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Corrosion of 9-12Cr ferritic–martensitic steels in high-temperature CO₂

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ABSTRACT

The high temperature corrosion behavior of two 9Cr and 12Cr ferritic–martensitic steel grades was studied under CO₂ pressures varying from 1 to 250 bar for exposure times up to 8000 h. No “breakaway” oxidation was observed. 9Cr steel grades suffered from fast parabolic uniform oxidation and fast carburisation. Increasing CO₂ pressure had very little effect on the oxidation rate but increased the carburisation rate. The corrosion behavior of both 12Cr steel grades differed and might be influenced by gas composition, minor elements or surface finish. A corrosion mechanism coupling oxidation and carburisation is proposed.

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1. Introduction

In the framework of the development of new generations of nuclear reactors and more specifically, Sodium Fast Reactor (SFR), a new concept of gas turbine with supercritical CO₂ (S-CO₂) Brayton cycle coupled to the secondary circuit (Na) is under study by several nuclear countries (France, Japan, South Korea, the USA).

In the reference S-CO₂ cycle (for a generic 900 MWt SFR with an additional intermediate sodium loop), the turbine inlet temperature is 515 °C and the maximum CO₂ pressure is fixed at 250 bar [1]. Considering that, in nuclear plants, the life time of the material constituting the heat exchangers should be, at least, thirty years, it is obvious that the candidate structural materials for its construction have to be chosen very carefully.

9-12Cr ferritic–martensitic (F–M) steels are candidates for applications in the high temperature parts of the cycle because of their good heat transfer properties and mechanical properties but their resistance to environmental degradation should be studied in detail.

This paper presents a part of the results which have been obtained throughout a collaborative work between two national research organisms, CEA (France) and JAEA (Japan). It focuses on the corrosion behavior of the following 9-12Cr ferritic–martensitic steel grades: T91[®] (CEA), Mod.9Cr-1Mo (JAEA), VM12[®] (CEA) and

P122[®] (JAEA). Their exact compositions are presented further in the paper in Table 1.

A tremendous amount of data exist on the corrosion behavior of 9Cr steel in high temperature CO₂ since it was studied extensively from the '60s in support of former British MAGNOX¹ and AGR² CO₂-cooled nuclear reactors [2]. In those reactors, the materials were exposed to CO₂ environments with 1–5 vol% CO at temperatures between 400 and 700 °C and total pressures between 1 and 60 bar. 9Cr-1Mo steel was chosen for the evaporative and primary superheater sections of the Commercial Advanced Gas cooled Reactor (CAGR). Recently, studies induced by the uprising interest on S-CO₂ cycle for power plants ended up to new papers on the corrosion behavior of 9-12Cr ferritic–martensitic steels in CO₂ at temperatures up to 650 °C and at higher pressures than MAGNOX and AGR reactors up to 250 bar [3–7]. Moreover, results on the corrosion behavior of 9-12Cr steels in CO₂ at temperatures between 550 °C and 700 °C have been presented in the literature for a few years in the framework of candidate materials for oxy-fuel combustion process in coal-power plants [8–10]. From a compilation of all these studies, it can be concluded that most of the 9-12Cr steels oxidize and carburise in CO₂ at temperatures higher than 500 °C. Their oxidation rate is more than two orders of magnitude faster than usual 18Cr austenitic steels [4]. They form a “protective” duplex oxide scale made of an outer magnetite/haematite

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¹ Magnesium oxide.

² Advanced Gas-cooled reactor.

Table 1
Chemical composition of the various studied steel grades (in wt%) as provided by the steel makers. The carbon content (*) of the CEA steel grades was measured by combustion infrared detection technique.

Name	Steel grade	Fe	C	Cr	Mo	V	Ni	Mn	Si	Nb	Others	N	Research organism
9Cr CEA	T91®	Balance	0.10*	8.63	0.95	0.21	0.23	0.43	0.31	0.09	Cu: 0.05	0.03	CEA
9Cr JAEA	Mod.9Cr-1Mo	Balance	0.10	8.73	0.96	0.22	0.07	0.43	0.40	0.01	/	0.05	JAEA
12Cr CEA	VM12®	Balance	0.16*	11.50	0.29	0.26	0.29	0.35	0.49	0.05	Co: 1.62 W: 1.50	/	CEA
12Cr JAEA	P122®	Balance	0.11	10.87	0.31	0.20	0.39	0.64	0.26	0.05	Cu: 1.03 W: 1.86	0.06	JAEA

Table 2
Experimental conditions of the various corrosion tests carried out at CEA and JAEA.

