Cr improves the mechanical properties of SiC ceramics. Corrosion tests in distilled water at T = 90 °C and immersion time of up to 4300 h revealed that Cr addition slows down corrosion processes in SiC ceramics. The average dissolution rate of SiC(Cr) samples in water is quite low and does not exceed the value of 0.16 μm/year.

PACS: 28.41.Kw; 81.05.Je

INTRODUCTION

A sealed container (or canister) for the disposal of high-level radioactive waste (HLW) and spent fuels (SF) is a key component of all deep geological repository programs. The container constitutes the only barrier within the overall multi-barrier disposal system which provides complete confinement of radionuclides. Therefore, attention is frequently focused on the performance of the canister, specially concerning the length of time during which the material stability and thus the barrier function can be guaranteed. Scientific and technological progress can improve both the performance of containers as well as the robustness of lifetime predictions. For many national radioactive waste disposal programs, optimization of these aspects is of primary importance. Therefore, nowadays R&D of container materials for the safe management of such waste is important and relevant [1].

There are a number of different concepts of containers for geological disposal of RAW, proposed around the world. Their configuration mainly depends on the type of waste disposal, the surrounding geological environment and the materials of the containers, aimed at minimizing the risks of their tightness failure [2]. For example, the geometric dimensions of containers differ depending on the type of waste: SF assemblies usually have length up to 4.5 m, while double-glazed cylinders for HLW usually have length up to 1.34 m. Traditionally, copper (Sweden and Finland) and carbon steel (Belgium, France, Switzerland, Czech Republic, Slovakia, and Hungary) are used for such containers.

One of the main issues in the operation of radioactive waste containers is safety, specifically to prevent dispersion of radionuclides to the surrounding environment. It is obvious that the release of radionuclides is possible at tightness failure, which occurs through the dissolution of the container material (corrosion), that is, a decrease in the wall thickness, which can lead to mechanical destruction of the container, and as a consequence – dispersion of radioactive waste into the environment [3].

The reduction of the wall thickness by environmentally induced corrosion is an important input to the structural analysis for some canister concepts. As the thickness reaches a critical value, stresses can lead to plastic collapse. The intrinsic materials properties can also be altered by hydrogen uptake, neutron embrittlement or preferential leaching/dissolution, which often leads to a reduction of the fracture toughness and to a larger risk of mechanical failure.

An overview of the currently planned container concepts and their expected exposure conditions showed that copper (e.g., Sweden, Finland, Canada, Korea, Taiwan) and carbon steels (e.g. Belgium, France, Switzerland, Czech Republic, Japan, Slovakia, Hungary) are the container materials that have been traditionally considered for the disposal of SF/HLW in countries with advanced disposal programs. The feasibility of containers made from these materials has been demonstrated and the required manufacturing technology is available and mature.

While steels provide a strong solution for this application, corrosion under anoxic conditions yields hydrogen gas which moves away from the canister surface by mass transport processes through both the engineered barriers of the repository and the geological barrier. In a closed system, such as a closed geological disposal facility, the gas can accumulate to the point of creating overpressure. All of the listed container materials have metallic conductivity, and therefore they prone to local electrochemical corrosion (pitting, intercrystalline and crevice corrosion), which is their significant drawback [4]. In order to provide alternative solutions to the use of steels for containers and thus limit the production of hydrogen in the long term, alternative materials to non-alloy steels have been studied in recent years in different countries.

Recent developments (e.g., copper coatings) considered in Canada and investigated in Switzerland [5], France and Japan have demonstrated that container optimization is indeed possible. Further alternative and novel container materials are also under consideration (e.g., steels with more controlled composition, Cu-based alloys and composites, ceramics, Zr alloys) [6, 7].

*Based on the results of KIPT's participation in EURAD project under Euratom research and training programme 2014–2018.

One of the prospective canister materials is silicon carbide (SiC), which is characterized by a strong Si-C ionic-covalent bond (5 eV), which results in unique mechanical (hardness up to 30 GPa) and physico-chemical properties. So hardness of SiC reaches up to 30 GPa, it practically does not interact with etchants (up to 400 °C) and has high inertness to chemical and radiation exposure [8]. Silicon carbide interacts with oxygen only at high temperatures; up to 1000 °C oxidation occurs very slowly, the maximum operating temperature in an oxidizing atmosphere is up to 1500 °C, and in an inert environment – up to 2700 °C [9]. Also SiC has high wear resistance and mechanical stability at high temperatures, high thermal conductivity and low coefficient of thermal expansion [10, 11].

