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A Study of NiFe(x)Cr(2-x)O4 by laser micro-raman spectroscopy

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The Study of Spinels by Laser Micro-Raman Spectroscopy

Standards of spinels, composed of two metals and oxygen with the formula AB_2O_4, are being created with known composition to identify spinels in samples of unknown composition by comparison with the spectra obtained from the standards. Laser micro-Raman spectroscopy allows the identification of chemical species based on their unique vibrational modes. The degree to which spinels of varying composition can be identified will be determined. This will aid in the study of the corrosion of steel by liquid metal. Spinels are a likely component of the oxide layer. Understanding the composition of the products of corrosion leads to an understanding of the processes involved in corrosion. This work is vital to the transmutation of nuclear waste**.**

A Study of $NiFe_xCr_{(2-x)}O_4$ by Laser Micro-Raman Spectroscopy

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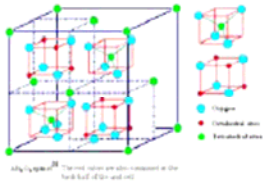
Introduction

Spinel standards with the composition $NiFe_xCr_{(2-x)}O_4$ were created to identify spinels in the unknown corrosion layer of corroded steel samples by comparison with the spectra obtained from the standards. Laser micro-Raman spectroscopy allows the identification of chemical species based on their unique vibrational modes. The degree to which spinels of varying composition can be identified was determined. This will aid in the study of the corrosion of steel by liquid metal. Spinels are a likely component of the oxide layer. Previous work has shown that the spinel, Fe_3O_4, is a major product of these corroded samples. However, due to the variety of metals within steel, other spinels can also be formed. Understanding the composition of the products of corrosion leads to an understanding of the processes involved in corrosion. This work is vital to the transmutation of nuclear waste.

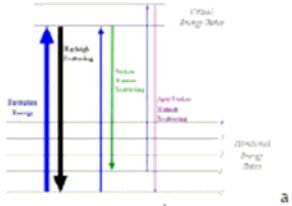


Materials and methods

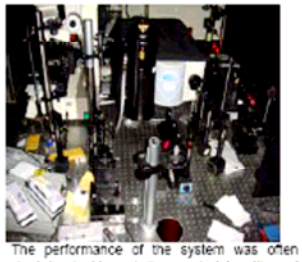
The spinels were synthesized by combusting aqueous solutions containing stoichiometric amounts of the appropriate metal nitrates and urea. The solution combusted at 350°C after excess water had boiled away.

Raman scattering is an inelastic light scattering process. Rayleigh scattered light has the same wavelength as the excitation light. Raman scattered light has an energy difference that corresponds to the vibrational energy levels of the molecule.

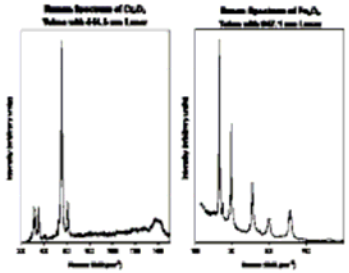
The excitation of vibrational modes resulting in photons of higher wavelength, lower energy, is termed Stokes scattering. Only Stokes Raman scattering was considered in this research.



a krypton laser, lasing at 647.1 nm, or an argon laser, lasing at 514.5 nm. The argon laser was added to the system this summer to reduce the difficulties caused by fluorescence.

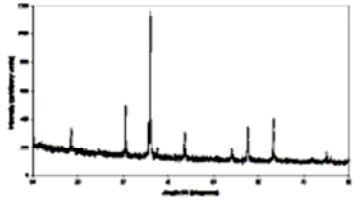


The performance of the system was often checked by looking at the peak intensities of strong Raman scatterers, such as Fe_2O_3 for the krypton laser, and Cr_2O_3 for the argon laser.

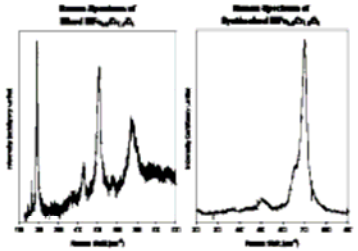


Results

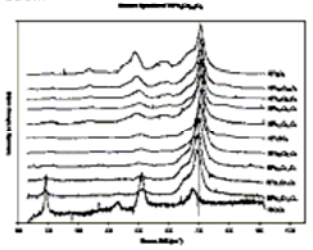
The spinels were successfully synthesized using the method described above. To verify that the powder produced had the spinel structure, several samples were tested using x-ray diffraction. The diffraction pattern obtained is consistent with the spinel structure.



The synthesized samples were then verified to be truly mixed spinels, with both Fe and Cr occupying sites in the same unit cell. This was done by comparing spectra of the synthesized spinels with spectra produced by mixing pure spinels in appropriate ratios.



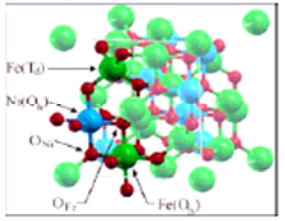
22 samples were synthesized, with over 50 spectra acquired, and changes in the Raman spectra were clearly evident as the composition of the spinel was varied. Some of the data is shown below:



Conclusions

By examining the major peak positions and relative intensities, the spinel composition can be identified to within 15%.

The 680cm^{-1} mode is a symmetric breathing mode of a tetrahedral NiO_4 "molecule." This mode increases in Raman shift from 677cm^{-1} to 703cm^{-1} quickly when going from the normal spinel, $NiCr_2O_4$, to $NiFeCrO_4$, but then stays relatively consistent from $NiFeCrO_4$ to the inverse spinel, $NiFe_2O_4$. This is due to the Ni being replaced by Fe in the NiO_4 "molecule."



$NiFe_2O_4$ inverse spinel unit cell[1]

Of course, real corroded steels will contain more than just Ni, Fe, and Cr, and thus further studies on other spinels will benefit this research.

Sources

[1] Foll, Helmut. "Ionic Crystals." http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_2/basics/b2_1_6.html (accessed July, 30 2008).

[2] Perron, H. "Structural investigation and electronic properties of the nickel ferrite NiFe2O4: a periodic density functional theory approach". *Journal of Physics: Condensed Matter* 19. (2007), [1-10].

Acknowledgments

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