



AFRL-RX-WP-TP-2010-4075

**SOLUTION ASSISTED LASER ABLATION SYNTHESIS OF
DISCRETE ALUMINUM NANOPARTICLES (Preprint)**

C.A. Crouse and J.E. Spowart

**Metals Development Section
Metals Branch**

E. Shin and P.T. Murray

University of Dayton Research Institute

**JANUARY 2010
Interim Report**

Approved for public release; distribution unlimited.

See additional restrictions described on inside pages

STINFO COPY

**AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE**

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.				
1. REPORT DATE (DD-MM-YY) January 2010		2. REPORT TYPE Journal Article Preprint		3. DATES COVERED (From - To) 01 January 2010 – 01 January 2010
4. TITLE AND SUBTITLE SOLUTION ASSISTED LASER ABLATION SYNTHESIS OF DISCRETE ALUMINUM NANOPARTICLES (Preprint)			5a. CONTRACT NUMBER IN HOUSE	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER 62102F	
6. AUTHOR(S) C.A. Crouse and J.E. Spowart (Metals Branch, Metals Development Section (AFRL/RXLMD)) E. Shin and P.T. Murray (University of Dayton Research Institute)			5d. PROJECT NUMBER 4347	
			5e. TASK NUMBER RG	
			5f. WORK UNIT NUMBER M02R4000	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Metals Development Section (AFRL/RXLMD) Metals Branch, Metals, Ceramics, and Nondestructive Evaluation Division Materials and Manufacturing Directorate, Air Force Research Laboratory Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command, United States Air Force			8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RX-WP-TP-2010-4075 University of Dayton Research Institute Dayton, OH 45469-0172	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force			10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/RXLMD	
			11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-RX-WP-TP-2010-4075	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				
13. SUPPLEMENTARY NOTES PAO case number 88 ABW-2009-4303, cleared 07 October 2009. The U.S. Government is joint author of this work and has the right to use, modify, reproduce, release, perform, display, or disclose the work. Submitted to Materials Letters. Paper contains color.				
14. ABSTRACT Discrete aluminum nanoparticles with an average particle size of 21 nm have been prepared by laser ablation of a metallic aluminum target submerged in dry tetrahydrofuran in the presence of 0.001 M oleic acid as a stabilizing ligand. The particles display high solubility and minimal aggregation while the absence of oleic acid leads to highly aggregated particles and a broader particle size distribution. O/Al ratios obtained from EDS analysis of single particles and small particle clusters suggests the particles produced are primarily metallic aluminum with minimal oxide content.				
15. SUBJECT TERMS nanomaterials, metals and alloys, laser processing				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 14
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified		
			19a. NAME OF RESPONSIBLE PERSON (Monitor) Jonathan E. Spowart	
			19b. TELEPHONE NUMBER (Include Area Code) N/A	

Solution assisted laser ablation synthesis of discrete aluminum nanoparticles

C.A. Crouse,^{*a} E. Shin,^b P.T. Murray^b and J.E. Spowart^a

^a Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433, USA

^b Research Institute, University of Dayton, Dayton, OH 45469-0172, USA

*Corresponding author. E-mail address: christopher.crouse@wpafb.af.mil (C.A. Crouse)

ABSTRACT

Discrete aluminum nanoparticles with an average particle size of 21 nm have been prepared by laser ablation of a metallic aluminum target submerged in dry tetrahydrofuran in the presence of 0.001 M oleic acid as a stabilizing ligand. The particles display high solubility and minimal aggregation while the absence of oleic acid leads to highly aggregated particles and a broader particle size distribution. O/Al ratios obtained from EDS analysis of single particles and small particle clusters suggests the particles produced are primarily metallic aluminum with minimal oxide content.