Possessing such properties, SiC-ceramic is undoubtedly a promising (alternative) container material for RAW deep-geological disposal. But it should be noted that additional studies of long-term corrosion processes in the conditions similar to geological disposal (T = 90 °C) are also needed.

The purpose of this article is to summarize the current state of the KIPT research within the framework of EURAD WP15 ConCorD (Container Corrosion under Disposal Conditions) in the field of SiC ceramics.

MATERIALS AND METHODS

When carrying out the research, we used test materials based on both pure SiC and chromium alloyed to improve the physico-mechanical properties.

Commercial SiC powder with an average particle size of 440 nm manufactured by Superior Graphite Co (USA) was used as the main raw material. Metallic Cr powder (purity 99.2%, particle size ≤ 125 μm) was used for SiC alloying. These powders were combined to obtain mixtures with the following Cr content (wt.%): 0.3, 0.5, 0.7, and 0.9. Powder mixtures were blended by ball-milling in liquid medium for 3 h. After drying mixed powders were sintered in laboratory hot pressing (HP) facility using following technological parameters: temperature T = 2000…2100 °C; exposure t = 30 min; pressure P = 40 MPa and heating rate v ~ 200 °C/min. Processing details are available in our previous publication [12].

As the result SiC(Cr) square slabs size of 25x25x4 mm with different Cr content (0.3…0,9 wt.%) were obtained.

The density of sintered samples was measured via pycnometer method.

Crystal structure and phase composition of samples was determined by XRD analysis. Diffraction patterns were collected using DRON-4-07 diffractometer in filtered Cu-Kα radiation (λ = 1.54187 Å).

Raman scattering measurements of samples were performed using Renishaw inVia spectrometer with Ar^+ laser excitation (λ = 514 nm).

Microhardness of the samples was measured by microhardness tester LECO LM700AT at a load of 200 g with holding time of 14 s.

Nanohardness of SiC(Cr) samples was determined by nanoindentation using the Nano Indenter-G200 system (Agilent Technologies, USA) equipped with Berkovich diamond tip. The depth of indentation was approximately 500 nm.

Long-term corrosion resistance tests were performed in distilled water at T = 90 °C (conditions close to geological disposal ones). Samples were placed in a container with distilled water for a total immersion time of 4300 h. After certain time intervals, samples were weighed on analytical balances. Before weighing samples were dried in dry air at 120 °C for 5 min.

RESULTS AND DISCUSSION

The appearance of obtained SiC(Cr) samples is shown in Fig. 1. The results of the density measurements are summarized in Table 1.

Fig. 1. Obtained SiC(Cr) samples (25x25x4 mm)

Table 1

Density of SiC(Cr) samples

Samples	Measured density, g/cm^3	From theoretical density of pure SiC, %
Pure SiC	3.161	98.5
SiC (0.3 % Cr)	3.108	96.8
SiC (0.5 % Cr)	3.181	99.1
SiC (0.7 % Cr)	3.167	98.7
SiC (0.9 % Cr)	3.129	97.5

Obtained results show how the change in the Cr concentration affects the density of SiC(Cr) samples. The maximum values 3.181 and 3.167 g/cm^3 were obtained in samples with a Cr content of 0.5…0.7 wt.%. A further increase in the Cr content to 0.9 wt.%, on the contrary, leads to the decrease in density. This may be related to the evaporation of Cr during the HP process, since its saturated vapor pressure when heated in a vacuum is several orders of magnitude higher. This phenomenon leads to intensive Cr evaporation and accelerates its mass exchange through the gas phase during the sintering, which also improves the uniformity of Cr distribution throughout the sample volume.

XRD analysis revealed that phase composition of all studied samples is almost identical (Table 2); as an example, the diffraction pattern of SiC(Cr) with the highest Cr content (0.9 wt.% Cr) is shown in Fig. 2.

