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NASA CONTRACTOR REPORT

SIZE AND SHAPE DEPENDENCE OF CO ADSORPTION SITES
ON SAPPHIRE SUPPORTED FE MICROCRYSTALS

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16. Abstract The surface structure and stoichiometry of γ -alumina substrates, as well as the size, growth characteristics, and shape of Fe-deposits on sapphire substrates have been investigated by LEED, AES, EELS, and XPS, as well as work function measurements, in conjunction with TEM observations. The substrates used in this work were the following: (a) new, clean γ - Al_2O_3 ; (b) same surface amorphized by Ar ion bombardment; (c) same surface re-generated by 650 C annealing; (d) amorphous alumina films on Ta slab; and (e) polycrystal alumina films, obtained by heating amorphous films to 600 C. Substrate cleaning was found to be most effective in producing a reproducible surface upon oxygen RF plasma treatment. The Fe nucleation and growth process was found to depend strongly on the type of substrate surface and deposition conditions. Ar ion bombardment under e-beam flooding, and subsequent annealing at 650 C was found an effective means to restore the original γ - Al_2O_3 (1102) surface for renewed Fe deposition. XPS measurements evidenced oxide-like bonds between Fe and the substrate, decreasing in probability with increasing deposit thickness. TEM observations corroborate the Fe island growth and revealed the dependencies on deposition parameters and surface conditions. In related work, the role of Zr doping in NiCrAl in suppressing S surface segregation was investigated by AES and XPS.		14. Sponsoring Agency Code	
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One frequently finds in the literature, when dealing with supported metal catalysts, that the catalytic activity has been related to the crystallite size and shape (1). Based on this observation, it has been proposed (2) to grow small Fe particles (microcrystals) on various alumina surfaces, such as on amorphous alumina with different preparation conditions and on single crystal alpha-alumina with different surface orientations.

The surface structure and stoichiometry of alpha-alumina substrates, as well as the size, growth characteristics, and shape of iron deposits on sapphire have been established by standard surface analysis techniques such as LEED, AES, EELS, XPS, and work function measurements, in conjunction with TEM observations.

The substrates used in this work were the following:

- (a) new (virgin) clean alpha-alumina ($1\bar{1}02$);
- (b) amorphized (by Ar-ion bombardment) α - Al_2O_3 ($1\bar{1}02$);
- (c) amorphized and subsequently recrystallized (by heating to 650 C) α - Al_2O_3 ($1\bar{1}02$);
- (d) amorphous alumina films (approximately 20 nm thick) supported on a Ta slab;
- (e) polycrystal alumina films (obtained by heating amorphous films to 600 C).

The nucleation process was found to depend strongly on the preparation conditions of the substrate. The different surfaces were characterized by Auger electron and energy loss spectra. Specifically, the ratio of the oxygen 501-eV peak to the aluminum 51-eV peak heights is a measure of the stoichiometry of the alpha alumina.

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Prior to any metal deposition, the alumina substrate had to be cleaned. The main impurity being carbon, one effective method to remove it from the substrate surface is known to be heating the specimen in vacuo to above 1100 C. According to our LEED results, however, a new (2x1) pattern was observed after annealing the alpha-alumina ($\bar{1}\bar{1}02$) surface at about 750 C. Above 850 C, the pattern changed to a structure close to (3x2). The 1/3 order beams were moving along the same directions upon changing the beam energy, which is characteristic of faceting. The latter pattern remained unchanged up to 1400 C, which is the maximum temperature the specimen could be heated to. Moreover, the ratio of the oxygen 501-eV to aluminum 51 Auger peak heights decreased above 700 C. This indicates a change of surface stoichiometry, and we concluded that heating above 700 C had to be avoided in our experiments, since this would change the surface structure of the alpha-alumina ($\bar{1}\bar{1}02$) substrate.

We have tried to circumvent this problem by cleaning the alumina (amorphous and crystalline) at room temperature with an oxygen RF plasma. To accomplish this, we admitted oxygen into the chamber containing the alumina specimens to a partial pressure of about 0.02 mbar and maintained the glow discharge with a Tesla coil, applied at an electrically insulated feedthrough (copper electrode with a clean aluminum plate of 3 cm² surface area attached to its end) into the chamber, for 10 - 30 seconds. During the discharge, the specimen was kept in front of the aluminum plate at a distance of about 2.5 cm. According to Auger measurements, carbon and nitrogen contaminants were thus completely removed from the alumina surface.

