NANO OVERVIEW

Nanocomposite Reactions in the Self-Propagating High Temperature Synthesis of Materials

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Researchers at Texas Tech University are developing superalloys from the combustion synthesis of nanostructured reactants. The composites consist of layered nano-scale thin (approximately 50 nm bilayer period) films or ultra−fine (approximately 35 nm diameter) particles that are in atomic scale proximity to each other but do not react until triggered. By combining reactants on the nano-scale, the product material is synthesized free of impurities and exhibits improved macroscopic properties. The aerospace industry has a need for coatings that protect against high temperatures, corrosion and wear. Nickel aluminide superalloys are being considered to support the new challenging environmental demands and requirements of industrial gas turbines.

Nanostructured thermite reactions are highly luminescent. An innovative technique for observing combustion synthesis has been developed that combines a high-speed video camera with a copper vapor laser. This system will allow measurements of flame propagation by peering through flames to record details of processes that would otherwise be totally obscured by the background light (Fig. 1).

For nano-powder media, results show that nanocomposites are dramatically more sensitive to ignition than traditional materials. The reduced time and energy required to initiate these reactions means the reactions themselves are more energy efficient[1]. The product superalloy has been shown to enhance the wear resistance by up to 50 %[2,3] from traditional NiAl alloys. Nano-particle additives are currently being considered that will further enhance the energetic nature of the composite, allowing product formation at even higher rates with further improved protective properties.

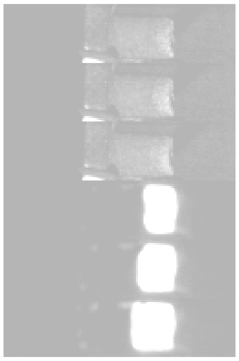

Fig. 1. Images of flame propagation A. with and B. without copper laser filtering system.

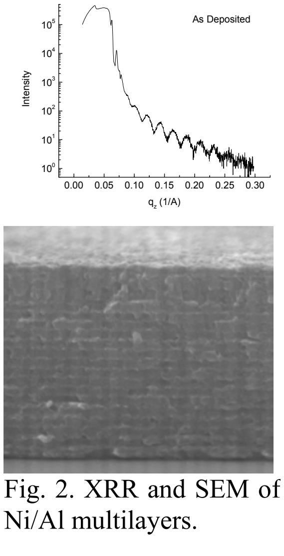

Fig. 2. XRR and SEM of Ni/Al multilayers.

We have studied interdiffusion kinetics through layer morphology of Ni/Al multilayer structures, with 50 nm bilayer period, as-deposited and following 10 minute anneals up through the melting temperature of Al. X-ray reflectivity measurements (Fig. 2) show interference fringes, characteristic of a well-defined multilayer stack, with ~ 1 nm interface roughness. Over a narrow anneal temperature range between 360 and 500°C these fringes diminish in amplitude and disappear,

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[1] "The Effect of Size Distribution on Burn Rate in Nanocomposite Thermites: A Probability Density Function Study," J. J. Granier and M. L. Pantoya, Submitted to *Combustion Theory and Modelling*, Aug. 2003.

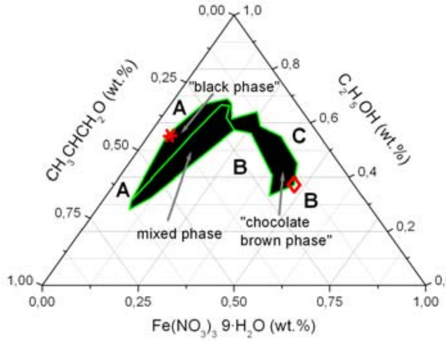
[2] "Nano-scale Reactants in the Self-Propagating High-Temperature Synthesis of Nickel Aluminides," E. Hunt, K. Plantier, M. Pantoya, Accepted for publication and in press *Acta Materialia*, September 2003.