Keywords: Nanomaterials; metals and alloys; laser processing

1. Introduction

The high energy density and reactive nature of aluminum nanoparticles (nAl) has catalyzed interest into their use as fuel and/or additives in many propulsion and pyrotechnic formulations. The reaction kinetics for Al combustion are governed by surface diffusion, therefore transitioning from micron-scale powders to nanoparticles has lead to remarkable enhancements in reaction rates due to an exponential increase in the specific surface area of the reactant materials. To meet the increasing demand for nAl, many synthetic approaches have been explored including wet chemical methods, *e.g.*

catalyzed reduction of alane precursors [1,2,3] and hydrogenolysis of organometallic precursors [4], as well as physical techniques, *e.g.* electrical explosion of Al wire [5], plasma vaporization/inert gas condensation [6] and laser ablation [7]. The pyrophoric nature of nAl requires passivation with a thin (2-6 nm) amorphous oxide layer at the particle surface to serve as a barrier to further oxidation of the underlying metal. Though effective, this method consumes active Al and can result in a material with more than 40% unreactive oxide by weight, as the particle size drops below 30 nm [8]. To avoid loss of active Al due to oxide formation researchers have explored alternative passivation routes including the use of hydrocarbon [9] and perfluorinated ligands [3], polymers [9], and transition metal oxide coatings [8]. Though these approaches produce products which are relatively stable to environmental oxidation, they provide little control over particle size and/or yield a highly aggregated product. To further enhance the potential for use of these materials in propulsion and pyrotechnic applications it would be desirable to have a discrete product with minimal aggregation in addition to tunable size control.

Laser ablation in aqueous and organic solvents has regularly been used as a route for producing noble metal and metal oxide nanoparticles [10]. Particle size control is shown to be dependent upon operating conditions (wavelength, power, etc.) and thus a variety of particle size distributions can be achieved by manipulation of the experimental parameters. Additionally, stabilizing agents (*e.g.* polymers and/or surfactants) can be added to yield a stable colloid or to prevent/minimize aggregation in the reactant products [10,11]. Herein we report, to the best of our knowledge, the first successful example of solution assisted laser ablation to yield discrete, organically capped nAl from bulk metallic Al substrates in a dry organic solvent (tetrahydrofuran) containing a stabilizing ligand (oleic acid) to minimize particle aggregation.

2. Experimental

The experimental setup is illustrated in Fig. 1. A 250-mL four-neck tapered sonochemical flask (Ace Glass, Inc.) was charged with a one inch Al target and fitted with three rubber septa and a nylon

#25 cell window holder (Ace Glass, Inc.) containing a calcium fluoride coated optical window (CVI Laser). Oleic acid (OA)(tech. grade, >90%) and tetrahydrofuran (THF) (anhydrous) were obtained from Sigma-Aldrich and used as received. Aluminum targets (99.9995%, 1 in. diameter) were obtained from Kurt J. Lesker Company. The flask was evacuated and purged with dry nitrogen a minimum of three times to remove air and moisture. A 0.001 M solution of OA in anhydrous THF (*ca.* 25 mL) was added until the solvent level was *ca.* 1 cm above the surface of the aluminum target. The reaction vessel was then purged with nitrogen and sealed. A focusing lens (focal length = 300 mm) was positioned above the reaction vessel yielding a 1 mm spot size on the target. A 1064 nm Nd:YAG laser, operating at 20 Hz with a beam power of 0.88 J/pulse, was used to ablate the aluminum target for 5 minutes. The reaction mixture was transferred via canula to a sealed vial where it was stored under nitrogen prior to analysis. Transmission electron microscopy (TEM) samples were prepared by drop drying the solution onto a 200 mesh Cu grid coated with a holey carbon film (SPI, Inc.). TEM images were obtained on a FEI Titan microscope operating at 300 kV. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed using an EDAX detector from 0-20 keV. Al₂O₃ nanoparticles (AMCN01, Accumet Materials Co.) were used as a standard for comparison of O/Al ratios. Particle size distribution data was obtained from diameter analysis of 471 particles from 10 separate TEM images and sample locations using ImageJ software.