An interesting result was obtained from the oxygen glow

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discharge experiments. The surface stoichiometry of the alumina substrates changed above a certain partial pressure of oxygen applied during the discharge. As was mentioned previously, the change of surface stoichiometry was measured by calculating the ratio of the oxygen 501-eV to aluminum 51-eV Auger peaks heights. This ratio increased between 0.02 mbar and 0.05 mbar with increasing oxygen pressure.

We also focussed our attention on the problem of removing iron deposits from the alumina ($\alpha\text{-Al}_2\text{O}_3$) surfaces and restoring the surface crystallinity, so the specimen could be reused for many deposition experiments without opening the UHV chamber. After deposition of a substantial amount of iron, the specimen was argon ion bombarded at 1 keV argon beam energy. Because of severe charging, it was, however, almost impossible to remove the iron deposit quantitatively from the alumina surface. The charging problem could be minimized by flooding the surface with a low-energy e-beam (0.1 microamperes at 700 eV beam energy) during the argon sputtering. The Ar ion current was about 8 microamperes. According to LEED and AES measurements, the iron could then be removed quantitatively, but the crystal was amorphized and the oxygen/aluminum AES peak ratio was decreased. Annealing at 650 C could, however, restore the surface crystallinity and stoichiometry of this amorphized alumina. Most likely, the heating caused a diffusion of oxygen from the interior to the alumina surface. After several Ar ion sputtering and annealing cycles, the rate of oxygen diffusion to the surface by heating decreased substantially, and thus the O/Al ratio remained small. The original O/Al stoichiometry could then be restored in another oxygen discharge.

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The iron was deposited in calibrated dosages (1-minute durations) from a wire source. According to quartz crystal thickness monitoring measurements, each dosage was equivalent to approximately 0.1 nm (or 1/3 monolayer of Fe(111)).

The Auger measurements during Fe deposition referred to the Auger peak heights of Fe(703 eV), O(501 eV), and Al(51 eV) versus the number of Fe dosages, whereby the O(501 eV) and Al(51 eV) peaks belong to the substrate. We used the high-energy (703 eV) Fe peak because the low-energy Fe peak (47 eV) overlaps with the substrate Al peak. Almost for all specimens, the Fe peak initially increased linearly with deposition time (number of dosages). At about the seventh dosage, the slope of the curves began to decrease. It then increased again after the 12th dosage. This is most likely due to two kinds of adsorption stages or two kinds of preferred sites. For the same number of dosages, the amount of iron that could be deposited on the surface was found to be unexpectedly higher on virgin $\text{Al}_2\text{O}_3(1\bar{1}02)$ than on amorphous alumina, and even smaller on the recrystallized $\text{Al}_2\text{O}_3(1\bar{1}02)$ (specimen type (c)). This is probably due to the preparation treatment. The virgin $\text{Al}_2\text{O}_3(1\bar{1}02)$ surfaces have many broken bonds and, therefore, many preferred nucleation sites. Heating to 650 degrees after Ar ion bombardment ("recrystallization") produces a better arrangement of the surface atoms, i.e., fewer defects and, consequently, fewer nucleation sites.

Because of charging, the Auger measurements at the very early stages of Fe deposition were not very reproducible. This problem was eliminated by using electron energy loss spectroscopy (EELS) (at a primary energy of 215 eV). The presence of Fe on the surface

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contributed a new loss peak with a loss energy of 55 eV in the EELS spectrum of alumina. The height of this loss peak was measured for the initial stages of iron deposition at RT, 300 C, 400 C, and 500 C substrate temperatures. As expected for nucleation under varying supersaturation conditions, the initial slopes of the loss peak-height versus Fe dosage curves decreased with increasing temperature. Furthermore, for the same temperature, the slope was substantially greater in the case of virgin single crystal alumina surfaces than for amorphous substrate films and recrystallized alumina.

According to the XPS measurements, when the Fe atoms are initially bound directly to the substrate, they form oxide-like bonds, which is evidenced by a shift of the XPS peak of the metallic iron to higher binding energies. A decrease of this shift, observed with increasing deposit thickness, suggests the growth of metallic Fe particles.

The TEM observations confirmed the previous measurements. At our prevailing conditions, iron forms small particles. The number density of these particles remains roughly constant while their size increases with the number of Fe dosages (flashes). For the same number of dosages, the number density of particles is smaller, and their size is larger, with increasing temperature. Also, for the same number of dosages, the number density and size of the particles are substantially greater on virgin Al_2O_3 ($\bar{1}\bar{1}02$) than on recrystallized alpha alumina or on amorphous alumina.