Test	Temperature (°C)	Pressure (bar)	Exposure time (h)	Gas flow	Test section diameter (cm)	Linear flow rate (cm/s)
CEA	550	1	1, 65, 350, 1000, 5000*	15 L/h, 11 L/h*	5.5, 12*	0.2, 0.03*
CEA	550	250	350, 1000	2.2 kg/h	5	0.2
JAEA	500, 550, 600	100, 200	Every 1000 h–8000 h	1.2 kg/h	0.7	From 8 to 22 depending on the (P,T) couple

layer with coarse columnar grains and an almost-as-thick inner Fe–Cr rich spinel oxide layer made of small equiaxed grains. Below the scale, Cr rich carbides form and their density and penetration depth increase with time. The duplex oxide layer grows according to a parabolic law. Corrosion mechanisms have been proposed to explain the duplex oxide growth [6,11–17] and carburisation below the oxide scale [9,18–20]. Besides, in studies on the corrosion behavior of 9Cr steel for CO₂ gas cooled reactors, it has been found that, after an incubation time depending on environmental and metallurgical parameters, the oxidation rate of 9Cr steel can suddenly “breakaway” into a faster linear growth mode. Such breakaway scales are very porous and can be in the form of many localised excrescences or a more uniform laminated scale [21,22].

The objective of this paper is to gather and interpret the numerous corrosion results obtained throughout CEA and JAEA experiments on two 9Cr and 12Cr ferritic–martensitic steel grades in order to propose a corrosion mechanism and a kinetic model of corrosion depending on the main environmental parameters (temperature and pressure). Long-term exposures of 9–12Cr steels – up to 8000 h – were carried out at JAEA in high pressure CO₂ at 500 °C, 550 °C and 600 °C. The occurrence of any “breakaway” oxidation in these tests was carefully checked. More specific short-term exposures – up to 1000 h – were carried out at CEA at 550 °C to study the influence of several parameters on the corrosion behavior of 9–12Cr steels such as the effect of the total CO₂ pressure, the effect of static or flowing CO₂ over the samples or the sample thickness.

Our results are discussed in the light of results taken from literature.

2. Experimental facilities and procedures

It is known that the corrosion behavior of 9–12Cr steels in CO₂ depends strongly on environmental parameters (CO₂ chemistry, temperature, gas flow rate, etc.) and metallurgical parameters (nature and amount of minor elements in the steel, surface finish, etc.). For these reasons, the parameters that the authors consider important to clarify are mentioned in the following paragraphs.

2.1. Materials

The composition of the 9–12Cr steel grades exposed in CO₂ at CEA and JAEA are given in Table 1.

The CEA samples were cut from the delivered plates or rods – 25 mm × 12 mm × 2 mm –, ground to 1200 grit surface finish and ultrasonically degreased in acetone–ethanol mixture before use. The surface roughness obtained after this procedure was measured by Michelson interferometer between 100 and 200 nm. The effect of

the sample thickness on the corrosion behavior was tested through the use of 0.1 mm, 1.5 mm and 5 mm-thick samples.

The JAEA samples were half cylinders with diameter equal to 1.4 mm or 1.9 mm and length equal to 15 mm. Their roughness was not measured but their surface preparation ensured a value below 1.6 μm. As a consequence JAEA sample roughness was higher than CEA sample roughness.

2.2. JAEA facility

The corrosion tests were carried out in a circulation loop made of austenitic stainless steel. A detailed flow diagram of the experimental test apparatus is shown in [5]. CO₂ was supplied from gas cylinders to the apparatus and pressurized at the desired CO₂ pressure using a higher-pressure CO₂ pump. Its purity was 99.995% (considered as “industrial” purity). It is very important to indicate the purity level of CO₂ used in the different experiments since it has been shown that the corrosion behavior of 9–12Cr steels depends on CO₂ purity [23,24]. The main CO₂ flow was injected into five sample lines and heated simultaneously to three testing temperatures, 500 °C, 550 °C and 600 °C, depending on the test section. The oxygen and water vapor concentrations in CO₂ were measured at atmospheric pressure continuously. During the corrosion tests, the water vapor concentration oscillated between 40 vpm and 130 vpm and the oxygen concentration was measured between a few vpm to several tenths of vpm. The JAEA corrosion data were obtained under two CO₂ pressures: 100 and 200 bar.

2.3. CEA facility

The corrosion tests were carried out at 550 °C in three different test apparatus to evaluate the influence of CO₂ pressure or CO accumulation in the gas phase on the corrosion behavior.

Corrosion tests in flowing CO₂ at atmospheric pressure were carried out in quartz tubular reactors. The purity of CO₂ used in these tests was the same as in JAEA corrosion tests, 99.995%. The oxygen partial pressure was measured in the isothermal section by using in-situ oxygen probe. The water concentration in CO₂ was monitored on-line via a capacitive-probe hygrometer positioned at the furnace entrance.

Corrosion tests under flowing CO₂ at 250 bar were carried out in two facilities. The first facility was used for studying corrosion under flowing high pressure CO₂ and was very similar to JAEA facility except that the CEA facility was not a circulation loop. CO₂ was renewed continuously. This facility was equipped with a zirconia oxygen probe and a capacitive hygrometer to measure the oxygen and the water vapor partial pressures at the inlet and at the out-

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