NASA CONTRACTOR REPORT

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High Resolution Surface Analysis by Microarea Auger Analysis: Computerization and Characterization

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16 Abstract
A custom scanning Auger electron microscope (SAM) capable of introducing a 3-5 keV electron beam of several nA into a 30 nm diameter sample area was fitted with a sample introduction system and was fully computerized to be used for materials science research (R. Browning, SEM 1983/IV, pp.1665-1663). The method of multispectral Auger imaging was devised and implemented (R. Browning et al., Inst. Phys. Conf. Ser. No.68, EMAG 1983, p.127 and EMAG 1985, p.231; R. Browning, J, Vac. Sci. Technol. A2 (1984) 1453 and A3 (1985) 1959; R. Browning et al., Appl. of Surf. Sci. 22/23 (1985) 145. The instrument was applied to various problems in materials science, including the study of the fiber/matrix interface in a SiC reinforced titanium alloy (H.J. Dudek et al., Surface and Interface Analysis 6 (1984) 274), the study of SiC whiskers in Al alloy 2124 (in cooperation with NASA-Langley), the study of NiCrAl superalloys (in collaboration with NASA-Lewis, ref. L.A. Larson et al., J. Vac. Sci. Technol. A1 (1983) 1029; J.L. Smialek et al., NASA Tech. Memo. 87168 (1985), the study of zircalloy specimens (in collaboration with Stanford University), and the microstructure of sintered SiC specimens (in collaboration with NASA-Lewis). The report contains a number manuscripts submitted for publication on these subjects.

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INTRODUCTION.

This report is the final report of the contract NNC 2-230. However as the principle investigator (R. Browning) is leaving Eloret Institute the report will cover not only the preceeding years work, Feb-1985 to Feb-1986, but also will sum up the general status of the work done while the principle investigator has worked under NASA contracts at Eloret. This will cover the 4.5 years Aug-1981 to Feb-1986.

The general direction of the work over the 4.5 year contract period has fallen into three broad and overlapping endeavors covering the application of Scanning Auger Electron Microscopy (SAM) to NASA related materials science problems. These three lines of endeavor were (a) the performance improvement of the NASA-SAM microscope, (b) the development of novel experimental methodologies, and (c) the actual generation of experimental data for input into the materials science effort of the various NASA centers.

(a) At the inception of the contracts it was apparent that the instrument, although technically advanced in respect of the electron optics, was still a prototype, and without a considerable design effort would remain largely a laboratory curiosity with little practical output. The proposals for the first two years of the contract period therfore dealt mainly with the modification of the instrumentation. This included the full computerization of the microscope and the building of a fast cycle sample introduction system, amongst other modifications. These modifications are described in more detail in a later section but in summary this investigator believes that the all the major instrumentation aims of those proposals were met. In consequence the instrument has now the most advanced capabilities for Auger imaging in the world bar none. The instrument can now be used both for regular and specialist materials science research and has produced results not obtainable with any other instrument or single technique.

(b) The field of Scanning Auger Microscopy is a relatively new one and still in a state of dynamic development with respect to both instrumentation and experimental methods. The development of specialized experimental methodologies that are particularly suited to NASA materials science problems has been singularly successful. Many of the NASA material science problems can best be described as the characterization of materials with small scale randomly distributed inhomogeneities. Systems such as precipitate hardened alloys and whisker hardened alloys fall into this category. The problem with such multicomponent systems is in their complexity, not only as small scale complex images but also but in the variety and quantity of possible (and unknown) inhomogeneities. The invention of multi-spectral Auger imaging under this NASA contract shows a nice symmetry in that the statistical multi-spectral imaging methods used for the analysis of NASA materials, are those same methods developed by NASA for remote multi-spectral image interpretation. These methods applied to Scanning Auger microscopy have solved many of the problems associated with the technique and have put the microscope at the forefront of international development in the field.

(c) The realization of the power of the microscope has taken a large proportion of the 4.5 year contract period and the immediate materials science benefits are not as extensive as a simple translation of time to results would demand. The results that have been produced on the instrument have however been of high quality. In one case results from the microscope may lead to a rethink of a materials science problem of considerable ecconomic importance and in other cases have produced quite unexpected results that may well impact on NASA's ceramic research efforts and the production of metal matrix composites. A further research effort initiated by the principle investigator in conjunction with NASA-Lewis and not involving the microscope has produced important insights into the high temperature oxidation of NiCrAl's. This is discussed in a separate section of this report.