The Auger spectra do not exhibit any difference between the virgin and recrystallized surfaces. However, the EELS spectra do show

some differences. The 34 eV loss peak of the virgin α -Al₂O₃ (1102) is much larger and sharper than that of recrystallized or amorphous alumina. Also, the 51-eV loss peak appears shifted toward lower energies by about 2 eV. This difference needs clarification.

In a related research activity, we investigated the surface segregation of minor constituents, in particular sulphur, during annealing of a NiCrAl superalloy at 750 C. The S surface segregation was measured by AES and XPS. It was found that by doping the alloy with 0.3% (Wt) of zirconium, the S segregation is suppressed, and upon annealing a Zr rich surface is produced. In order to separate bulk and surface effects, several monolayers of Zr were evaporated onto undoped NiCrAl and annealed up to 750 C. Sulphur still readily segregated to the surface, indicating that the apparent competition for surface segregation is not a free surface effect but a consequence of the NiCrAlZr bulk matrix. A paper on this research has been submitted for publication and is included as Appendix 1 to this report (3).

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The role of some minor constituents in NiCrAl
superalloys: II The effect of a surface layer of
zirconium on the segregation of sulphur.

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ABSTRACT

Annealing of a NiCrAl superalloy in UHV at 750° C will quickly produce surface segregation of some minor constituents, particularly sulphur. This effect can be measured using AES and XPS. By doping the alloy with 0.3%(Wt) of Zr the sulphur segregation is suppressed and on annealing a Zr rich surface is produced. In order to separate bulk and surface effects several monolayers of Zr were evaporated onto undoped NiCrAl and annealed up to 750° C. Sulphur still readily segregated showing that the apparent competition for segregation to the surface is not a free surface effect but a consequence of the NiCrAlZr bulk matrix.

INTRODUCTION.

The cyclic oxidation resistance of NiCrAl superalloys can be improved by the addition of small concentrations of rare earths such as Zr, Y, Nb or Hf. This improvement in resistance to oxidation and thermal cycling is mainly due to the large increase in the strength of adherence of the oxide scales to the alloy when doped with less than 0.5% (Wt) of the rare earth. Recent studies¹⁻⁴ including paper I⁵ on the UHV annealing of doped and undoped NiCrAl alloys, suggest that the suppression of sulphur segregation and the alternative segregation of Zr or Y to the metal/oxide interface may be the critical factor in reducing oxide spalling. Sulphur is widely regarded as an agent in the reduction of interfacial strengths (e.g.⁶), while the high free surface energies of Zr or Y might be expected to increase adherence.

In paper I doped and undoped NiCrAl alloys were heated in UHV and the surface specific techniques of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to measure the concentrations of the surface segregants. The major findings were that the surface of an undoped Ni15Cr13Al became covered in a saturation coverage of sulphur (~ 0.5 monolayers) after heating up to 750°C. In contrast the surface of the same NiCrAl doped with 0.3% (Wt) of Zr or Y became covered with a Zr or Y enriched layer under the same conditions. In the case of the Zr doping the segregation of sulphur appeared to be entirely suppressed.

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At first sight it is surprising that the Zr or Y would compete with sulphur in segregating to a surface as sulphur has a very low surface free energy (0.078J/m^2) compared with Zr(2.79J/m^2) and Y(1.160J/m^2)⁷. Indeed it is not at all clear from simple arguments that Zr should segregate at all,^{8,9} having both a large negative free energy of mixing¹⁰ (and reaction¹¹) with Ni and a higher surface free energy than Ni, Cr or Al. In fact elemental segregation to a free or internal surface of a metal matrix is very complex and could be driven by a variety of mechanisms. Surface free energy, relative atomic size¹² or surface contamination^{13,14} could all be factors and with a complex multi-component multi-phase material such as NiCrAl+Zr+S any argument, without a great deal of experimental evidence, must be somewhat tentative. This being said however it is not unreasonable to point out that the segregation of sulphur is strongly suggested by its low surface free energy while the Zr(or Y) segregation mechanism is most likely determined by the difference in atomic radii of the larger rare earth atoms in the γ phase Ni alloy (+28% for Zr, +43% for Y). Given these two mechanisms the suppression of the sulphur segregation would not be predicated on the segregation of the Zr as it is not readily apparent that the two mechanisms would interact. One of the several possible explanations for the apparent competition in segregation is that there is a competition for surface sites on the γ phase NiCrAl. Site competition is unlikely for not only are Zr and S chemically very different but the driving force

of one mechanism would be independent of the surface (Zr atomic radius) while the other would clearly favour a sulphur surface despite Zr segregation. However it is important to show that the rare earth/sulphur interaction is a bulk effect and not a competition for surface sites on the NiCrAl. This can be done by simply pre-coating the undoped NiCrAl with Zr from an evaporation source and annealing.

