High Temperature Mechanical Properties of Ti(C,N)-Co-Mo₂C Cermets

A. Gallardo-López[1, a], A. Morales-Rodríguez[1], A. Domínguez-Rodríguez[1]

J. M. Córdoba[2], M. A. Avilés[2], F. J. Gotor[2]

[1]Departamento de Física de la Materia Condensada, Universidad de Sevilla-CSIC, Apdo. 1065, 41080 Sevilla, Spain

[2]Instituto de Ciencia de Materiales de Sevilla, CSIC-USE, Avda. Américo Vespucio 49, 41092 Sevilla, Spain

[a]angela@us.es,

Abstract. The creep behavior of a TiC_xN_{1-x}-Co-Mo₂C cermet has been investigated at temperatures between 1100-1200ºC in an inert atmosphere to assess the one step mechanically induced self-sustaining reaction synthesis and pressureless sintering process, and the influence of the Mo₂C additive in the high temperature mechanical properties of this cermet. The samples deform plastically at the chosen temperatures, and values of the stress exponent ($n=1.7\pm0.6$) and activation energy ($Q= 4.3\pm0.5$ eV) have been estimated from uniaxial compression tests. No significant grain growth has been detected after deformation. The reproducibility of the creep tests compared to other compositions indicates that the Mo₂C addition contributes to increase notably the resistance to high temperature oxidation of the samples, so that the plastic behavior is not affected by oxidation when deformation experiments are performed in an inert atmosphere.

Introduction

Titanium carbide and titanium nitride can form a solid solution TiC_xN_{1-x} with high wear resistance, high melting point, good thermal conductivity, and chemical stability at high temperatures, among other convenient properties [1]. When combined with metals, namely Ni or Co, the resultant cermets unite the hardness and wear resistance of the titanium carbonitride phase with the ductility and toughness of the metal. These cermets have a variety of industrial applications in cutting tools and other instruments, which require very high wear resistance, and provide a good alternative to conventional WC-Co materials [2]. However, their applications are somehow restricted to high-speed finishing and cutting operations provided their high thermal conductivity, which minimizes thermal stress and cracks. Since the cutting speeds in service can therefore be very high, temperatures as high as 1000ºC can be reached by these cermets. This means that besides improving the toughness of the Ti(C,N)-based cermets, which is still a major goal nowadays, their resistance to plastic deformation and high temperature mechanical properties needs to be extensively investigated.

The microstructure of Ti(C,N)-based cermets can range from a typical ceramic structure, with a limited amount of metal at the grain boundaries of the hard phase, to a metal skeleton structure with ceramic particles embedded if high metal contents are used. A key aspect to achieve high mechanical performance and good mechanical properties is to control the ceramic-metal bond during sintering. For that reason, a number of additives are currently used in this process, mainly binary carbides such as TiC, TaC, WC or Mo₂C. While TiC and TaC are cubic carbides which enhance hardness, Mo₂C is known for improving the wetting of the ceramic into the metallic bond, and also for improving the high temperature deformability in Ti(C,N)-based cermets [3]. When several ceramic components are employed, the typical core-rim microstructure is developed during sintering for the carbonitride grains [4]. The core consists of undisolved titanium carbonitride, and the rim, which is formed during a solution-precipitation process in the liquid melt, can be also

subdivided in two regions, an inner rim and an outer rim with different heavy elements content. The rim inhibits grain growth and coalescence of the carbonitride grains during the sintering process.

Many aspects have to be considered to obtain a Ti(C,N)-based cermet with good mechanical properties in the low and high temperature range, beginning with the starting powder of the ceramic carbonitride phase, whose characteristics will determine the quality of the hard phase. Chemical purity, particle size distribution, and stochiometry of the powder are the major issues; in particular the ratio C/N is critical in the morphology of the ceramic phase [5], affecting the thermal conductivity and the oxidation behavior of the final product [6]. These factors can be controlled by the synthesis method. Mechanical milling has strong advantages such as its low cost and its capability of producing ultrafine powders, nano-structured materials, and very homogeneous final materials [7]. Besides, it does not need solvents and it is a low temperature process. Powders obtained by mechanical milling possess increased sinterability due to their refined microstructure and the high amount of induced defects. Therefore they react at higher speeds and lower temperatures. Reactive milling processes consist of mechanical milling followed by a solid-state reaction. If chemical reactions induced by milling are exothermic enough, a self-sustaining reaction similar to self-propagating high-temperature synthesis (SHS) can be initiated within the milling jar at room temperature after a critical milling time. This kind of mechanochemical process is generally called mechanically induced self-sustaining reaction (MSR) [8].