II. INSTRUMENT MODIFICATIONS.

The modifications to the Scanning Auger Microscope instrumentation have covered a wide range of different aspects. The most critical in terms of the quality of information from the microscope was the computerization of the microscope control and data aquisition. This was critical in that the signal-to-noise characteristics of the microscope and the complex contrast mechanisms in Auger imaging require moderately sophisticated signal processing and a careful evaluation of the information. The next most important area of modification was the fitting of a rapid cycle specimen introduction system. This introduction system has itself gone though a process of development culminating with the replacement of the microscope specimen stage with a totally new x,y,z stage more suitable to the needs of rapid specimen cycling. The more recent developments with the instrumentation have been with the addition of a fine point ion milling gun and the reorganization of the ion cleaning gun and gas handling system. There have been a series of more minor, but not unimportant, modifications. The SEM detector has been changed from a Channeltron to a novel sintillator and light tube arrangement. This detector is used both for SEM and ion imaging and has considerably improved the quality of the SEM information. There have been a series of on going modifications to the pumping system with the addition of a turbo pump, differential gas line pumping, vacuum air lock, and bakeout ovens. The purpose of all these modifications to improve the integrity and speed of the pumping system. The electron gun has undegone minor modifications to improve its bakeability, reliability and ease of adjustment. The electron gun seating also has been modified to improve its mechanical reliability and vibration stability. There have been numerous modifications to the instrumentation electronics some of which are described below under the heading of microscope computerization.

ii.i Microscope Computerization.

The signal characteristics of the Auger microscope are compex and digital processing is necessary to obtain meaningful results. The Auger signals are very low level and on a large background. Counts of from 100 to 1000 electron counts on a background of 10000 counts in a 100ms sampling period would be typical. The reduction and interpretation of this low level signal is complicated by two factors, firstly the field emmision proccess is very noisy giving beam current fluctuations of 10%, and secondly the Auger yeild mechanisms are multiple and complex. A multiple signal channel approach was decided on to produce enough information to normalize beam current fluctuations and discriminate against 'unwanted' contrast such as topographical contrast. The long aquisition times for signal collection also suggested that the control of the SEM scans as well as the Auger instrumentation should be attempted. A radical overhaul of the electronics was therefore instituted and a fully computerized raster scan control and Auger scan control and data collection system was built. This sytem was based on a Hewlett-Packard 9845B computer and a specialized SEM/Auger microscope interface unit. This interface unit was built at NASA entirely by the principle investigator. Multiple signals can be collected simultaneously and several modes of operation were made possible by the combination of digital signal proccessing and digital SEM output. The software for the collection of spectra, linescans, images, SEM images, data smoothing, data expansion, filing, housekeeping and operating the microscope have been developed continuously over the 4.5 year priod of the NASA contacts and are still being developed. The system is dicussed in technical detail in **ref 1.** . The data system has been very successful not only in enabling the merits of the electron optics to be realised but also in making the collection of data a routine, relisble and prompt process. The data system has offered the additional benefit, not shared by commercial systems, of inhouse software control. Software control in this context also means experiment control and this has lead to the invention of several new techniques in Auger microscopy. **Ref 2.**

III. NOVEL SAM METHODS FOR MATERIALS SCIENCE.

Two factors have influenced the development of experimental methodologies for analysing NASA related materials. The first factor is the signal characteristics of the Auger microscope and the second factor is the nature of the materials. The are a variety of problems inherent in extracting meaningful elemental compositions from Auger signals. Firstly the Auger signal is low level and noisy and secondly the information depends in a complex way on the probe beam/specimen interaction. The Auger yield can be strongly dependent on specimen topography, matrix effects, diffraction effects and surface preparation methods as well as bulk elemental concentration. Clearly the complex contrast effects and the low level signal interact to reduce the quality of the Auger information and imply long aquisition times to get sufficient accuracy, either for quantitative determinations from spectra or for planometric measurements from images. Spectra are typically collected over 100-1000s and images over 1000-10000s. This imposes considerable constrants on the mechanical stabiltiy of the specimen stage and on the stability of the probe forming electronics if the ultimate spatial resolution of the microscope is to be achieved. In fact the stabilities are not nearly good enough and limit the spatial resolution of spectral measurements to 2000A at best. Higher spatial resolution can be achieved if measurement time is short but then a limited amount of information can be collected.

