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Journal of the European Ceramic Society 33 (2013) 1349–1361

www.elsevier.com/locate/jeurceramsoc

Original article

The ZrC–C eutectic structure and melting behaviour: A high-temperature radiance spectroscopy study

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Received 30 July 2012; received in revised form 4 December 2012; accepted 10 December 2012
Available online 11 January 2013

Abstract

A fast spectro-pyrometer has been employed for radiance measurements of zirconium carbide samples laser-heated to very high temperature, for compositions $0.7 \leq C/Zr \leq 2.61$ and in a spectral range $0.550\ \mu m \leq \lambda \leq 0.900\ \mu m$. The ZrC–C eutectic temperature has been taken as the radiance reference. The measured normal spectral emissivity (NSE) ε_λ of solid zirconium carbide is close to 0.6 at 0.650 μm, in agreement with previous literature. Its high-temperature behaviour, value in the liquid, carbon-content and wavelength dependences in the visible-near infrared range have been determined here for the first time. Liquid zirconium carbide seems to interact with electromagnetic radiation in a more metallic way than the solid. A considerable NSE increase has been observed at increasing carbon content, which can be interpreted on the basis of preferential growth along the "c" plane of the carbon lamellae in the eutectic structure.

Keywords: Eutectics; Laser heating; Optical properties; Spectroscopy; Zirconium carbide

1. Introduction

1.1. Zirconium carbide

Zirconium carbide is a high-melting refractory material of both scientific and technological interest. Thanks to its high physico-chemical stability up to very elevated temperature (melting point of stoichiometric ZrC around 3700 K[1–5]), it can be used for extreme applications, and also as a high temperature reference material.[6] High mechanical strength up to high temperature is typical of ZrC, which is metallic in its electrical, magnetic, and optical properties. Its good resistance to the diffusion of CO_2 and some fission products (Ag), as well as the low neutron absorption cross section of zirconium, make of it a good candidate material as nuclear fuel coating in high temperature Generation IV reactors.[7,8] In aerospace applications, ZrC is mostly employed as thermal shield.[9,10] It is also a good candidate material for high-temperature solar absorbers.[11] However, a complete understanding of the thermodynamic, mechanical, and heat transport properties of ZrC_x is still limited by the lack of thorough characterisation as a function of non-stoichiometry.

From a fundamental research viewpoint, new results have been recently published on phase equilibria of the system Zr–C, for compositions $0.7 \leq C/Zr \leq 2.61$ and in the temperature range $1500\ K \leq T \leq 4000\ K$.[1] These results were obtained by an original experimental approach based on laser-heating under controlled atmosphere.[12] In the present research, which can be considered as a deepening and a completion of that previous work,[1] the invariance of the eutectic ZrC–C temperature on a broad composition range[6] is used as a reference for the thermal radiative behaviour of the Zr–C binary system. Such an approach can be understood by observing the high-temperature phase boundaries optimised by CALPHAD calculations[13] in the Zr–C binary eutectic phase diagram reported in Fig. 1 (after Ref. 1), together with the solidus, liquidus and eutectic data

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http://dx.doi.org/10.1016/j.jeurceramsoc.2012.12.008

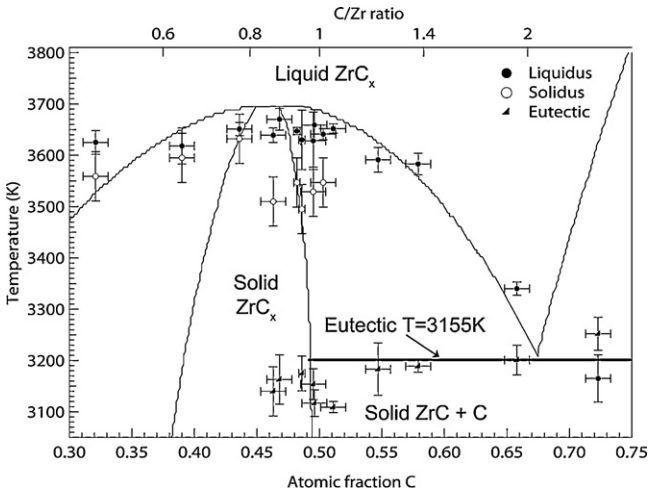

Fig. 1. The high-temperature zirconium–carbon eutectic phase diagram assessed by Fernandez Guillermet.[13] Experimental data points were recently measured by laser heating and fast pyrometry by Jackson et al.[1]

points recently measured by laser heating and fast pyrometry by Jackson et al.[1] As it can be noted, the low-carbon limit for the three-phase coexistence line (solid ZrC, liquid ZrC and eutectic ZrC–C) at the eutectic temperature has been assessed to be slightly hypo-stoichiometric ZrC, and it extends to the pure carbon end member.

