

Synthesis of Homogeneously Dispersed Nanoscale M50-Type Steel Powders via Polymeric Surfactants

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INTRODUCTION

Nanostructured materials in comparison to conventional coarse-grained materials have unique properties by virtue of their nanometer-sized grains, crystallites, or phases.¹⁻³ Although there exist several physical methods⁴⁻⁷ for the synthesis of nanoscale materials, the chemical methods^{8,9} offer several advantages such as precursor design at the molecular level, means to control particle size and size distribution, better chemical homogeneity, and also cost efficient bulk production in some cases.

M50 steel, an iron-based alloy composed of 4.0% Cr, 4.5% Mo, 1.0% V, 0.8% C, and balance Fe (in wt %) is used widely in the aircraft industry as main-shaft bearings in gas-turbine engines because of its good wear and rolling contact fatigue.¹⁰ Conventional M50 steel has large micron-sized carbide particles which act as fatigue crack initiation sites in the bearing material.^{11,12} In contrast, we can expect an improvement in the mechanical properties of such structural materials by reducing the grain size as well as the precipitate (defect) size.

The most pressing problem of making nanophase powders of multicomponent compositions such as M50-type steel is the difficulty in controlling elemental homogeneity on the nanometer scale. Such homogeneities, if present, can adversely affect the mechanical properties of the final product. Surfactants, by steric and electronic effects, can control agglomeration between fine metal particles and such polymeric surfactants have been previously used to produce well-dispersed metal particles such as iron^{13,14} as well as bimetallic palladium-copper nanoscale colloids.¹⁵

We report in this communication the use of a poly-

meric surfactant to synthesize M50 steel nanopowders. Also reported are the microstructural and other analytical characterizations of the nanopowders.

EXPERIMENTAL

Chemicals and Instrumentation

All manipulations for the preparation of the powders were performed in the dry-box or by Schlenk line techniques. For the sonochemical reaction, the reactants, iron pentacarbonyl, $\text{Fe}(\text{CO})_5$; bis(ethylbenzene)chromium, $\text{Cr}(\text{Et}_x\text{C}_6\text{H}_{6-x})_2$ ($x = 0-4$); bis(ethylbenzene)molybdenum, $\text{Mo}(\text{Et}_x\text{C}_6\text{H}_{6-x})_2$ ($x = 0-4$); and vanadium hexacarbonyl, $\text{V}(\text{CO})_6$, were purchased from Strem Chemicals. In addition, a surfactant, poly(vinyl pyrrolidone) (PVP), that was added to the reaction flask was purchased from Sigma Chemical Co. The solvent decalin was distilled over CaH_2 and degassed by bubbling argon through it for at least 5 h.

Ultrasonic treatment was done by means of a high-intensity ultrasonic probe (Sonic and Materials, Model VC-600, 0.5 in a Ti horn, 20 kHz, 100 W cm^{-2}). X-ray powder diffraction data for the as-synthesized powders (coated with mineral oil) were collected on a Norelco/Phillips diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$ Å). Scanning electron micrographs (SEM) were taken on a Cambridge (Mark 250) electron microscope fitted with an X-ray analyzer. Transmission electron micrographs (TEM) were taken on a JEOL 200CX electron microscope with an accelerating voltage of 200 kV.

Synthesis

Synthesis Without Surfactant. A dispersion of 20 g (0.102 mol) of $\text{Fe}(\text{CO})_5$, 1.40 g of $\text{Cr}(\text{Et}_x\text{C}_6\text{H}_{6-x})_2$, 1.03

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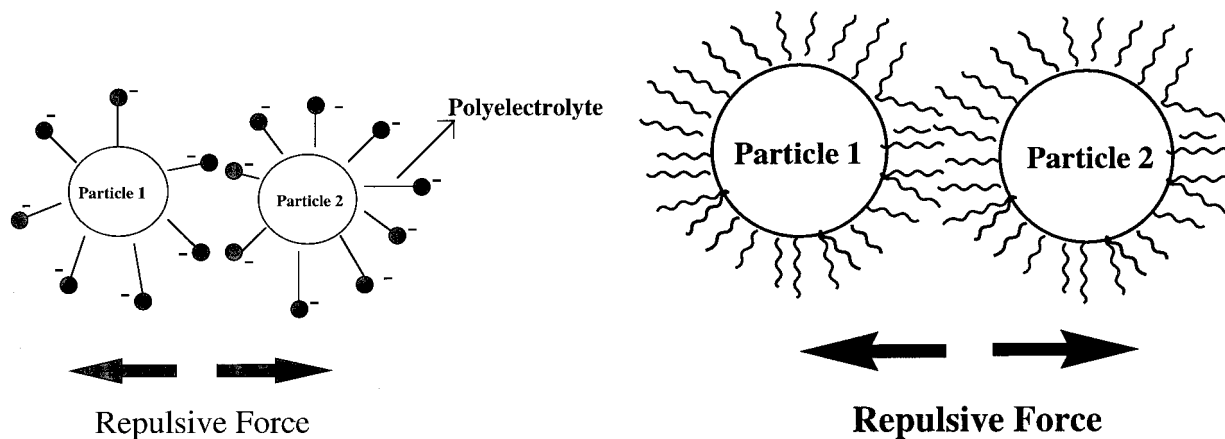


