Intermetallics 65 (2015) 35–41

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Isothermal and cyclic oxidation behaviour of hot-pressed MSi_2 compounds (with $M = V$, Ti, Cr)

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ARTICLE INFO

Article history:
Received 16 February 2015
Received in revised form
19 April 2015
Accepted 12 May 2015
Available online 5 June 2015

Keywords:
A. Intermetallics
B. Oxidation
C. Powder metallurgy
D. Microstructure

ABSTRACT

The oxidation resistance of MSi_2 compounds with $M = V$, Ti, Cr was investigated from 450 to 950 °C in air under isothermal and cyclic conditions. Vanadium, chromium and titanium disilicide were not subjected to the pest phenomenon at 650 °C over 800 1-h cycles. The results demonstrated very low weight gains regardless of the testing conditions. Oxidation tests were also performed over long duration (1000 h) to identify the oxidation products. The MSi_2 compounds were all subjected to the simultaneous oxidation of M and Si despite the formation of a protective silica scale. Increasing the duration of oxidation enhanced the protective properties of the silica scale. Therefore, short-term measurements (by thermogravimetry) did not allow an extrapolation of the MSi_2 lifetime. The formation of molten V_2O_5 induced a higher oxidation rate of VSi_2 and delayed the establishment of the protective silica scale compared with $CrSi_2$ and $TiSi_2$.

1. Introduction

Some refractory metal disilicides, such as $MoSi_2$, possess the ability to develop protective silica layers [1] from relatively low temperatures (from 550 °C for $MoSi_2$ in a water-vapour-containing atmosphere) to very high temperatures (1700 °C). These materials have thus been used as heating elements (Super Kanthal) [2] or as protective coatings for Mo-based alloys [3,4] for several decades. However, this compound also disintegrates into a powder in the temperature range of 400–550 °C mainly because of mechanical stresses developing during oxidation [5,6]. In fact, silicide compounds are commonly reputed to be brittle at low temperatures.

Recent studies [7–10] demonstrated that coatings made of metal disilicides MSi_2 (with $M = Ti$, V and Cr) can protect vanadium alloys from oxidation under various conditions (isothermal in impure helium or in air at 650 °C, impure Na at 550 °C, cyclic oxidation up to 1100 °C). In these cases, the catastrophic oxidation of disilicide compounds was never evidenced, corroborating the results of [11–13]. These authors suggested that metal silicide composed of a metal of the first series of transition metals did not exhibit the catastrophic oxidation behaviour. Consequently, such materials, which display rather high melting temperatures, could be of interest for applications in the 600–1000 °C range, which is usually covered by chromia-forming alloys. The advantage of silica-forming materials instead of chromia-forming ones lies mainly in the high stability of silica in highly corrosive environments, such as those containing chloride and sulphate salts [14].

It is therefore of interest to characterise the oxidation behaviour of these three compounds under both isothermal and cyclic conditions. This study was conducted to determine the ability of MSi_2 materials to develop silica in the temperature range of 450–950 °C in air and to verify the lack of susceptibility to catastrophic oxidation of these brittle materials. The oxidation behaviour of these compounds in air is discussed regarding their physico-chemical properties.

2. Experimental methods and materials

2.1. Manufacturing of MSi_2 compounds ($M = V$, Ti and Cr)

The manufacturing process presented hereafter has been employed to prepare MSi_2 compounds because melting methods (inductive or arc melting) systematically induced porosities and cracks during solidification and cooling. Such melted samples are not suitable to perform the aimed oxidation study; this is the reason why the powder metallurgy route was employed to obtain

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http://dx.doi.org/10.1016/j.intermet.2015.05.005

MSi_2 dense samples.

The first step for MSi_2 preparation trough the powder metallurgy route consists of inductive melting of stoichiometric mixtures of pure metals and silicon (high-purity Ti 99.7%, Cr 99.99%, V 99.7% and Si 99.9999%) in a water-cooled copper crucible. The melting was performed three times for each ingot to achieve high compositional homogeneity. Then, the ingots were hand-crushed into a powder until a grain size of less than 80 µm was obtained. A sample of the powder was retained for X-ray characterisation. The rest was densified by uniaxial hot pressing under argon to produce dense MSi_2 samples. For uniaxial hot pressing, the powder was introduced onto a graphite die previously coated with boron nitride (BN) spray. BN works as a diffusion barrier between graphite and metallic powders and thus limits the formation of carbides. The die was heated to 1200 °C for 4 h under a pressure of 27 MPa, after which the load was removed, and the heating was stopped. The cooling time to room temperature was approximately 4 h. Under these conditions, the densification percentage of the manufactured specimens was higher than 98%. The specimen dimensions were approximately (Ø 25 mm, h 12 mm). To study oxidation, parallelepedic coupons of 10 mm × 10 mm × 2 mm were cut from their respective ingots of VSi_2, $TiSi_2$ and $CrSi_2$, and the surface was ground down to 1200 grid (SiC paper).