Normally images are collected with a short aquisition time per picture element and it is this form of information that has the potentially highest spatial resolution. Conventional Auger images however just have one Auger transition measured per picture element and do not contain sufficient information to normalize against other contrast effects besides elemental concentration. Further single elemental images because of specimen drifts cannot be accurately compared with other images. The use of multispectral imaging gives images that not only have good spatial correspondance but also the technique allows the information to be manipulated to improve the signal separation from unwanted contrast such as specimen topography. The image statistical methods used for manipulating images from multispectral remote sensing equipment can be applied with only minor modifications in methodology and have been very succesful in their application to Auger imaging. The differences in methods are due to the fact that the specimen can be imaged repeatedly over the same area with different collection parameters, unlike LANSAT, and the signal to noise ratios are generally poorer than those used in remote sensing. The methods of image partition are therefore different because an interactive partioning/collection loop can be used to chose the best collection parameters and the best partioning scheme. This is also normally done with reduced pixel images, often only 32x32, to save calculation and collection time while increasing sampling time per pixel. A further difference is the magnification can be changed to isolate particular features and naturally this removes much of the uncertainty in partioning, thus many of the more complex automatic classification schemes are not needed. The use of the Hotelling transform has been largely confined to first pass classification as a method of reducing the multidimensional space to two significant dimensions. Other information such as specimen current is also combined with the Auger information using this transform. In some cases this can markedly improve feature contrast, although it can add too much information. A new transform has been invented that not only reduces the dimensionallity of the image information, but also contains normalization. The ratioing of one dimension by another can in some circumstances enhance the presentation of the information and provide some topographicall normalization. This method has been very successfully applied to specimens of metal matrix composites. These multispectral methods are also vital in the analysis of inhomogeneous materials. The typical metallographic or ceramic specimen is composed of a fine random dispersion of phases. These phases can either form the bulk of the material or can be dispersed in a single phase matrix that may compose 95% of the material. The type, association, and quantity of these dispersed phases are often the information that is needed. As these phases range in size from Angstoms to several microns the highest spatial resolutions are required for accurate representation of the material. Multispectral imaging can be used to answer these questions by representing the image information in a form that shows the separation of compositions and can be used to measure the significance of a single pixels information Random image fields that may just look like noise in a single element image can therefore be quantified in a way not possible with conventional approaches. The first calim published for a quantified Auger image was made using these methods. The elemental compositions of phases can be deduced even from a field of very small randomly dispersed phases as the correlations show trends and standard metallurgy supplies the likley elemental associations. **Refs · 3,4,5,6,7.**

IV. MATERIALS SCIENCE APPLICATIONS.

Several systems have been investigated using the SAM instrument. These systems have included metal matrix composites, superalloys, zircalloy, and SiC ceramics.

Metal matrix composites based on Ti alloys were investigated in collaboration with the DFDLR West Germany. These Ti6Al4V matrix composites were model systems with aligned SiC fibers. Using the SAM it was possible to show that the Ti and SiC had reacted to form Ti5Si3 and TiC, and that the TiC was forming a diffusion barrier to the reaction.[8] Specimens of Metal matrix composites based an aluminium alloy Al2124 were analysed for NASA-Langley. The results showed that the SiC wisker material used in the composite had reacted with the matrix to change the precipitate behavour of the matrix. Further the reaction products were not localized at the wisker/matrix interface.[9,10]

NiCrAl super alloys were investigated in collaboration with NASA-Lewis. Using SAM the oxidized material was found to have a phase distribution that was consistant with the diffusion of Al to the surface.[11] Little other information was obtained directly from the SAM but NiCrAl was instead investigated using Auger and XPS in a hot stage UHV instrument. This proved to be very succesful and showed the interaction beween the dopants in the NICrAl used to promote oxide scale adherence and the posioning effects of sulphur. Refs 12,13,14,15.

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Zircalloy specimens were investigated in collaboration with Stanford University. These specimens were from nuclear fuel cladding material prone to stress corrosion cracking. The findings showed that against all expectations that carbon rich surface inhomogeneities may well play a vital part in the iodine related SCC failure of this material. Ref 16.

In collaboration with NASA-Lewis the microstructure of specimens of sintered SiC were investigated. SAM is particularly siutable for studying these materials as the Auger yield for light elements is still high, unlike the case for the X-ray microprobe. SAM showed in the case of corroded SiC that the grain boundry films found by SEM were merely remnants of SiC grains and not a special grain boundry phase as had been suspected from X-ray microprobe studies. Studies of different noncorroded SiC showed the effects of production techniques on the microstructure. Boron carbide is added to the SiC powder to facilitate sintering. Under a nitrogen atmosphere the B4C reacts to form boron nitride and free carbon. This had not been suspected before and only B4C and free C had been previously detected. These products were only found in this study in vacuum sintered SiC. Refs 17, 18,

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