CONF-970806--1

LA-UR- 97-872

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Submitted to: To be presented at the Eleventh International Conference on the Strength of Materials, Prague, Czech Republic, August 25-29, 1997 to be published in Journal of Materials Science and Engineering A

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Vanadium-Spinel Composites for Structural Applications in Hostile Environments

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ABSTRACT

Vanadium-spinel composites are promising materials for structural applications in radiation environments. Powders of two Vanadium-spinel composites, 20/80 vol. %, were prepared by (a) ball milling mixtures of vanadium and spinel powders (alloy VSLP) and (b) through a self-sustained reaction synthesis of vanadium, MgO, and Al powders (alloy VSHP). These powders were consolidated by hot isostatic pressing. Most of the V and spinel domains in the the compacts are sub-micron in size. The compacts have K_{IC} toughness values of 3.9, about three times the toughness obtained by hiping mixtures of commercial powders.

Keywords: composites, radiations resistance, toughness

INTRODUCTION

In 1996, Sickafus et al. [1] proposed that a composite of vanadium metal and $MgAl_2O_4$ spinel could potentially be a good candidate for structural applications in a deuterium-tritium magnetic fusion reactors. A simple analysis of the published properties of V and $MgAl_2O_4$ [1] suggested that the vanadium-spinel composite should have a number of attractive properties: good radiation resistance (e.g., absence of volume swelling during particle irradiation); high melting point and creep resistance, good thermal shock/fatigue resistance (the thermal expansion coefficients of V and $MgAl_2O_4$ are well matched); good thermal conductivity, especially if the vanadium phase in the composite is continuous; and good toughness and strength: Preliminary

tests showed that spinel bonds readily to metals and this should lead to both high hardness and toughness. These parameters, however, are strongly related to the microstructure. To test these predictions, Ustundag et al. [2] fabricated three vanadium-spinel composites at the volume ratio 40/60, 50/50, and 60/40. These composites were prepared by mixing commercial vanadium and spinel powders and consolidating the mixture by hot pressing in graphite dies. The vanadium powder had an average particle size in the range 5-15 μm (including particles as large as 45 μm) whereas the spinel powder had an average particle size of about 10 μm . The properties of these compacts (density, microstructure, hardness, coefficient of thermal expansion, and toughness) were measured [2]. A sample of the 50/50 V/spinel composite was also irradiated *in situ* at ~ 20K with 1.5 MeV Xe^+ ions to a fluence of 5.0×10^{15} ions cm^{-2} . All the grains in the sample retained their crystal structure for an ion dose that corresponds to approximately 5 dpa at a depth of 50 nm in spinel and 8.5 dpa in vanadium. The only measured property that did not reach expectations was the fracture toughness, which ranged from 2.7 to 3.3 $\text{MPa m}^{1/2}$. The observed easy fracturing of the V phase suggested that it may contain impurities, notably oxygen which, when present even at the ppm level, can drastically raise the ductile-to-brittle transition temperature of vanadium.[3] Another undesirable characteristic of these alloys was the rather large grain size of the constituents. It was speculated that a finer domain two-phase alloy would also increase the fracture toughness by blunting the crack propagation.

The goal of the present work was to produce a fine-structure composite of vanadium and spinel using mechanical alloying (MA), followed by hot isostatic pressing. By starting from pure and dried powders, we expected to obtain a lower oxygen content in the sintered V phase.

EXPERIMENTAL PROCEDURE

Two vanadium-spinel composites, 20/80 % by volume, denoted VSLP and VSHP, were prepared by different methods. The VSLP alloy was prepared from commercial vanadium powder (-325 mesh, 99.5% pure from Aldrich, Milwaukee, WI) and commercial MgAl_2O_4 (99% pure, from ALCOA, Bauxite, AR). A 5-gram mixture of these powders was vacuum dried at 150°C . The mixture was then mechanically alloyed for 10 h in a SPEX 8000 shaker mill [Edison, NJ], using a tungsten carbide vial and a single 12-gram ball. The ball mill was located inside a glovebox which contains Ar gas with less than 1 ppm O_2 and water vapor.