In this work, the creep behavior of a $TiC_{0.76}N_{0.24}$ + 15wt.% Co (CoTi) + 5wt.% Mo_2C cermet, produced by one step mechanically induced self-sustaining reaction followed by pressureless sintering, has been analyzed to validate the production method, the C/N ratio, and the binary carbide additive in the high temperature mechanical properties of the resulting cermet.

Experimental Procedure

In this study, samples with $TiC_{0.76}N_{0.24}$ + 15wt.% Co (CoTi) + 5wt.% Mo_2C have been deformed under uniaxial compression at constant load and temperatures between 1100-1200ºC to achieve plastic deformation, with stresses ranging from 27-91 MPa in an inert (Ar) atmosphere. The Ti(C,N)-based cermet has been synthesized by MSR, using a modified planetary mill to achieve solid-gas reactions at constant pressure [9]. Ti, C (as graphite), Co, and Mo_2C of high purity were milled in the planetary ball mill in a high purity N_2 atmosphere, until a mechanically self-sustained reaction was achieved. The green bodies where then conformed by cold isostatic pressing, and pressureless sintered at 1400ºC during 1 h in an inert He atmosphere. Although the starting powder carbonitride composition was $TiC_{0.5}N_{0.5}$, the reaction of Ti with Co during the milling to form an intermetallic compound (CoTi), resulted in the higher C/N ratio of the carbonitride phase written throughout the paper. The whole production process is detailed elsewhere [10].

The samples where cut into parallelepipeds with dimensions of 2.5 x 2.5 x 5 mm³ with a precision diamond saw, and then rectified in order to ensure the parallelism of the surfaces. The samples where then mounted on alumina pellets and tested in a prototype machine with a cantilever system, which ensured constant load for creep tests with alumina rams. The ensemble rams+sample was enclosed into an alumina hollow cylinder, which allowed a constant gas flow (Ar) during the experiment to ensure an inert atmosphere and prevent oxidation of the samples. The furnace had $MoSi_2$ resistors, and an additional thermocouple was placed beside the sample inside the alumina cylinder. The deformation of the sample was registered by an extensometer and it was continually recorded versus time. The temperature changes were all carried out at 10ºC/min.

The mechanical data have been analyzed using the standard high temperature power law for steady state deformation:

$$\dot{\varepsilon} = A\sigma^n \exp(-Q/kT) \tag{1}$$

where A is a parameter depending on the microstructure, n is the stress exponent, Q is the activation energy for the deformation process, and k is the Boltzmann constant.

The microstructure of the samples before and after the creep tests was studied using a JEOL 6450LV scanning electron microscope equipped with backscattered electron detectors, which provide compositional contrast in the images, and a microanalysis X-ray energy dispersive spectrometer (EDX), which allows chemical analysis of the different phases of the cermet. Sections parallel to the compression axis were cut from the deformed and as-received samples, and all the surfaces were polished up to 1 μm with diamond paste. No etching was used on the samples, since thermal attack resulted in oxidation of the polished surfaces. The carbonitride grains were characterized by measuring the equivalent planar diameter, $d = \left(\dfrac{4 \cdot area}{\pi}\right)^{1/2}$, and the shape factor,

$F = 4\pi \dfrac{area}{(perimeter)^2}$, using ImageJ software.