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EXPERIMENTAL APPARATUS AND SAMPLE CHARACTERISTICS

The experimental apparatus which has been previously described⁵ includes a high resolution double pass cylindrical mirror analyser (CMA), integral electron gun, and a Phi dual anode X-ray source for XPS measurements.

The specimen was prepared from a Ni15Cr13Al billet. The specimen was sectioned to 10x10x0.05 mm and polished to 600 diamond grit with no other treatment. The specimen was mounted on tungsten wire legs and heated resistively. A W5Re/W26Re thermocouple was used for temperature measurements. The sample was cleaned in UHV by heating and argon ion bombardment cycles and was used for the experiments described in paper I. The Zr evaporation source has been previously described.¹⁵

METHODS AND RESULTS.

The Zr evaporation source was first characterized by plotting the $N'(E)$ Zr Auger peak at 92 eV¹⁶ as a function of evaporation time. It can be seen from fig 1 that the change in slope at the nominal one and two monolayer points is reasonably clear cut. The ratios of the slopes for $M_2 / M_1 = 0.69$ and $M_3 / M_2 = 0.54$ are not the same as reported by Davis¹⁷ for Zr on W ($M_2 / M_1 = 0.51$, $M_3 / M_2 = 0.53$). However in this work on NiCrAl there is some overlap with the Ni transition at 102 eV and the apparently high initial growth of the Zr 92 eV signal is influenced by the decrease in the Ni 102 eV signal. If the Zr 116 eV transition is used the ratio of the slopes $M_2 / M_1 = 0.53$. This is in agreement with calculations based on the model and calculations of Davis¹⁷ (perfect hcp overlayer) and the mean free path of Seah and Dench¹⁸. The figures are $a = 0.317/\sqrt{2}$ nm, $E = 116$ eV, $\lambda_m = 2.13$ and $M_2 / M_1 = 0.53$. Thus despite the nature of the argon ion cleaned polycrystalline multiphase alloy surface it seems that the Zr overlayer is initially forming by monolayer growth. For Zr on Ni alloys this is not unreasonable for given the large negative heat of mixing over the whole of the composition range¹⁰ the Ni-Zr interaction might be expected to dominate the growth kinetics^{19,20}

After this characterization of the Zr source and the growth kinetics an estimated two monolayers of Zr was evaporated onto the ion cleaned NiCrAl. The sample was then annealed in

steps of 100°C from 450°C to 750°C for 5 mins at each step. Between each annealing step the sample was returned to room temperature for analysis by AES and XPS. The effects of the annealing can be seen from the spectra shown in fig 2. Included for comparison is a spectrum from the annealed undoped NiCrAl without a Zr overlayer.

There are several changes apparent due to the annealing. The Ni and Al peaks at 51 eV and 60 eV increase, the 92 and 116 eV Zr peaks decrease and the peaks at around 150 eV increase to a similar extent as the S peak on the Zr free surface. Also however the oxygen peak at 510 eV decreases markedly. The ratio of the 116 eV peak height to the 148 eV peak height of Zr has been variously reported in the literature at between 1:2 and 1:12 depending on the amount of surface contamination and the history of heating.^{16,20,21} In this case the ratio of 1:47 and the similarity of the peak shapes between the S on the untreated NiCrAl unambiguously show that S has surface segregated. This is confirmed by the XPS spectrum B of fig 3. Unfortunately the shape of the S (148/152) Auger peak does not appear to be strongly predictive for the surface state of the S on Ni^{22} (c.f. Fe^{23}) although the formation of a sulphide, either Zr or Ni, may be energetically favoured it is known from catalysis that the S saturates without a bulk sulphide being formed on Ni and there is no reason to suppose that this will be different for Zr. The spectra of fig 2 show moreover that the S has rapidly diffused through the surface alloy of NiCrAl+Zr of spectrum D fig 2 and does not appear to

have stabilized Zr at the surface by the formation of a Zr sulphide.