3. Results and Discussion

Aluminum nanoparticles were prepared by solution assisted laser ablation of an Al target submerged in a 0.001 M OA solution in THF, and also in THF without any OA. As prepared these particles become suspended in solution and remain in solution for a period of several months, Fig. 2. TEM micrographs of the products are presented in Fig. 3. The OA stabilized nAl (OA-nAl) particles are noticeably discrete (non-aggregated) with a narrow size distribution displaying an average diameter of 21 nm as shown in the particle size distribution graph, Fig. 3(d). Some larger particles and fragments, 100 nm or more, are

also occasionally observed as shown in Fig. 3(b). Solubility of the product is in part due to the small particle size and their discrete nature but also the presence of an OA coating at the particle surface provides a hydrophobic shell which enhances miscibility with common organic solvents. As shown in Fig. 3(c), ablation in the absence of OA also leads to the formation of nAl, however, these particles are highly aggregated with only a small percentage of the particles remaining discrete.

EDS spectra, Fig. 4, were collected to analyze the O/Al ratios for the discrete OA-nAl. These ratios were compared to O/Al ratios obtain for commercial Al₂O₃ particles to qualitatively understand the chemical state of the OA-nAl. Spectra were acquired from both single particles and clusters of particles present on the TEM grids. Low O/Al ratios (Table 1), obtained from comparing the intensities of the aluminum signal (1.44 keV) to the oxygen (0.46 keV) signal, suggests that the particles mostly remain as metallic aluminum and are not fully oxidized during the synthesis or upon exposure to atmospheric conditions.

Previous reports on the preparation of nAl by laser ablation in a liquid phase [12] suggested the formation of nAl with an average particle size of 50 nm or less, however, no evidence was provided confirming the state of Al as either metallic or oxide. Moreover, the experimental design consisted of an ablation target formed from compressed Al powder with distilled water as the liquid phase. Due to the passivated oxide layer present on Al powders the ablation target would contain an elevated oxide content compared to a bulk metal target. Additionally, Al readily reacts with water to form aluminum oxide and oxide-hydroxides [13], therefore one might expect that the primary product would be aluminum oxide nanoparticles and not metallic nAl as suggested. To circumvent these complications in our studies we have chosen to perform all experiments under air-free conditions by operating with dry organic solvents under inert atmospheres. High purity Al sputtering targets were selected to minimize the presence of oxidized Al in the system. Additionally, bulk Al is perhaps the most stable starting material from which Al nanoparticles can be prepared, thereby eliminating the use of expensive and

sensitive powders and/or organometallic precursors. Previous literature reports have utilized the coordination of various carboxylic acid ligands to the metallic Al surface to prevent oxide passivation of the particles [3,14]. With similar intentions, OA was added to our reaction mixture in an attempt to inhibit oxidation of the produced metallic nAl through formation of an organic layer at the particle surface immediately upon particle formation. The presence of OA additionally aids in minimizing aggregation and promotes solubility of the nanoparticle product in the reactant solution. EDS spectra of the OA-nAl demonstrate relatively low oxygen content, which can be partially attributed to oxygen contained within the OA ligand. XPS analysis does confirm the presence of oxidized Al suggesting that an oxide layer is still present or that some of the smaller particles are partially oxidized. It is unclear whether this oxidation occurs during the reaction or upon sample preparation and exposure to the atmosphere but in either case OA was not completely successful at inhibiting oxidation although it does prevent aggregation. Similar results have been reported for the sonochemical synthesis of Al nanoparticles in the presence of an OA/dodecane mixture [14].

4. Summary

Discrete metallic nAl have been successfully prepared by laser ablation of an Al target in the presence of a dry organic solvent, THF. Aggregation of the particles was minimized through the addition of OA, whereas particles produced in the absence of OA readily form aggregates with only a small amount of particles remaining discrete. OA also appears to impart some control over the average particle size of the product leading to a narrow, unimodal size distribution displaying an average particle size of 21 nm. The discrete nature and small particle size allow for the preparation of stable particle suspensions in THF with the particles remaining suspended for months. This work provides a novel and unique route towards the synthesis of stable, discrete metallic nAl from stable and inexpensive Al precursors.