Table 2

Phase composition of SiC(Cr) samples

Cr, wt.%	Phase	Content, wt.%	Lattice parameters, Å
0.3	SiC-6H	94.5	a = 3.080; c = 15.113
	SiC-4H	2.4	a = 3.078; c = 10.061
	C	3.1	a = 2.46; c = 6.75
0.5	SiC-6H	95.5	a = 3.080; c = 15.112
	SiC-4H	2.8	a = 3.079; c = 10.064
	C	1.7	a = 2.46; c = 6.71
0.7	SiC-6H	94.0	a = 3.080; c = 15.114
	SiC-4H	2.3	a = 3.079; c = 10.061
	C	3.7	a = 2.46; c = 6.76
0.9	SiC-6H	91.1	a = 3.080; c = 15.114
	SiC-4H	2.9	a = 3.079; c = 10.064
	C	6.0	a = 2.46; c = 6.75

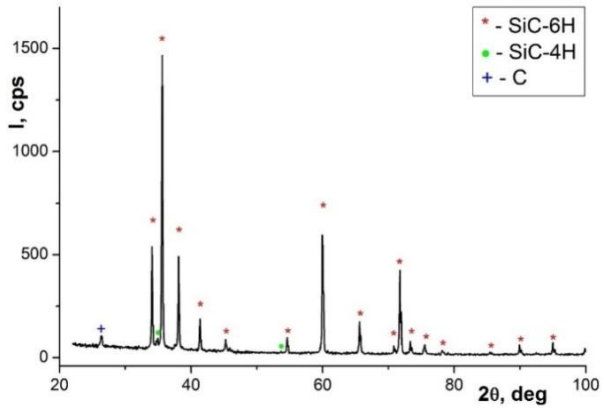

Fig. 2. Diffraction pattern of the SiC (0.9 wt.% Cr) sample

Analysis established the presence of 2 SiC polytypes (6H and 4H) in all Cr-doped samples, as well as a small amount of carbon C. The main constituent phase is SiC-6H (weight fraction is about 96%, lattice parameters are: a = 3.080 Å; c = 15.112 Å). It should be noted that 4H and 6H polytype modifications of SiC are identical in their physico-mechanical and electro-chemical properties [13]. Therefore, a trace of SiC-4H polytype in the samples does not affect their properties. A small amount of carbon is detected on the surface of the samples due to their contact with the graphite mold. Also, it is important to note the absence of chromium Cr peaks on diffraction patterns (3 strongest Cr peaks are expected to be at 2θ angles of 44.39, 64.58, and 81.73°). Chromium is a heavier element than silicon and carbon and has a higher "scattering capability" than SiC. Therefore, with higher Cr content (0.9 wt.%) its diffraction peaks should be detected. On the other hand, Cr is a strong carbide-forming element and the absence of peaks related to chromium may indicate the formation of chromium carbides, the "scattering capability" of which is much less than that of Cr.

The Raman spectra of pure SiC and SiC(Cr) samples are presented in Fig. 3. These spectra feature peaks at 767.5 and 788.0 cm^{-1}, which correspond to the 6H–SiC polytype. Increase in chromium content (> 0.7wt.% Cr) leads to a broadening of these peaks, which may indicate the presence of an amorphous phase [14, 15].

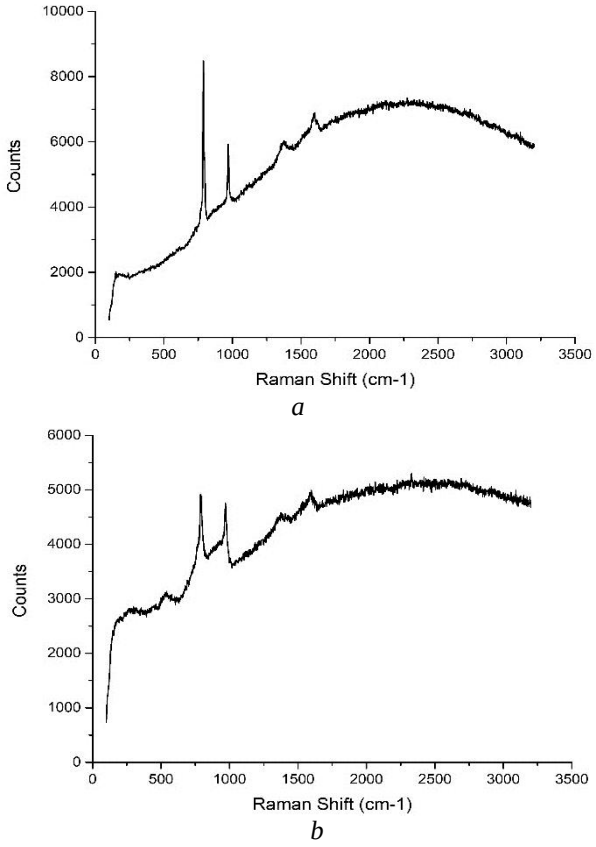

Fig. 3. Raman spectra of samples: a – pure SiC; b – SiC with 0.9 wt.% Cr

The results of microhardness measurements are shown in Fig. 4. Microhardness of pure silicon carbide is 22.8 GPa, which corresponds to the known literature data (20…26 GPa) [13, 16].