Figure 1 (a) Mechanism of electrostatic stabilization, (b) mechanism of steric stabilization.

g of $\text{Mo}(\text{Et}_x\text{C}_6\text{H}_{6-x})_2$, and 0.063 g (0.00028 mol) of $\text{V}(\text{CO})_6$ in dry decalin was sonicated at 50% of maximum vibration amplitude (sonochemical reactor horn) for 7 h at room temperature in a sonochemical reactor fitted with a condenser and gas inlet and outlet tubes connected to a mercury bubbler. The color of the solution turned dark and then black within a few minutes and this reaction mixture was sonicated until the formation of shiny metallic particles was observed on the walls of the reaction vessel. The sonication was then stopped and the decalin solvent was removed from the reaction flask via vacuum distillation. Fine black powder (yield: 6.13 g) remained at the bottom of the reactor, which was then isolated and transferred to a vial before the compaction.

Synthesis with Surfactant. The procedure for this synthesis is the same as stated above except that 1.0 g of poly(vinyl pyrrolidone) (MW = 40,000), a polymeric surfactant, was added to the reaction flask in addition to the above precursors. Extremely fine powder parti-

cles were observed as a colloidal solution in the decalin solvent in contrast to the shiny metallic particles observed in the above synthesis without the surfactant.

RESULTS AND DISCUSSION

Role of Surfactants

Surfactants^{16,17} are defined as surface-active agents. These chemicals when present at the surface of a colloid prevents the constituent particles from aggregation. Unprotected particles in a dispersion are constantly in Brownian motion and will rapidly agglomerate as a consequence of van der Waals attractive forces. Polymers can stabilize and therefore prevent aggregation in colloids pri-

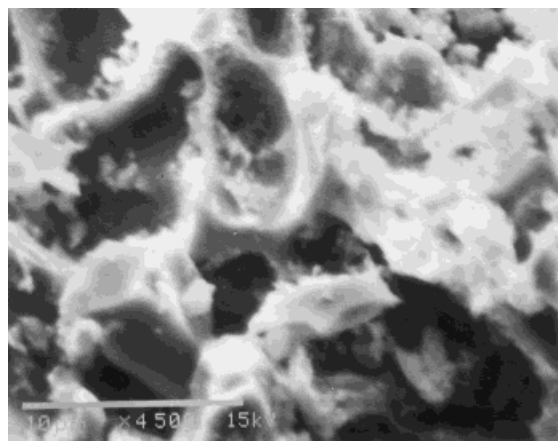


Figure 2 SEM micrograph of sonochemically synthesized M50 steel powders (without surfactant).

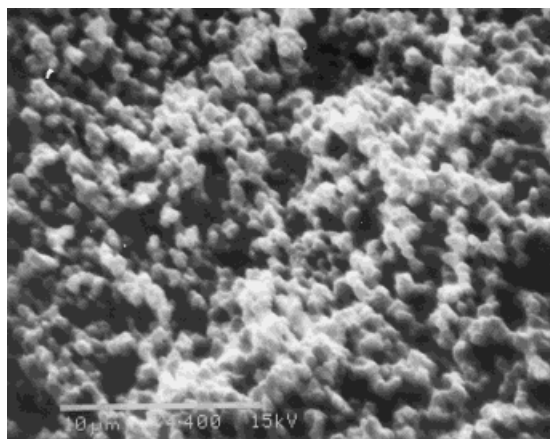


Figure 3 SEM micrograph of sonochemically synthesized M50 steel powders (with surfactant).