Acknowledgment

Funding for this work was made available by Air Force Research Laboratory, Materials and Manufacturing Directorate, via Air Force Office of Scientific Research and the University of Dayton, Research Institute. Their support is gratefully acknowledged. This research was performed while the primary author (C.A. Crouse) held a National Research Council Post-doctoral Research Associateship.

Figures

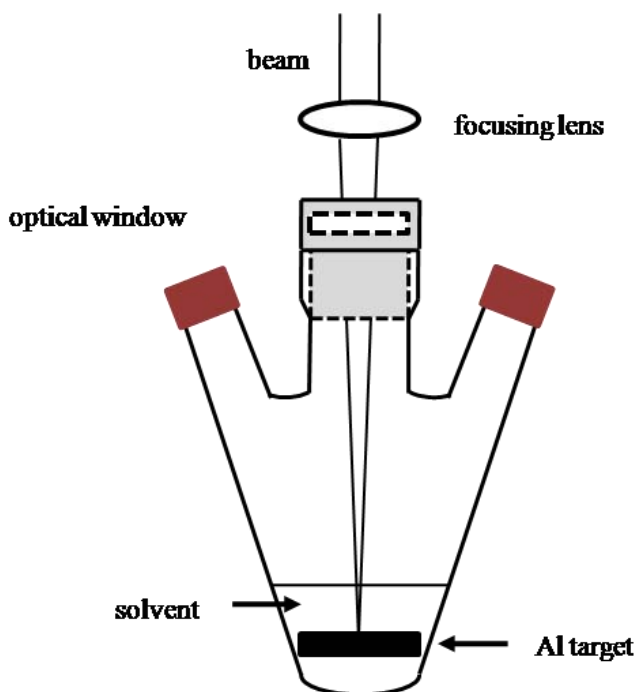


Fig. 1. Schematic of the experimental setup.

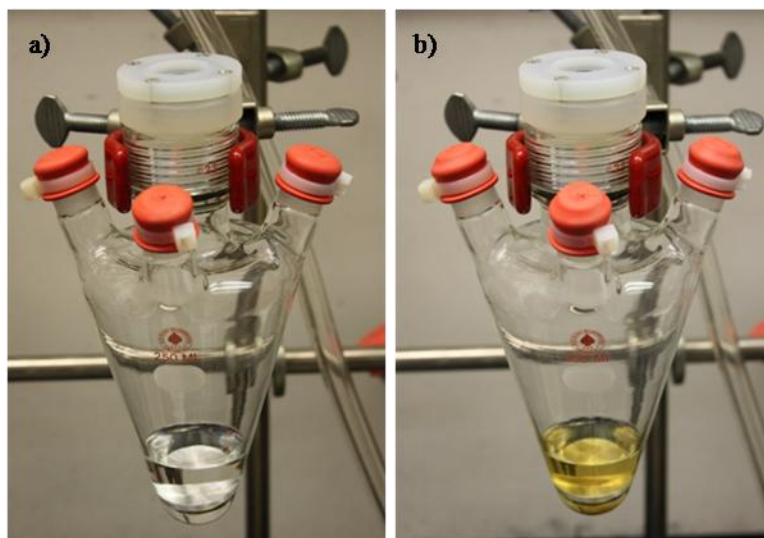


Fig. 2. Digital images of the reaction taken a) before and b) after ablation (5 minutes).