The VSHP alloy was prepared by a reaction synthesis route starting from a mixture of V_2O_5 , MgO , and metallic aluminum in the molar ratio 3:5:10. A 5-gram charge of these powders was dried in vacuum and was then mechanically alloyed in the same SPEX mill. The three components react according to $3 \text{V}_2\text{O}_5 + 5 \text{MgO} + 10 \text{Al} \rightarrow 6 \text{V} + 5 \text{MgAl}_2\text{O}_4$. Figure 1 shows x-ray diffraction patterns of the initial powder mixture and after various milling times. It is clear that the reaction described by Eq. (1) occurs sometime between $\frac{1}{2}$ and 1 h of MA.

Fig. 1. X-ray diffraction patterns during the synthesis of the VSHP alloy powder. (a): initial mixture of V_2O_5 (all unlabeled Bragg peaks), MgO , and Al . (b): after 0.5 h of MA. (c): after 1 h of MA. (d): after 10 h of MA.

The VSLP and VSHP powders were loaded into tantalum cans which were then evacuated and sealed by e-beam welding. The cans were hot isostatic pressed at 0.2 MPa and 1350°C, keeping at pressure for 45 min. The products were rods, 2-cm diam. and 5 cm long. Samples were cut from the compacts using a water-cooled high-speed diamond impregnated saw.

The polished surfaces were examined by scanning electron microscopy. The same surfaces were studied by x-ray diffraction. The x-ray spectra were deconvoluted using the Los Alamos GSAS Rietveld analysis routine. Hardness measurements were done using a diamond Vickers indenter. The toughness of the samples was deduced from the length of the radial cracks that formed at the corners of the Vickers indents for loads ranging from 10 to 30 N. The elastic constants of the alloys were measured by a resonant ultrasound spectroscopy (RUS) technique [4]. The RUS data indicated that the two-phase alloys were isotropic and gave the values for the two independent elastic moduli.

RESULTS

Figure 2 is a SEM micrograph of the VSHP alloy. The vanadium appears as the light phase and the spinel as the dark phase. The pyramidal depression at the lower right of the figure was formed by the Vickers indenting probe. Two out of the four radial cracks extending from the corners of the indent are also visible. The horizontal crack runs straight, without encountering any large vanadium precipitates. The vertical crack, however, is observed to change direction at various places, whenever it encounters a large vanadium particle. This indicates that the vanadium phase is contributing to the toughening of the composite. The cracks do not seek the V-spinel interfaces which appear to be at least as strong as the matrix.

The toughness of the composites was determined from the length of the surface radial cracks.[5] The advantages of this technique (simplicity; applicable to small samples) are offset by various complications. The major problems are: (1) the accuracy to which the cracks can be

measured, and (2) the assumption that the sub-surface cracks are either one or the other of two idealized crack systems (the 'penny-shaped median' or the "Palmquist" types), which may or may not be the case for the material in question.

Fig. 2. SEM micrograph of the

VSHP sample.

For the present samples, we analyzed the data using theoretical models deduced for both crack systems. For the 'penny-shaped median' crack type we used the model of Anstis *et al.* [6] which predicts, $K_c = 0.016 (E / H)^{1/2} [P / (l + a)^{3/2}]$, where E is the Young's modulus, H the hardness, P the load, l the average crack length, and a is half the diagonal of the indent. For the 'Palmquist' crack type we used the model of Niihara *et al.* [7], as modified by Srinivasan *et al.* [8], which predicts $K_c = 0.0123 (E)^{0.4} (H)^{0.1} (P / l)^{1/2}$. The indentations were obtained for loads of 10 to 30 N, in increments of 4 N. Ten indents were made at each load and the crack lengths were measured from calibrated optical micrographs. The hardness was deduced from linear fits to load vs. (indent-area) plots. The Young's moduli were deduced from the RUS elastic moduli measurements.