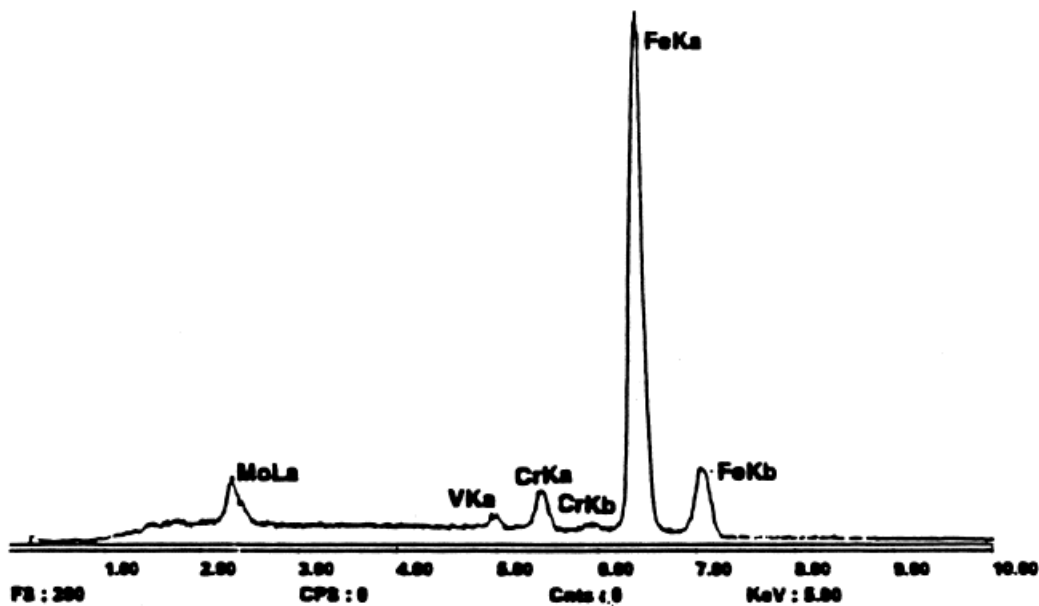


Figure 4 EDAX analysis of sonochemically synthesized steel powders (with surfactant).

marily by two methods: (a) electrostatic stabilization and (b) steric stabilization. In the first method, the use of polymers such as polyelectrolytes stabilize small particles by adsorbing onto them and causing the particles to ac-

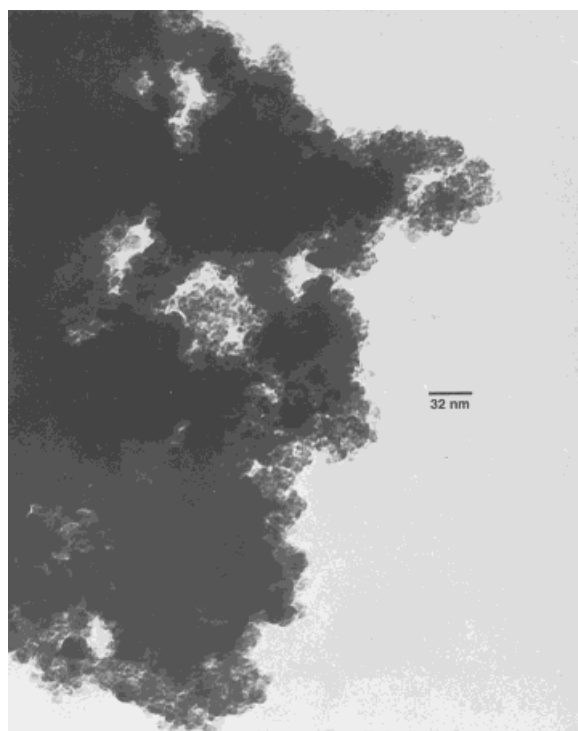


Figure 5 TEM micrograph of sonochemically synthesized M50 steel powders (without surfactant).

quire a charge of the same sign [Fig. 1(a)], thereby repelling one another by the formation of an intermediate electrical double layer which tends to keep the two particles from coming into close contact. In the case of steric repulsion, the polymers are adsorbed onto particles [Fig. 1(b)] and form a very closely packed adsorbed layer. Approach of the particles is prevented by two methods: Either the polymer groups from each layer form a simple physical barrier which they are unable to interpenetrate, thereby resulting in steric repulsion, or because the adsorbed polymer has loops extending into the solution which then create a local osmotic effect where solvent molecules can