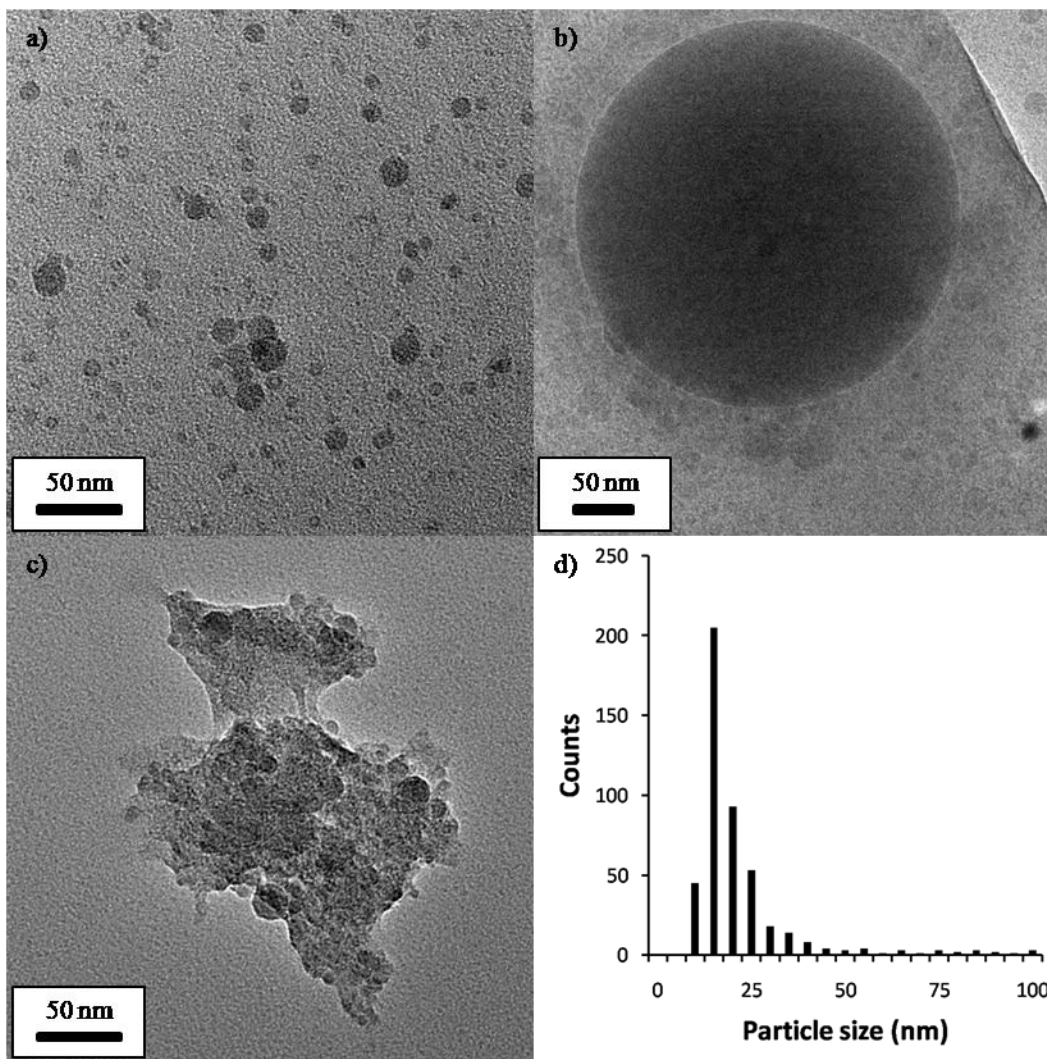


Fig. 3. TEM micrographs of (a ,b) discrete OA-nAl, c) nAl produced in THF without OA and, d) particle size distribution for OA-nAl.