Results and discussion

Microstructure of the as-received material. The as-received sintered samples were found to be fully dense, although a few processing cracks and cavities existed, as can be observed in Fig.1 (cavities are distinguished in black color). The zones with the highest amount of pores are located in regions with a lack of metallic (Co) binder phase. Three phases can be distinguished in this cermet. The metallic binder (bright grey phase) is homogeneously distributed around the ceramic carbonitride grains (dark grey phase), some of which exhibit the typical core-rim structure. The characteristic inner and outer rims were not observed in our samples due to the low content of Mo$_2$C. Finally, small grains (bright white phase) are located at the ceramic-binder interfaces. The analytical microscopy performed on these bright white grains shows that they correspond to accumulations of the Mo$_2$C additive. The EDX analysis performed on the binder phase showed that its composition consists of an intermetallic compound of titanium and cobalt with iron impurities in a very small amount. The ceramic phase has equiaxed grains ($F = 0.82\pm0.06$) with an average grain size of titanium carbonitride of 2.4 ± 1.2 μm.
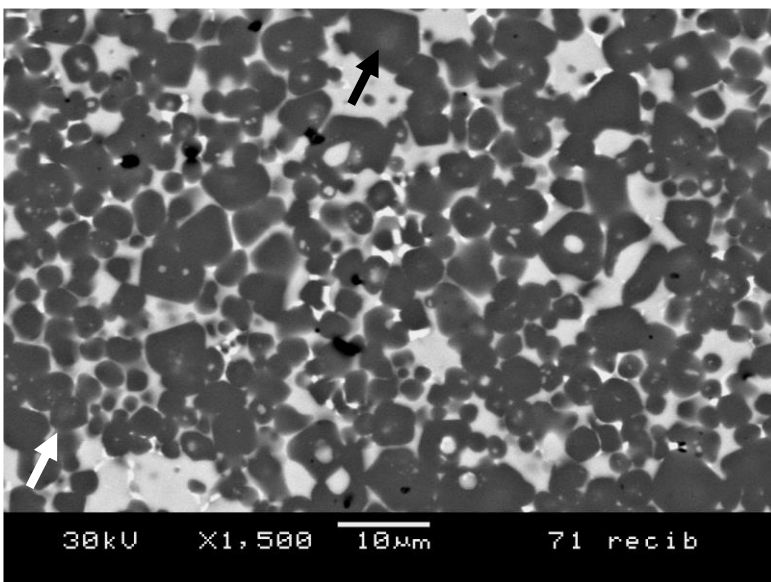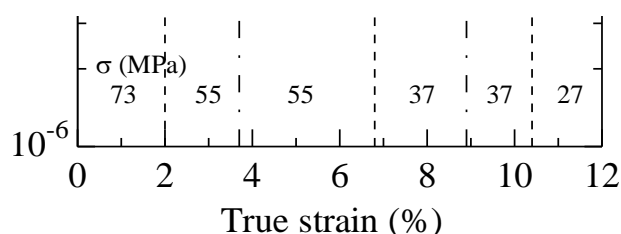

Fig. 1. SEM micrograph of the as-received cermet. The arrows point at carbonitride grains with the distinct core-rim structure.
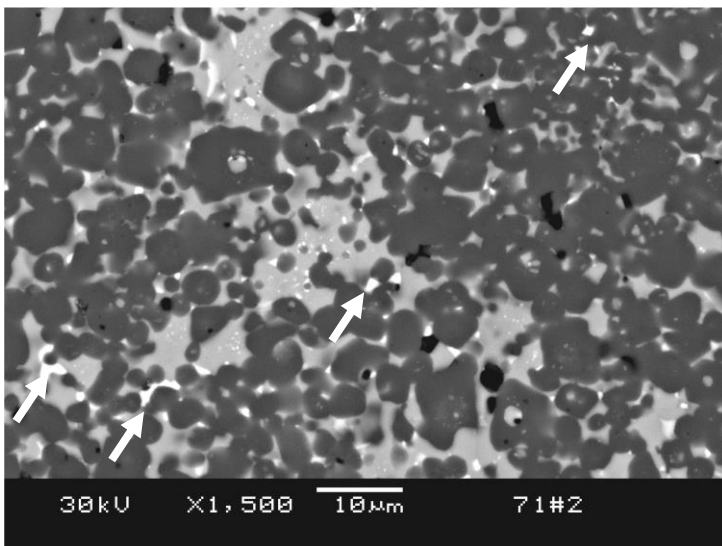
Creep results. The stress exponent from creep experiments with controlled incremental load steps has been estimated, and the activation energy of the deformation process has also been

calculated from temperature changes in the creep test. The values obtained for these two parameters have been $n = 1.7 \pm 0.6$ for the stress exponent, and $Q = 4.3 \pm 0.5$ eV for the activation energy. This activation energy is comparable to that of C diffusion in TiC (4.2 eV) [11]. Typical strain-rates ($\dot{\varepsilon}$) ranged from $3 \cdot 10^{-6}$ s^{-1} to $6 \cdot 10^{-4}$ s^{-1}. The results of the creep tests were very reproducible, indicating that no oxidation was interfering with the plastic deformation of the samples. The samples were deformed up to a 10-14% strain (ε), showing no significant deterioration after the tests other than a very thin oxidized surface film. Typical creep test data (strain rate versus strain) are plotted in Fig. 2.