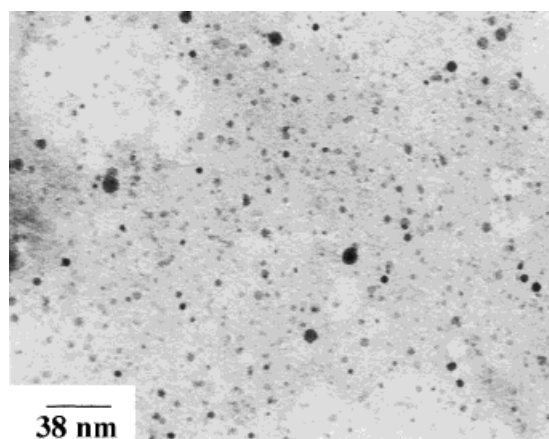


Figure 6 TEM micrograph of sonochemically synthesized M50 steel powders (with surfactant).

Histogram of Current Image	Frames :	1
Feature : Max Diameter	Objects :	859
Unit : nm	Max Cnt :	281
Classes : 30	Min Val :	1.3332
Underflow: 0	Max Val :	52.363
Overflow : 0	Tot Sum :	6260.4
	Mean :	7.2881
	Std Dev :	6.1008

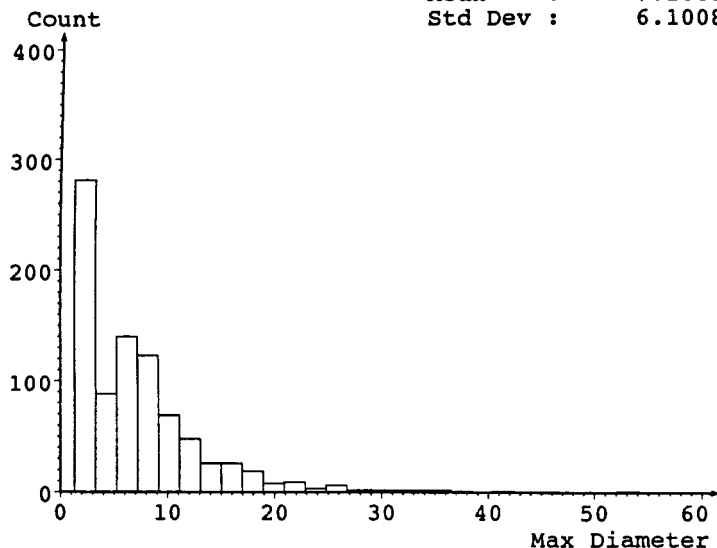


Figure 7 Particle-size analysis of sonochemically synthesized M50 steel powders (with surfactant).

diffuse into the overlap region to produce a repulsive force. Therefore, the use of polymeric surfactants aids in producing homogeneously dispersed, discrete, and deglomerated metal particles by the above chemical synthesis techniques.

Analytical Characterizations

SEM/EDAX and TEM microscopy were used to examine the microstructure of the M50 steel powders produced with and without the addition of the surfactant.

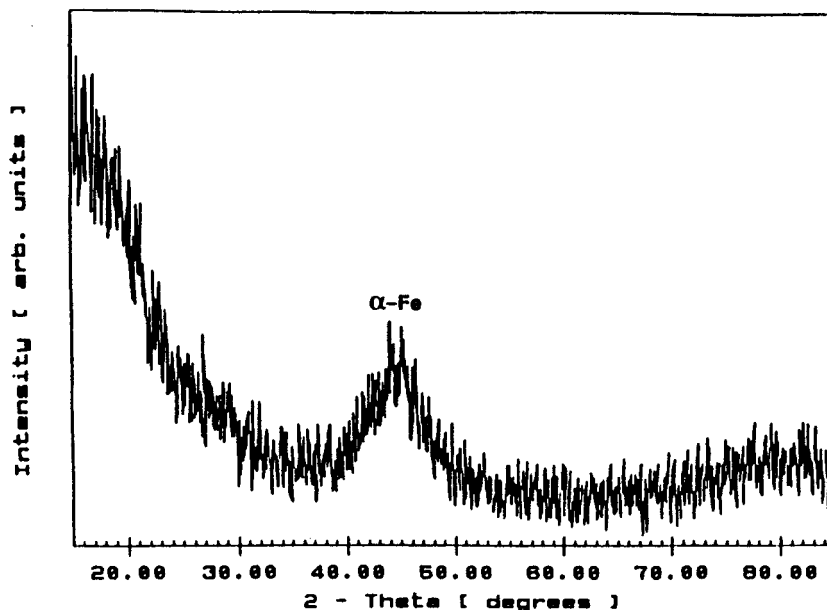


Figure 8 X-ray diffraction spectrum of the as-synthesized M50 steel powders.