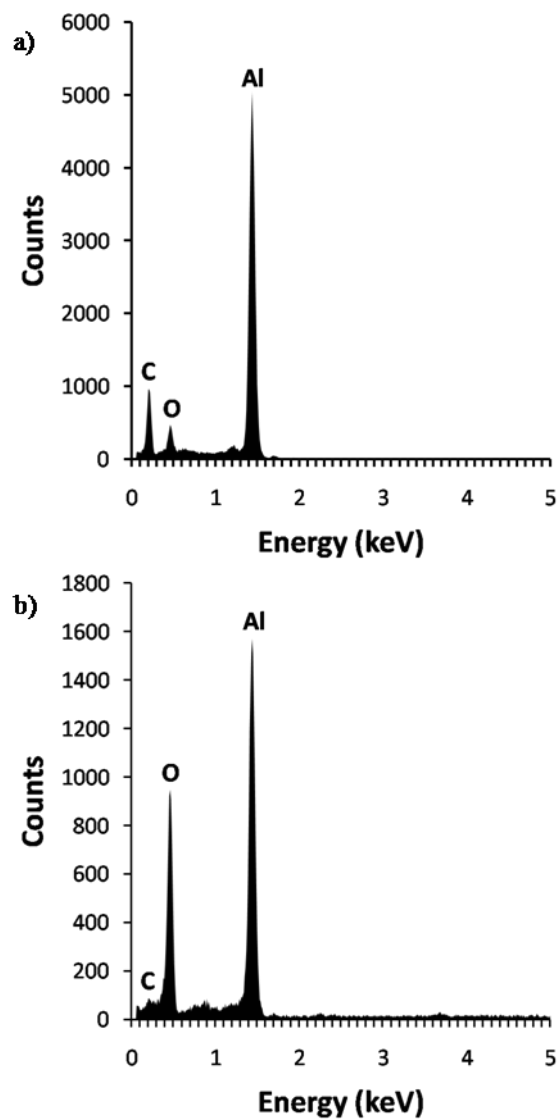


Fig.4. EDS spectra of a) discrete OA-nAl nanoparticles and b) Al₂O₃ nanopowder (control).

Table 1 O/Al ratios obtained from EDS analysis of OA-nAl and Al₂O₃ nanoparticles

Sample	O/Al
Single particle	0.094
Clustered particles	0.159
Al ₂ O ₃ (control)	0.603

References

- 1 Meziani MJ, Bunker CE, Lu F, Li H, Wang W, Gulians EA, Quinn RA, Sun Y-P. ACS Appl Mat Interfaces 2009;1:703
- 2 Haber JA, Buhro WE. J Am Chem Soc 1998;120:10847
- 3 Jouet RJ, Warren AD, Rosenburg DM, Bellito VJ, Park K, Zachariah MR. Chem Mater 2005;17:2987
- 4 Cokoja M, Parala H, Schroter M-K, Birkner A, van den Berg MWE, Grunert W, Fischer RA. Chem Mater 2006;18:1634
- 5 Ivanov YF, Osmonoliev MN, Sedoi VS, Arkhipov VA, Bondarchuk SS, Vorozhtsov AB, Korotkikh AG, Kuznetsov VT. Prop Explos Pyrot 2003;28:319
- 6 Pivkina A, Ivanov D, Frolov Yu, Mudretsova S, Nickolskaya A, Schoonman J. J Therm Anal Cal 2006;86:733
- 7 Park K, Rai A, Zachariah MR. J Nanopart Res 2006;8:455
- 8 Foley TJ, Johnson CE, Higa KT. Chem Mater 2005;17:4086
- 9 Kwon Y-S, Gromov AA, Strokova JI. Appl Surf Sci 2007;253:5558
- 10 Zhang J, Lan CQ. Mat Lett 2008;62:1521
- 11 Compagnini G, Scalisi AA, Puglisi O. J Mater Res 2004;19:2795
- 12 Kim D, Jang D. Appl Surf Sci 2007;8045:8049
- 13 Wefers K, Mirsa C. Oxides and Hydroxides of Aluminum, Alcoa Laboratories, 1988, Alcoa Technical Paper No. 19, Revised
- 14 Fernando KAS, Smith MJ, Harruff BA, Lewis WK, Gulians EA, Bunker CE. J Phys Chem C 2009;113:500