Addition of chromium to SiC increases the microhardness of samples, which reaches the maximum value of 25.5 GPa at chromium content of 0.5 wt.%. Further increase in Cr concentration up to 0.9 wt.% results in a decrease in microhardness of SiC(Cr) to 21.7 GPa. Such behaviour can be explained by the formation of chromium carbides and/or silicides at higher Cr concentrations.

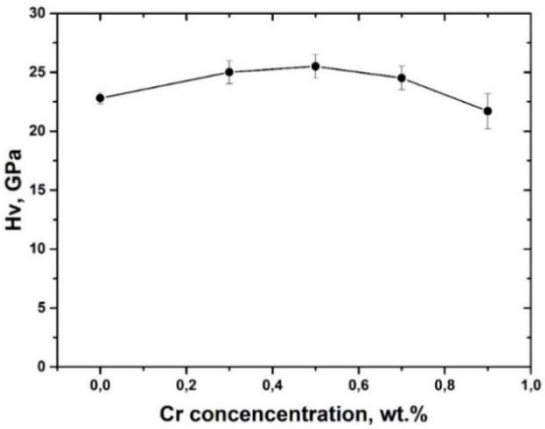

Fig. 4. Microhardness of SiC(Cr) samples depending on Cr content

Results of nanoindentation are shown in Table 3 and Fig. 5. It can be seen that the addition of Cr in the range from 0.3 to 0.7 wt.% increases the nanohardness compared to pure SiC. The maximum value of 37.8 GPa was reached at 0.5 wt.% of Cr. Increasing the Cr content to 0.9 wt.% leads to a sharp decrease of nanohardness from 37.8 to 27.0 GPa. This reduction of nanohardness can occur due to the formation of a number of Cr_xC_y and Cr_xSi_y phases. Obtained results are in good agreement with microhardness values.

Table 3

Nanohardness (H) and Young's modulus (E) of SiC samples with different Cr concentration

Sample №	Cr, wt.%	H, GPa	E, GPa
1	0	31.0	439
2	0.3	33.4	464
3	0.5	37.8	522
4	0.7	35.9	487
5	0.9	27.0	235

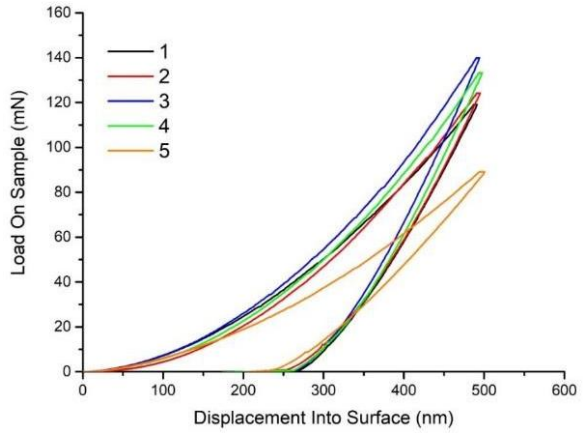

Fig. 5. The load-unload curves vs. Cr concentration of SiC(Cr) samples

The results of the long-term corrosion tests in distilled water are shown in Fig. 6. As it can be seen corrosion of both pure SiC and SiC(Cr) samples has staged character. In the first 500 h of testing, all samples showed fairly rapid dissolution. Then, in the SiC(Cr) samples, an increase in mass is observed (500…1000 h). Further, in the intermediate stage the dissolution process stabilizes, a slowdown of corrosion processes in the samples is observed. However, after 3500 h of testing, a significant acceleration of dissolution is observed for all samples.

Similar corrosion behaviour of Cr-doped silicon carbide was observed in water at a temperature of 350 °C and a pressure of 16.8 MPa [17], but differs considerably in time.

Most likely, this is due to the lower test temperature (90 °C), at which the formation of the protective Cr_2O_3 film is much slower. The sharp dissolution of the samples after 3500 h is probably related to the dissolution of the surface on which the protective films were not formed. Probably, selected Cr concentrations (0.3…0.9 wt.%) are not sufficient for the formation of a dense and continuous Cr_2O_3 protective film on the surface of the SiC(Cr) samples. However, the average dissolution rate of SiC(Cr) samples in distilled water is lower than that of pure SiC and does not exceed 0.16 μm/year.

