



## Internal oxidation of Ag–VC composites

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### ABSTRACT

The internal oxidation (IO) of Ag–VC composites containing 5 vol.% of carbide was examined at three oxidation temperatures (350, 400, 600 °C). Two mechanisms were observed due to the formation of double oxides with relatively low-melting points. At temperatures below the lowest eutectic point *in situ*, or diffusion less IO, was observed with the formation and growth of oxide layers surrounding the initial carbide. At temperatures above the eutectic point IO resulted in the formation of liquid oxide pools, which grew in size and developed into a network of oxides within the metal matrix. The kinetics confirmed the presence of two distinct mechanisms.

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## 1. Introduction

Internal oxidation, oxidation beneath the surface of an alloy or composite, has been studied extensively for single-phase alloys. Wagner's [1] pioneering work in this field resulted in a mathematical model of internal oxidation which is still widely used today. Considerable research of internal oxidation of single-phase alloys has been reviewed by Rapp [2] and again recently by Douglass [3]. While the quantitative study of two-phase alloys effectively began with Meijering's model of two-phase alloys [4,5], due to the increased complexity of internal oxidation in two-phase alloys as compared to single-phase alloys, the three models developed by Meijering for three different levels of solubility of the reactive element in the matrix include a number of parameters which are extremely difficult to measure, making their applicability difficult. This difficulty was overcome to some degree by Gesmundo et al. [6,7], who examined two-phase binary alloys by returning to Wagner's model and comparing the theoretical values with the effective experimental values, thus introducing measurable quantities and offering new insight into the kinetics of two-phase alloys [8].

Two modes of oxidation have been observed in two-phase materials, the appearance of which depend on the solubility of the alloying element within the base metal. The first mode of oxidation, known as *in situ* or diffusionless internal oxidation, is

observed when the alloying element or secondary phase or particle is insoluble in the metal matrix [9]. This results in the oxidation of the secondary phase at its initial location with no appreciable displacement. The second mode of oxidation, known as the diffusive mode of oxidation, results in the precipitation of oxide particles from the solid solution. Both mechanisms of internal oxidation have been observed to appear simultaneously in two-phase alloys such as Ag–1.3 at.% Te [10,11] and Ag–1.3 at.% Se [12,13] alloys.

The mechanism of internal oxidation in the absence of an external scale was studied in silver–vanadium carbide composites. Because of the large permeability of oxygen through the silver matrix and the instability of the silver oxide Ag<sub>2</sub>O above 190 °C, silver alloys and composites are highly suitable for the study of internal oxidation. The solubility of oxygen in silver was measured and can be expressed in an atomic or mole fraction as [14–19]:

$$C_0^S = 6.69 \times 10^{-2} \exp\left(-\frac{49.62}{RT}\right) \quad (\text{atomic or mole fraction}) \quad (1)$$

where  $C_0^S$  (at.% or mol.%) is the solubility of oxygen in the metal (atomic or mole fraction) under the oxygen pressure prevailing at the alloy surface,  $R$  is the universal gas constant and  $T$  (K) is the temperature. Furthermore, the diffusivity of oxygen through silver is expressed as:

$$D_0^S = 3.66 \times 10^{-3} \exp\left(-\frac{46.1}{RT}\right) \quad (\text{m}^2 \text{s}^{-1}) \quad (2)$$

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where  $D_0^S$  ( $\text{m}^2 \text{s}^{-1}$ ) is the diffusion coefficient of oxygen in a solvent metal.

The use of carbides as a reinforcement for silver can add both durability and anti-sticking properties to the composite, resulting in longer lifetimes for such applications as electrical contacts. Vanadium carbide is an especially interesting reinforcement for the study of high temperature internal oxidation since its oxides have relatively low-melting points, resulting in the formation of liquid products of oxidation. The formation of these low-melting point oxides has been known to cause catastrophic external oxidation in certain steels and alloys [20].

Due to the nature of composite materials such as metal alloys, which differ from other two-phase materials mainly in the scale and function of the secondary phase, the chemical dissimilarities between the carbide and the base metal will result in a virtually immiscible carbide particulate reinforcement within the base metal. Furthermore, the silver–vanadium phase diagram [21,22] indicates that very limited solubility exists between the two solid components. Internal oxidation in the solid state is thus expected to proceed through the *in situ* mechanism with the final distribution of oxides equivalent to the initial distribution of the carbide particles. Because of the relatively large size of the vanadium carbide particles, oxidation is expected to be only partial as the internal oxidation front moves through the composite. The appearance of liquid double oxides at higher temperatures of oxidation is expected to increase the rate of transport of reactants to the reaction surface and thus increase the rate of oxidation.

This work will examine the mechanism of the internal oxidation of Ag–VC composites containing 5 vol.% carbide by investigating the development of various oxide phases and their composition. The temperatures of oxidation were chosen so as to observe both the development of the microstructure in the presence of solid oxides, as well as in the presence of liquid oxides. In an effort to gain further insight into the mechanism associated with the microstructural developments, the kinetics of internal oxidation were also examined according to the procedure described by Gesmundo [6,23].

