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PLASMA TORCH PRODUCTION OF Ti/Al NANOPARTICLES

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ABSTRACT

Using the Aerosol-through-Plasma (A-T-P) technique high surface area bi-cationic (Ti-Al) oxide particles of a range of stoichiometries were produced that showed remarkable resistance to sintering. Specifically, we found that homogeneous nanoparticles with surface areas greater than 150 m^2/gm were produced at all stoichiometries. In particular, for particles with a Ti:Al ratio of 1:3 a surface area of just over 200 m^2/gm was measured using the BET method. The most significant characteristic of these particles was that their sinter resistance was far superior to that of TiAl particles produced using any other method. For example, A-T-P generated particles retained >70% of their surface area even after sintering at 1000 C for five hours. In contrast, particles made using all other methods lost virtually all of their surface area after an 800 C treatment.

INTRODUCTION

Ti-Al ceramic compounds have attracted interest, due to their high surface area and good thermal stability, for applications in automotive catalytic converters, components expose to high temperature in electric and electronic devices, shield material in nuclear reactors, and tools for a melting furnace (1). The textural, structural, and surface properties of these compounds are strongly influenced by the method of synthesis; techniques like precipitation, impregnation, and grafting have been used to prepare materials with tailor made surface areas, acid/ basic properties and defined porosity structures. (2-5).

Of particular interest to our team is the potential use of TiAl as a catalyst support material for automotive three-way catalysts. High temperatures affect all the components of the catalytic converter, the support sinters and can suffer a phase change, reducing the total surface area. The active metal particles sinter, resulting in a decrease in the fraction of the metal available for catalytic reactions (6-9). This low sintering resistance can be countered to some extent by the addition of elements as Ti, Ce and Zr as structural promoters, which also stabilizes the very extensive alumina support against sintering (9-13). An enhanced oxygen storage capability is also a key feature in modern catalytic converters in order to boost the oxidation of CO, NO_x and hydrocarbons (7, 11-14)

Ti-Al oxides are among a handful of materials capable of 'buffering' the oxygen concentration in automotive exhaust. Experience indicates that mixed oxides, such as Al-Ce, Al-Ce-Zr, Ce-Zr, and Ti-Al are potentially the best oxygen 'buffers'. That is, each is at least moderately stable at elevated temperature and each includes one ion capable of changing oxidation state at around 650 C. Hence, each can act as an oxygen 'buffer' during episodic spikes away from stoichiometry in gasoline engine exhaust. During fuel excess excursions Ce and Ti ions in oxide compounds have proven to concomitantly accept electrons and release oxygen, and during fuel lean excursions, they can give up electrons and bond with more oxygen. In addition to suitable chemistry support materials must be thermally resistant. That is, they must retain most of their surface area even after many hours at temperatures encountered by catalytic converters in automotive exhausts (ca. 650 C).

The present work is specifically focused on the surface area and sinter resistant of A-T-P produced Ti-Al oxides of three different cation ratios; 1:3, 1:1 and 3:1. Parameters employed in evaluating the suitability of A-T-P produced particles for three way catalysts include: surface area/gram, particle size distribution and resistance to sintering. It was found in this study that A-T-P produced Ti-Al particles showed superior characteristics for these properties relative to A-T-P produced particles of other composition (15-17), and enhanced thermal stability relative to TiAl nanoparticles generated using more conventional techniques. First, some of the samples had BET surface areas greater than 200 m^2/gm initially. Second, TEM examination showed that, in most cases, the particles were uniformly small, with a tight particle size distribution and an average particle size of order 10 nm or less. Third, even after sintering for five hours at 800 C, three of the samples (all of the 'second set') had surface areas greater than 130 m^2/gm. This indicates that the A-T-P produced particles are far more sinter resistant than TiAl particles produced using other techniques.