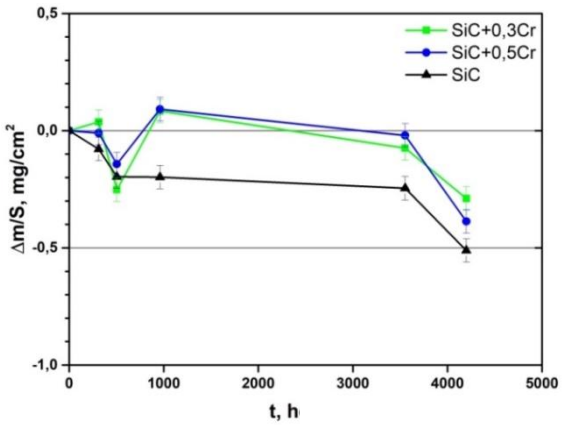

Fig. 6. Mass gain of SiC and SiC(Cr) samples as a function of immersion time in distilled water at 90 °C

Similar SiC dissolution processes were also observed in autoclaves under different test conditions (temperatures 290…330 °C, pressure 7…15 MPa, pH 5.6…7.2, oxygen and hydrogen concentrations 1.0 ppm O_2 and 0.3…3.57 ppm H_2) [18]. Dissolution of SiC can reach 0.3 mg/cm^2 in 1440 h at water temperature of 290 °C and an oxygen concentration of 1.0 ppm O_2. In other work CVD SiC samples showed mass loss in the range of 0.01…0.03 mg/cm^2 for 40 h in water at 300 °C and 8.5 MPa [19]. The mechanism of oxidation and dissolution of SiC in the water of BWR and LWR reactors is described in detail in [20]. The equations for hydrothermal corrosion of SiC in water at 300 °C [18] are given below:

$$SiC + 2H_2O = SiO_2 + CH_4 \uparrow, \quad (1)$$

$$SiO_2 + 2H_2O = Si(OH)_4. \quad (2)$$

In other words, it was found that parts of the SiC samples were corroded by the formation of silica and the subsequent dissolution of silica in water.

CONCLUSIONS

The influence of chromium additives on the mechanical properties and chemical stability of SiC as an alternative material for SF/HLW containers has been studied.

The positive effect of Cr addition on the mechanical properties of SiC ceramics was revealed. The highest values of microhardness (25.5 GPa) and nanohardness (37.8 GPa) have SiC(Cr) samples with 0.3…0.5 wt.% of Cr content.

Oxidation and dissolution of SiC and SiC(Cr) samples has staged character. It was established that Cr addition slows down corrosion processes in SiC ceramics under conditions simulating the geological disposal of radioactive waste (in distilled water at T = 90 °C). There is an increase in mass of the SiC(Cr) samples between 500 and 1000 h of testing, which may be due to the formation of a protective Cr_2O_3 film. But after 3500 h of testing, it begins to dissolve again.

The average dissolution rate of SiC(Cr) in water is quite low, and does not exceed 0.16 μm/year.

ACKNOWLEDGEMENTS

This research has received funding from Euratom research and training programme 2014–2018 under EURAD project, grant agreement # 847593.

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Article received 09.07.2024

КЕРАМІКА НА ОСНОВІ SiC ЯК МАТЕРІАЛ КОНТЕЙНЕРІВ ДЛЯ ГЕОЛОГІЧНОГО ЗАХОРОНЕННЯ РАВ

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Проведено дослідження кераміки SiC, легованої хромом, як перспективного матеріалу для контейнерів геологічного захоронення РАВ. Зразки досліджували за допомогою рентгенівської дифрактометрії, раманівської спектроскопії, вимірювань мікротвердості, наноіндентування та випробувань на корозійну стійкість. Отримані результати показали, що легування 0,3…0,7 мас.% Cr у SiC покращує механічні властивості SiC-кераміки. Корозійні випробування у дистильованій воді при T = 90 °C та часу витримки до 4300 год виявили, що додавання Cr призводить до сповільнення корозійних процесів у SiC-кераміці. Середня швидкість розчинення SiC(Cr) у воді досить низька і не перевищує значення 0,16 мкм/рік.