The SEM micrograph of the as-synthesized powders without the surfactant (Fig. 2) shows the presence of highly agglomerated particles as well as chunks of material having micron-sized particle sizes. In contrast, the micrograph of the sample produced with the addition of a surfactant (Fig. 3) at identical magnification shows a porous coral-like morphology and a more homogeneous and much less agglomerated microstructure. Spot EDAX (energy dispersive analysis by X-ray) analysis in several randomly selected regions of the powder sample (with surfactant) shows the peaks of Fe, Cr, Mo, and V in the expected ratios (Fig. 4).

TEM micrographs were taken for the powder samples produced with and without surfactants. The TEM microstructure of the powders produced without surfactants (Fig. 5) shows a very agglomerated structure composed of smaller particles having mean particle diameters between 5 and 10 nm. In contrast, a more homogeneous distribution of the particles is observed for powders produced by addition of the surfactants (Fig. 6). In addition, these particles are also more discrete and degglomerated. An image analysis on the TEM micrograph shown in Figure 7 shows a relatively wide particle-size distribution with particles having a mean diameter of ≈ 7 nm. The XRD analysis of the as-synthesized powders (with surfactants) revealed a rather amorphous pattern as shown in Figure 8 with a very broad peak with fwhm of approximately 5° in 2θ units and centered around $44\text{--}45^\circ$.

CONCLUSIONS

M50 steel powders were synthesized with and without the addition of polymeric surfactants. This work has demonstrated that surfactants are very effective in producing homogeneous and discrete multicomponent alloy powders. The mean particle sizes as determined by TEM showed that sizes as low as 7 nm were obtained for the ultrasound-assisted synthesis of these metal nanopowders. EDAX analysis proved that the powders synthesized in the presence of a surfactant exhibited high compositional homogeneity on the nanometer scale. Consolidation of these powder samples via vacuum hot pressing and the microstructural and mechan-

ical properties of the resulting compacts will be reported in a separate publication shortly.

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REFERENCES

1. R. W. Seigel, *Mater. Sci. Eng. A*, **168**, 189 (1993).
2. H. Gleiter, *Nanostruct. Mater.*, **6**, 3 (1995).
3. J. C. Parker and R. W. Seigel, *Nanostruct. Mater.*, **1**, 53 (1992).
4. S. C. Davis and K. J. Klabunde, *Chem. Rev.*, **82**, 152 (1982).
5. G. Messing, S. Zhang, and G. Jayanthi, *J. Am. Ceram. Soc.*, **76**, 2707 (1993).
6. W. R. Cannon and S. C. Danforth, *J. Am. Ceram. Soc.*, **65**, 324 (1982).
7. T. Kameyama, K. Sakanaka, and A. Motoe, *J. Mater. Sci.*, **25**, 1058 (1990).
8. K. E. Gonsalves, S. P. Rangarajan, A. Garcia-Ruiz, and C. C. Law, *J. Mater. Sci. Lett.*, **15**, 1261 (1996).
9. K. E. Gonsalves, S. P. Rangarajan, C. C. Law, C. R. Feng, G. M. Chow, and A. Garcia-Ruiz, *ACS Symposium Book Series 622*, American Chemical Society, Washington, DC, 1996, chap. 15, p. 220.
10. J. E. Bridge, Jr., G. N. Maniar, and T. V. Philip, *Metal Trans.*, **2**, 131 (1993).
11. F. Kayser and M. Cohen, *Metal Progr.*, **61**, 79 (1952).
12. W. B. Pearson, *A Handbook of Lattice Spacing and Structures of Metals and Alloys*, Pergamon Press, New York, 1958, vol. 1.
13. T. W. Smith and D. Wychick, *J. Phys. Chem.*, **84**, 1621 (1990).
14. I. Nakatani, M. Hijikata, and K. Ozawa, *J. Magn. Mater.*, **122**, 10 (1993).
15. J. S. Bradley, E. W. Hill, C. Klein, B. Chaudret, and A. Duteil, *Chem. Mater.*, **5**, 254 (1993).
16. I. Piirma, *Polymeric Surfactants, Surfactant Science Series*, Marcel Dekker, New York, 1992, Vol. 42.
17. M. R. Porter, *Handbook of Surfactants*, Chapman and Hall, New York, 1991.