[3] "The Role of the Al_2O_3 Passivation Shell Surrounding Nano-Aluminum Particles in the Combustion Synthesis of NiAl," J. J. Granier, K. B., Plantier and M. L. Pantoya, Submitted to the 30th International Symposium on Combustion, Nov., 2003.

indicating elevated interface roughening. However, fringes are observed for anneal temperatures both below and *above* this range, indicating the presence of well-defined layers with smooth interfaces. A kinetic model, in which nanocrystal domains of intermetallic nickel aluminides form at the interfaces, is developed to quantify the annealing induced interface roughness. This model predicts a temperature range over which the interface roughness, resulting from interdiffusion, grows due to nanocrystal formation. The model allows us to quantitatively interpret this interesting result, and is in agreement with previous calorimetry studies. X-ray diffraction allows us to identify the phases produced by annealing at these different temperatures, showing that they evolve from Al-rich to Ni-rich compounds with higher temperature. This is expected from Bené's rule for interdiffusion. A Letter is in press.[4]

A new approach has also been developed for combining nano-scale reactants using sol-gel chemistry. This approach will improve the homogeneity of the reactant mixture thereby improving the microstructure of the product and may allow the super alloy to exhibit macroscopic properties with further improved protective behaviors. The synthesis approach has begun with a study of the oxidizing skeleton formation in the iron (III) nitrate nonahydrate ($Fe(NO_3)_3\ 9H_2O$) – ethanol (C_2H_5OH) – 1,2-epoxypropane (propylene oxide (CH_3CHCH_2O)) ternary system with the purpose of estimating the composition boundaries and phase composition for derived gels. Iron (III) nitrate nonahydrate ($Fe(NO_3)_3\ 9H_2O$) was dissolved in ethyl alcohol. The completely dissolved $Fe(NO_3)_3 9H_2O$ was placed in an ultrasonic bath with a specified amount of propylene oxide (PPO) added to this solution. The sol was immediately filtered by 0.20 μm PTFE membrane filter. This procedure was applied to 150 sols of different compositions of iron (III) nitrate nonahydrate/ethanol/PPO in an effort to obtain a ternary phase diagram for this system[5]. Gels were subjected to a drying procedure for preparation as xerogels.

Figure 3 shows a ternary phase state diagram of iron (III) nitrate nonahydrate/ ethanol/PPO. The gel time varied between 150 s and 10 days depending on the composition. The optical microscopy analysis of wet gels having gelation time less than 300 s showed that gels contained two different phases. The gels, dried for one week at room temperature, have a deep brown color phase and a red-radish color phase. After conventional annealing at 200°C for 12 hours, the color of the phases transformed to black and chocolate-brown. It was established that the single phase gel containing only a "black phase" was formed in the left part of the ternary phase state diagram (* in Fig. 3) that contained a large amount of ethanol and PPO. In the "chocolate brown phase" the gelation time decreases with increasing PPO and, in some cases, with increasing ethanol. The gelation time for all sols in this area varied from 25 min to 3 hrs.



It was establish by FTIR studies, that all derived gels were transformed to amorphous α-FeOOH phase after 6 hrs. of annealing at 300 °C. At 700 °C the amorphous α-FeOOH phase crystallized to α-Fe_2O_3 phases. The optimum nanocomposite parameters were obtained for composites having a density of 10-15% of theoretical maximum density. From this point of view, the aerogels derived from the "black phase" part of the ternary phase diagram are appropriate candidates for making energetic nanocomposites with optimum characteristics.

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[4] "Influence of nanocrystal growth kinetics on interface roughness in nickel–aluminum multilayers" D. Aurongzeb, M. Holtz, M. Daugherty, J. M. Berg, A. Chandolu, J. Yun, and H. Temkin, accepted by Appl. Phys. Lett. (Dec. 2003).

[5] "Ferrihydrite Gels Derived in the $Fe(NO_3)_3 9H_2O$-C_2H_5OH-CH_3CHCH_2O Ternary System," E. F. Talantsev, M. L., Pantoya, C. Camagong, B. Lahlouh, S. M. Nicolich, and S. Gangopadhyay, Submitted to the *Journal of Non-Crystalline Solids*, Oct. 2003.