2.2. Oxidation tests

The isothermal oxidation tests were performed at 450, 550, 650, 750, 850 and 950 °C for 50 h in dry air using a SETARAM TAG1750 symmetrical thermobalance with an accuracy of 1 µg. For VSi_2 samples, a SETARAM T92 of 3 µg accuracy was used for temperatures higher than 650 °C because the expected oxide of vanadium forming in air from 681 °C corresponds to liquid V_2O_5 [15]. Then, the risk of contamination of the experimental devices by liquid V_2O_5 when performing the experiments at temperatures higher than 681 °C was high. The samples were hung in the hot zone of the thermobalance furnace with a platinum wire. Small pieces of tubular alumina (0.8 mm diameter) were placed around the platinum wire to prevent interaction between platinum and the silicide samples. Synthetic dry air (H_2O amount lower than 3 ppm) was introduced into the reaction chamber with a flow rate of 1.5 L/h. The samples were heated at 10 K/min up to the test temperature and cooled down to room temperature at a rate of 5 K/min. The curves presented here show only the mass gain once the temperature dwell was reached. Long-duration isothermal oxidation tests were also performed for as long as 1000 h in a tubular furnace in the lab atmosphere. All samples were placed in alumina crucibles.

Cyclic oxidation tests (1-h annealing – 10-min cooling) were performed at 650 °C by placing the specimens in a tubular furnace in air. During the cooling, the specimens were removed from the furnace and regularly hand-weighed to evaluate the mass variation during 850 cycles; the measurements were made using an analytical balance with a precision of 0.1 mg. The cyclic oxidation conditions allowed the evaluation, in a single experiment, of both the oxidation resistance and the effect of thermo-mechanical stresses applied to the oxide scale - substrate system. It should be a severe test for materials susceptible to catastrophic oxidation.

2.3. Metallographic characterisation

A Philips X'Pert Pro diffractometer with a θ–2θ Bragg Brentano geometry and monochromatic Cu Kα1 radiation (1.5418 E) was employed to identify the crystal structure of the main phases in the oxidation products. The crystal structure of each compound was identified by matching the characteristic X-ray diffraction (XRD) peaks with the International Center for Diffraction Data (ICDD). Metallographic observations were performed using a JEOL JSM-7600F equipped with an SDD-type EDX detector coupled with an Oxford INCA WAVE WDS spectrometer.

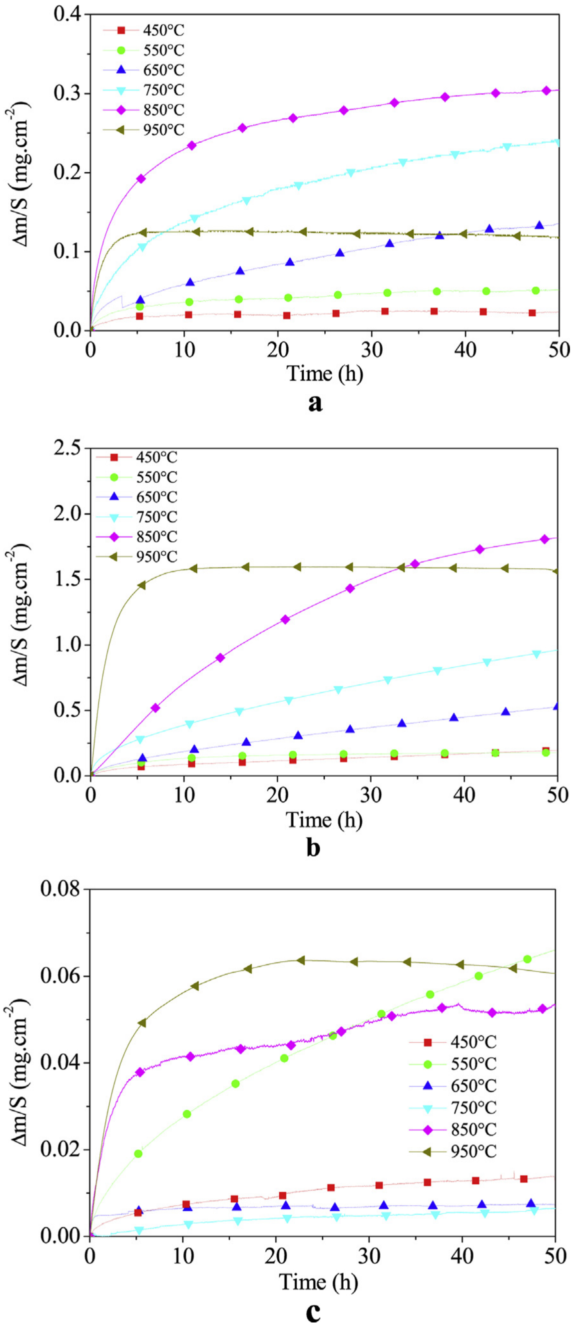

Fig. 1. Mass gain vs. time curves recorded during the isothermal oxidation of MSi_2 from 450 °C to 950 °C: a) $CrSi_2$, b) VSi_2 and c) $TiSi_2$.

Before cutting and grinding, the oxidised samples were covered by an electroplating layer of Ni to prevent the degradation of oxidation products. Next, samples were cut transversally to characterise the cross sections, embedded with a cold epoxy resin, ground from 240 to 2400 grid with SiC paper, and polished using a colloidal SiO_2 suspension.