## 2. Materials and methods

Ag–VC composites were created using powder metallurgical methods producing a composite consisting of 5 vol.% of carbide. The vanadium carbide powder consisted of particles  $>45 \mu\text{m}$  in size, while the silver powder was on average  $6 \mu\text{m}$  in size. The powder mixture was then placed in a container, alcohol was added to produce a pasty texture and the container was rotated on rollers for 4 h at a rate of  $70 \text{ min}^{-1}$ . This produced an even distribution of carbide particles dispersed throughout the silver powder. The mixed powder was then mechanically pressed to 140 bar to form round tablets with a final thickness between 2 and 3 mm. Sintering of the tablets at  $900^\circ\text{C}$  for 4 h was performed in a quartz tube vacuumized to  $10^{-5}$  mbar and placed into a preheated horizontal tube furnace. In order to determine the degree of sintering that occurred, the theoretical density of the tablets was calculated and compared to the density measured using the Archimedes method. These values were in good agreement (theoretical  $\rho_t = 10,290 \text{ kg m}^{-3}$ ; measured  $\rho_m = 10,030 \text{ kg m}^{-3}$ ) indicating that the sintering process was successful.

The cross-sectional microstructure of the composites was observed after sintering using a scanning electron microscope (SEM) (JEOL 5610) (Fig. 1). The cross-section revealed a homogeneous distribution of vanadium carbide particles within the silver matrix, with little or no visible porosity. No oxidation was observed to have occurred during the sintering process. These tablets were then cut into  $8 \text{ cm} \times 8 \text{ cm} \times 3 \text{ cm}$  samples and prepared for

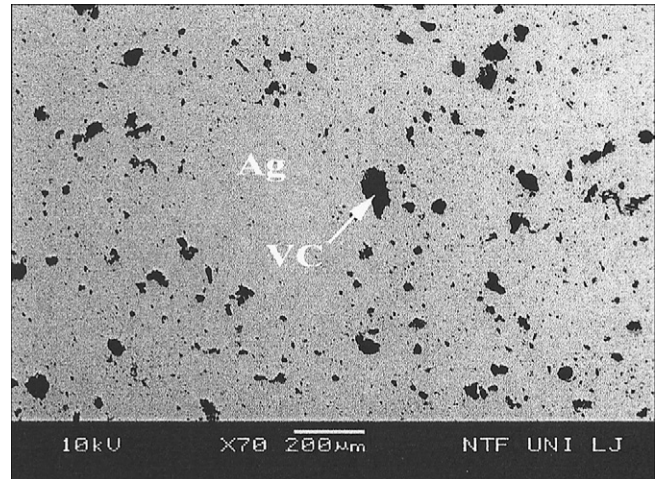


Fig. 1. Microstructure of sintered Ag–VC composites. The image is SEM backscattered electron image.

oxidation. Prior to oxidation, each sample was abraded using 4000 grit silicon carbide abrasive paper and cleaned in alcohol and acetone. Each sample was then placed in a horizontal tube furnace preset to the temperature of oxidation with a constant flow of oxygen of  $45 \text{ ml min}^{-1}$ . Both the temperature and duration of oxidation were varied in order to observe the microstructural development.

The oxidized samples were then observed using SEM and the various developing phases identified using energy dispersive X-ray spectroscopy (EDS) (iXRF 500) and X-ray diffraction (XRD) (Philips PW 3710, monochromatic  $\text{Cu K}\alpha$  X-rays, wavelength =  $0.15406 \text{ nm}$ ). In order to characterise the kinetics of oxidation, thermogravimetric analysis (TGA) (NETZSCH – STA 449 Jupiter) was performed at three different oxidation temperatures ( $350, 400, 600^\circ\text{C}$ ).

### 2.1. Ag–V–O ternary system

Of the Ag–V–O ternary system, only the quasi-binary phase diagram  $\text{Ag}_2\text{O}$ – $\text{V}_2\text{O}_5$  was found in the literature [14] (Fig. 2). This

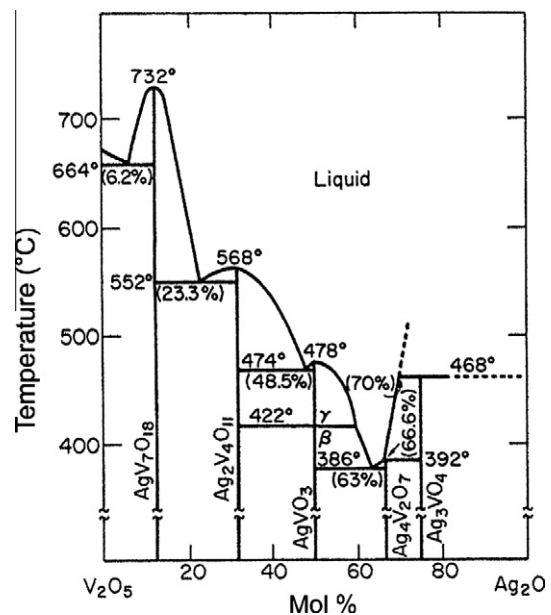


Fig. 2.  $\text{V}_2\text{O}_5$ – $\text{Ag}_2\text{O}$  quasi-binary phase diagram [14].

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