Table I summarizes the mechanical properties of the two 20/80 vanadium-spinel composites prepared in this work, as well as those of one of the previous 50/50 vanadium spinel composite [2]. The elastic properties and hardness of the VSLP and VSHP composites are quite similar. The VSHP alloy has a slightly higher toughness than the VSLP alloy. Both alloys,

however, have higher toughness than the large-grain VS-3 alloy studied previously [2]. This is significant in view of the fact that the present composites have much less vanadium. Although the toughness of monolithic spinel is only $\approx 1.4 \text{ MPa m}^{1/2}$ [9], the measured toughness of the VSHP composite, close to $4 \text{ MPa m}^{1/2}$, is still too low for its intended application as structural material.

Table I. Mechanical Properties of Vanadium-Spinel Composites

Sample ID (V/spinel) Vol. %	E (GPa)	G (GPa)	ν	H (GPa)	K_c ($\text{MPa m}^{1/2}$) Median model Eq. (2)	K_c ($\text{MPa m}^{1/2}$) Palmquist model Eq. (3)	K_{Ic} ($\text{MPa m}^{1/2}$) Chevron notch (Ref. [10])
VSLP (20/80)	249	97.4	0.28	12.4	3.24	3.37	
VSHP (20/80)	249	95.9	0.29	12.1	3.90	3.94	
VS-3 (50/50)	270	-	0.27	4.7			2.66

Fig. 3. Curve (a): X-ray diffraction ($\text{Cu}, K\alpha$) pattern from the VSHP composite. Curve (b): difference between the curve (a) and the Rietveld analysis fit (on an 100x expanded scale).

The reasons for the low toughness become apparent when we analyze the x-ray diffraction data. Fig. 3 shows the x-ray diffraction pattern and Rietveld fit for the VSHP sample. A similar refinement was obtained for the VSLP sample. Notice that the (200) Bragg peak of vanadium is split. This indicates that the vanadium is present both in the bcc and bct structures. The bct phase is stabilized by oxygen.[11] The Rietveld analysis enabled us to estimate the volume fraction of both phases and the results are given in Table II. The refinement also provided accurate values for the lattice parameters of the two vanadium phases. The interstitial oxygen in the bcc phase was deduced from the measured lattice parameter and the data of Henry *et al.*[12] For both alloys, the calculated oxygen content were close to 4 at %, and this agrees with the room-temperature equilibrium value for bcc vanadium in equilibrium with the bct V_9O phase.[11] Using the data in Table II we deduced the average oxygen content in the vanadium phase to be 6.7 and 5.8 at.% for the VSLP and VSHP alloys, respectively. This compares favorably with the 15 to 20 at.% oxygen content in the vanadium of the previous alloys [2].

Table II. Results of the Rietveld refinement of the x-ray diffraction data

Sample ID (V/spinel) Vol. %	Vol. % bcc V	Vol % bct V (V_9O)	a for bcc V (nm)	Average O content in V (at. %)
VSLP (20/80)	46	54	0.3047	6.7
VSHP (20/80)	64	36	0.3043	5.8
VS-1 (50/50) (Ref. xxx)	0	100	-	15 to 20

DISCUSSION

The main goal of using the MA synthesis route was to increase the toughness of the V-spinel composites over the value previously obtained by hot pressing a 50/50 mixture of

commercial powders. Although the present 20/80 alloys contain much less vanadium, their toughness is higher by a factor of about 3. The increase is most likely due to (a) a better distribution of the vanadium phase as sub-micron size domains and (b) a lower oxygen content in the V phase. The VSHP alloys prepared by a novel reaction synthesis route is especially promising since it resulted in the lower content of oxygen in the vanadium phase. Future work will address the synthesis of V-spinel composites in the presence of excess aluminum and/or magnesium, which we expect will further reduce the oxygen content and increase the toughness of the composites.

Acknowledgement: This work was supported by the US Department of Energy. Office of Basic Energy Sciences.

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