Fig. 2. Strain rate versus strain plot of a typical creep test with incremental load steps and temperature steps, showing the temperatures and stresses used in the experiment, and the individual values of stress exponent (n) and activation energy (Q) obtained from each load or temperature change respectively.

The microstructure of the deformed samples did not show significant changes with respect to as-received samples. Grain size of the deformed samples has been estimated as $d = 2.3 \pm 1.2$ μm, and the shape factor $F = 0.80 \pm 0.06$, so no grain growth or grain deformation was detected after high temperature creep of the samples. No decohesion of the grains by cavitation has been observed. Grains maintain their size and shape, which is characteristic of a grain boundary sliding (GBS) deformation mechanism. Some pockets of additive Mo$_2$C are signaled by arrows on the micrograph.

Fig. 3. SEM micrograph of the microstructure of the deformed cermet. The carbonitride grains retain their initial equiaxed shape and size, indicating that the macroscopic deformation of this phase is preferentially grain boundary sliding.

The absence of grain deformation after a considerable strain is characteristic of a superplastic behavior and has also been reported for fine grained ($d \sim 1$ μm) materials. Grain size should have a strong influence on the deformation behavior. The model of Ashby and Verral [12] for superplastic deformation by grain sliding assumes that the grains do not exhibit significant deformation in the end of the process. Accommodation takes place by diffusion in the bulk or in the grain boundaries.

Both aspects, mechanical parameters (stress exponents $n \sim 2$) and microstructural observations (no significant changes in the microstructure of the deformed samples, size and shape of grains unchanged after deformation) agree with a grain boundary sliding deformation mechanism, which could be accommodated by C diffusion inside the carbonitride grains, according to the estimated activation energies. Other authors [13] with a very similar material (HIP sintered TiC$_{0.7}$N$_{0.3}$ + 18 vol.% Co + 6.4 vol.% Mo$_2$C) have proposed a similar GBS mechanism, where the accommodation process includes a possible cobalt infiltration in the grain boundaries. However, these authors found that grains became cohesionless after deformation, although the samples where deformed to smaller strains (3%). Comparisons can also be established with studies of the high temperature plastic flow of TiC + 20wt.% Mo$_2$C + 20wt.% Ni cermet [3] (tested under uniaxial compression) with a grain

size (d=1.93 μm) comparable to our material. Authors report values of n=0.6, smaller than ours, grain growth with increased strain at different strain-rates, which we do not observe, and also propose a sliding along contiguous carbide grain boundaries mechanism. Previous results of plastic deformation in cermets synthesized and sintered by the same method, but with different C/N ratio and using Ni as metallic binder and no carbide addition ($TiC_{0.75}N_{0.25}$ + 15wt%. Ni (Ni_3Ti + NiTi) and $TiC_{0.79}N_{0.21}$ + 15 wt.% Ni (Ni_3Ti)), showed poorer results in terms of influence of oxidation in the high temperature plastic behavior. Though the sample with higher C content (and Ni binder) exhibited a higher flow stress, the cermets in this study possess enhanced mechanical properties at high temperatures due to the additive Mo_2C, which improved their resistance to oxidation.

Conclusions

A $TiC_{0.76}N_{0.24}$ + 15wt.% Co (CoTi) + 5 wt.% Mo_2C cermet synthesized by a mechanically self-sustaining reaction and pressureless sintered has been deformed plastically in uniaxial compression at temperatures in the range 1100-1200°C. The C/N ratio chosen, as well as the use of Co as metallic binder and Mo_2C as additive, has avoided interference of oxidation on the high temperature deformation of the samples, thus achieving totally reproducible results of strain rate for identical external conditions of temperature and stress.

Values for stress exponent of n=1.7±0.6 and activation energy Q= 4.3±0.5 eV have been estimated from the creep tests. The grain size and shape factor have been estimated on as-received and deformed samples. The samples after deformation do not exhibit grain growth nor grain shape changes nor cavitation as found by other authors for similar cermets. A grain boundary sliding deformation mechanism accommodated by C diffusion in Ti(C, N) is compatible with our results.

Acknowledgements

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