EXPERIMENTAL

Liquid Aerosol A-T-P Method- The fundamentals of the A-T-P process for generating oxide nanoparticles, particularly multi-cationic, from liquid precursors is thoroughly described elsewhere (15). Briefly, the process for bi-cationic particles consists of dissolving salts of two different metals in water and then sending the liquid/dissolved salts through the plasma torch (operated at approx. 90% of atmospheric pressure) as an aerosol. The solid nanoparticles and micron scale particles produced via this method in the torch are then trapped on filter paper. In this case the two salts employed were Al(NO3)3•xH2O (x~9) (99.999% from Alfa Aesar), and Ti(NO3)4•4H2O (99.9+% from Aldrich). The ratio of the dissolved salts was selected to create an aerosol with the targeted Ti/Al ratio as previous work has shown that the atomic ratio in the aerosol closely matches that of the homogenous composition particles. The aerosol gas was a mixture of argon (5 sccm) and oxygen (5 sccm) and the plasma gas was pure Ar (10 sccm). The torch was operated at 850 W in all cases.

Analysis of the particles employed the same instruments and techniques described in earlier reports (15-17), all found at the Universtiy of New Mexico: transmission electron microscopy (TEM, JEOL 2010), scanning electron microscopy (SEM,5200 Hitachi), nitrogen isotherm determination of surface area (BET, Micromeretics ASAP 2000) and x-ray diffraction (XRD, Philips Powder). The particle size distribution shown was determined by hand measuring more than 200 particle images (TEM).

Sintering was performed in oxygen flows (50 cc/min, STP) in a Netzche TGA/DSC. A fresh sample was used for each temperature. The protocol was to raise and lower temperature at 25 C/min and to hold fresh material at the selected temperature for five hours

RESULTS/DISCUSSION

TEM Images, Figure 1, show that the unsintered material (fresh from the torch) consists of very small particles for all three compositions. Also, in agreement with XRD results, those particles with the highest titania content (3:1) were the most crystallized (Figure 1b). XRD results indicate that the crystal phase seen is the anatase phase of titania. There is no signal from any phase associated with aluminum or an aluminum alloy. Although the data is not conclusive, it is possible that the surface of these is amorphous alumina (Figure 1b). This would be consistent, for example, with very compelling images obtained for Ce-Al particles. For Ce-Al oxides it is clear that particles had a ceria core and an amorphous alumina shell (15).

Figure 1: *TEM of Ti/Al Oxide Particles, Set 1.* A) At a composition of 75Ti/25Al only nanoparticles are found and the average size is clearly of the order 10 nm. B) At higher magnification it is clear that a large fraction of each particle is crystallized, apparently in the Anatase TiO2 phase. C) At a 50Ti/50Al composition a few 'large' particles (ca. 0.1 micron) are found.

The fact that a bimodal distribution of particles exists (Figure 1c) in some cases supports the extension of an earlier model of nanoparticle formation during the A-T-P process 'expansion and shattering' (15) to the Ti-Al system. That is, we suggest nanoparticles of TiAl form when a gas (probably nitrogen or nitrogen oxide) created during the decomposition of the precursor molecules, causes a nearly 'plastic' form of the ceramic, present during the high temperature encountered in the plasma, to expand as a hollow shell. In the afterglow, this shell shatters because of stresses induced by rapid cooling (thermal shock). The shattering process creates nanoparticles. This model is distinctly different from the standard model of nanoparticle formation in conventional aerosols (16,17).

It must be noted that the images in Figure 1 are taken from Set 1 of the Ti-Al particles. As the BET measurements make clear (Table I), the two samples, made by two operators (Set 1- KL; Set 2- LC), each ostensibly using an identical procedure, yielded particles with very different initial surface areas. The size 'gap' does narrow as the sintering temperature is raised.

The remarkably high surface areas of Set 2 particles raise a question: Are the BET surface areas correct? The tentative answer is yes, with caveats. Statistically, the BET measures are excellent. The correlation coefficients were greater than 0.999 for all samples, the y-intercept was zero to the highest accuracy possible to determine.

Moreover, the changes with surface area (below) with sintering trend in a fashion consistent with expectations. What are the caveats? Perfectly spherical particles with an average size of 10 nm and a density of 3.8 gm/cm^3 (best estimate) have a surface area of about 40 m^2/gm. Yet, as shown in Figure 2, the BET surface area of particles with an average diameter of 'about' 10 nm as determined from TEM images, have a measured BET surface area (Table I) of 106 m^2/gm. Is one measure correct and not the other? Possibly both are correct. The particles can have both the diameter distribution shown in Figure 3, and the surface area of Table I, if the 'roughness factor' of the surface is about 2, or if the particles have some porosity.