Although this system was not considered as an ITC90 reference,[14–16] the ZrC–C eutectic temperature has recently been established to be 3155 K with great accuracy and precision (reproducibility of ±1 K) and suggested as a high-temperature invariant point.[6,17] This last investigation has inspired the current thermal radiance spectroscopy approach for the determination of the normal spectral emissivity ε_λ (or NSE), and some related properties. NSE is an important electro-optical property of a material surface, and an indispensable parameter for the pyrometric measurement of its temperature.

1.2. Theoretical background

1.2.1. Radiance

The spectral radiance[18] L_λ is defined at a point on a surface at temperature T as the radiant power within an infinitesimal wavelength λ interval per unit projected area and unit solid angle. For an ideal blackbody it follows Planck's radiation law in a medium with refractive index n:

$$L_{\lambda b}(T) = \frac{c_{1L}}{n^2 \times \lambda^5}\left[\exp\left(\frac{c_2}{n \times \lambda \times T}\right) - 1\right]^{-1} \quad (1)$$

where $c_{1L} = 2 \times h \times {c_0}^2$ is the first radiation constant and $c_2 = h \times c_0 \times k_B$ is the second radiation constant. c_0 is the speed of light in vacuum, h is Planck's constant, and k_B Boltzmann's constant. For the purposes of the present work, the index of refraction was always taken to be equal to 1 (being the current medium air or an inert gas close to atmospheric pressure), whereas a value[18] of 14,388 μm K was used for c_2. A blackbody is a surface (material or geometrical) that emits or absorbs all radiant flux of all wavelengths and polarisations incident upon it from all possible directions. For a prescribed temperature and wavelength, no surface can emit or absorb more thermal radiation than a blackbody.

1.2.2. Emissivity

The ability of a real surface to emit thermal radiation at a given wavelength λ, as compared to that of a blackbody at the same temperature, is expressed in terms of its spectral-directional emissivity ε_λ.

$$L_\lambda(T) = \varepsilon_\lambda(T) \times L_{\lambda b}(T) \quad (2)$$

Eqs. (1) and (2) can also be expressed in terms of radiance temperature[18] T_λ, defined as the temperature at which a perfect blackbody source would emit the same thermal radiation as the sample under investigation at a given wavelength λ.

$$L_\lambda = \frac{1}{\lambda^5} \times \frac{\varepsilon_\lambda}{e^{C_2/\lambda T} - 1} = \frac{1}{\lambda^5} \times \frac{1}{e^{C_2/\lambda T_\lambda} - 1} \quad (3)$$

T_λ is therefore a function of T, ε_λ and λ. Since pyrometers in the present work were always set up near normal with respect to the sample surface, the angle dependence of ε_λ was not considered and, 'emissivity' will always refer to normal spectral emissivity NSE. The determination of ε_λ constitutes in many cases a difficult experimental task. One direct method to measure it is based on Kirchhoff's law that relates ε_λ to the spectral reflectivity ρ_λ and the spectral transmissivity τ_λ. The sum of these three parameters should equal unity for a surface at the thermodynamic equilibrium with its environment. For opaque materials ($\tau_\lambda = 0$), it reduces then to

$$\varepsilon_\lambda = 1 - \rho_\lambda \quad (4)$$

Eq. (4) yields the spectral emissivity at a certain wavelength when the reflectivity is measured at the same wavelength. This sort of measurement can be performed by means of a laser beam and an integrating sphere.[19,20] Another direct approach to the measurement of NSE consists in drilling a blackbody hole in the sample material, and comparing the radiance emitted by the blackbody cavity with that directly measured on the sample surface far away from the hole. Such a method was applied to zirconium carbide by Grossman.[21] However, both approaches can be experimentally awkward, especially at very high temperature where the sample chemical stability is poor and the thermal radiation background plus the radiation absorption due to vaporisation are often hard to minimise.

Spectral emissivity is measured in the current research with a multi-channel spectro-pyrometer.[22,23] Such an approach is technically more flexible than the reflectance measurements. Typically, the sample radiance can be measured with a high time resolution (1 kHz) while the sample is heated in a vessel under a controlled gas pressure. The sample morphology, which can considerably change in case of vaporisation or melting, has only a limited influence on the radiance measurement if the spectro-pyrometer spot is sufficiently small compared to the sample surface. On the other hand, multi-channel pyrometry is known to be a low accuracy technique, compared to direct reflectivity measurements, due to the poor numerical stability