It is interesting to extrapolate the data in one sense. Specifically, as the ratio of surface area to volume for nearly spherical particles is inversely proportional to diameter, it appears that the particles with the highest BET surface area (>200 m2/gm) probably have an average diameter of about 5 nm.

Figure 2: *Particle Size Distribution (Diameter) for Set 1, 0.25Ti/0.75Al Particles.* Particle sizes were binned by diameter, and almost all were found in the 0-5, 5-10, 10-15 and 15-20 nm bins, although one particle with a diameter of 100 nm was found. The mean size is approximately 8 nm.

Figure 3 has been prepared in order to compare the results of this study with the results of earlier studies using non-A-T-P methods. The A-T-P produced particles presented the lowest initial surface area when compare with particles of equivalent composition prepared by coprecipitation and sol-gel methods; however, even among those non A-T-P methods there is a great variation in the values reported between studies, reinforcing the statement that the textural, structural, and surface properties of these compounds are strongly influenced by the method of synthesis. **Figure 3** *Initial surface area (as produced) for Ti-Al particles prepared using alternative methods.* The A-T-P sets of particles have the lowest surface area when compare against coprecipitated particles reported by Ramirez et al. (18), sol-gel (Miller et al. reference 19) and non-alkoxide gel (Sivakumar et al. reference 20).

Due to the fact that one of the key features of the Ti-Al materials is their high temperature resistance, sintering experiments were performed by treating the particles for five hours at elevated temperature in a Netzche TGA/DSC. It is clear that the particles, both Set 1 and 2, are resistant to sintering at temperatures at least as high as 1000 C (Figure 4). Indeed, it is remarkable that the particles in Set 2 have surface areas greater than 130 m^2/gm even after treatment at 800 C for five hours. It also is apparent that at 1200 C the particles lose virtually all surface area.

TEM studies of the samples after sintering are qualitatively consistent with the BET measurement. As seen in Figure 4, after sintering at 800 C 'necks' form between the particles and a network of partially sintered particles forms. After treatment at 1200 C there is virtually nothing that appears 'particulate'. The material has sintered to form a single, nearly homogeneous solid.

Figure 4: *Surface Area as a Function of Temperature.* In all cases samples were treated for five hours at the temperature shown. Set 1 and Set 2 data show similar trends although it is clear that the particles in Set 1 are far smaller initially.

It is notable that the resistance to sintering compares well with that reported elsewhere for high surface area, sinter resistant particles (19, 21). That is, other than our own finding (see Figure 4), we have not found any reports of materials with a surface area of greater than 100 m^2/g after sintering at 1000 C, or materials that retain more than 70% of the initial surface area after this treatment, as shown in Figure 5.

Figure 5- Comparison of NORMALIZED Surface Area Losses: A-T-P Generated Al-Ti samples vs. literature reported samples of similar composition prepared using alternative methods; non-alkoxide gel (Sivakumar et al. reference 20) and sol-gel (Escobar et al. reference 21). Notably, only the A-T-P particles show any stability above 900C.

CONCLUSIONS

Uniquely sinter resistant TiAl oxide particles can be synthesized using the Aerosol-through-Plasma (A-T-P) technique. First, we found nanoparticles with surface areas greater than 150 m^2/g were produced over a broad range of cation ratios. Second, at all cation ratios the A-T-P particles retained more than 70 % of the initial surface area after calcination at 1000 C for 5 hrs. In contrast, TiAl oxide particles made using other techniques lost virtually all their surface area after sintering at only 900 C.

Some findings in this study also support suppositions regarding the characteristics of A-T-P particles put forth in earlier publications. First, the occasional finding of 'large' TiAl particles (i.e.> 100 nm diameter) is consistent with the postulate that nanoparticles form during A-T-P synthesis due to a mechanism unique to the A-T-P process: the shattering of larger, hollow particles. Second, the finding that the particles have a core-shell structure, with an amorphous alumna shell and a TiO2 core supports a proposition previously put forward by our team: the stability of particles is enhanced by the existence of phase segregation, particularly the formation of an amorphous alumina shell. In conclusion, the A-T-P technique is a novel and effective method of obtain Ti-Al nanoparticles with a narrow size distribution and high sintering resistance.

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