After annealing the specimen was cleaned using argon ion bombardment. The Argon ion cleaning rapidly removed S and Zr from the AES spectra but Zr(3d) was persistent in the XPS spectra. Between 10 and 20 monolayers of Zr were then evaporated onto the NiCrAl specimen. The Zr spectrum was never free of oxygen after evaporation so no determination of the relative elemental Zr peak heights was possible. Annealing in steps as previously described to 750°C showed that Ni and Al rapidly diffused through the Zr overlayer and that the 150 eV Zr peak separated into the 148 and 152 eV peaks that appear to be characteristic of S.

CONCLUSION.

The simultaneous presence of a Zr enriched near surface alloy and surface sulphur on a NiCrAl specimen shows that the apparent competition between the surface segregation of S and Zr is not a free surface effect. That is the action of Zr in suppressing the segregation of S in Ni₁₅Cr₁₃Al_{0.5}Zr at temperatures up to 750 °C is a bulk effect and would be expected to be true for internal surfaces and interfaces as well as the free surface.

The rapid diffusion of Zr into the NiCrAl and the Ni into the Zr is consistent with the negative heat of mixing despite the apparent difficulty of the atomic radii mismatch between Zr and γ Ni.

The results suggest that the mere presence of a Zr doped NiCrAl, albeit only a few monolayers of doped alloy, is not sufficient to stop the diffusion of S to a surface. The implication is that the action of Zr on S is not a surface or alloy effect but a chemical effect during the high temperature stages of alloy preparation.

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FIGURE CAPTIONS

Fig.1 The growth of the 92 eV Zr N^{1s} Auger peak with number of evaporations. For Zr on NiCrAl with a substrate temperature of 20°C.

Fig.2 Auger spectra from A) NiCrAl annealed to 750°C. B) C) D) and E) NiCrAl precoated with two monolayers of Zr annealed to indicated temperature under conditions described in text.

Fig.3 X-ray photoelectron spectrum of NiCrAl coated with two monolayers of Zr and annealed up to 750°C.

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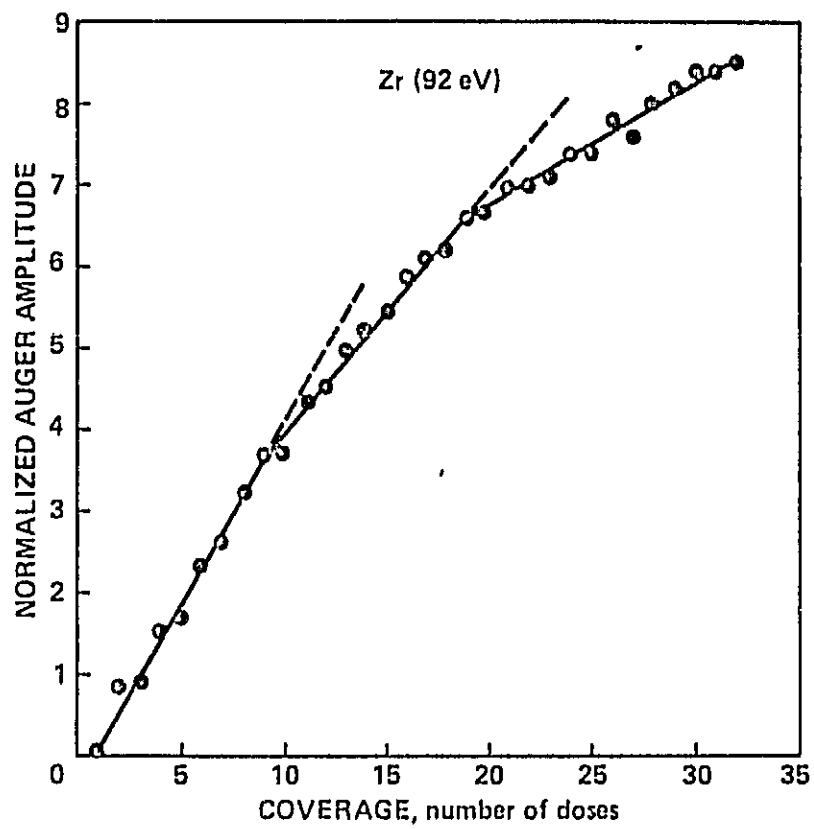
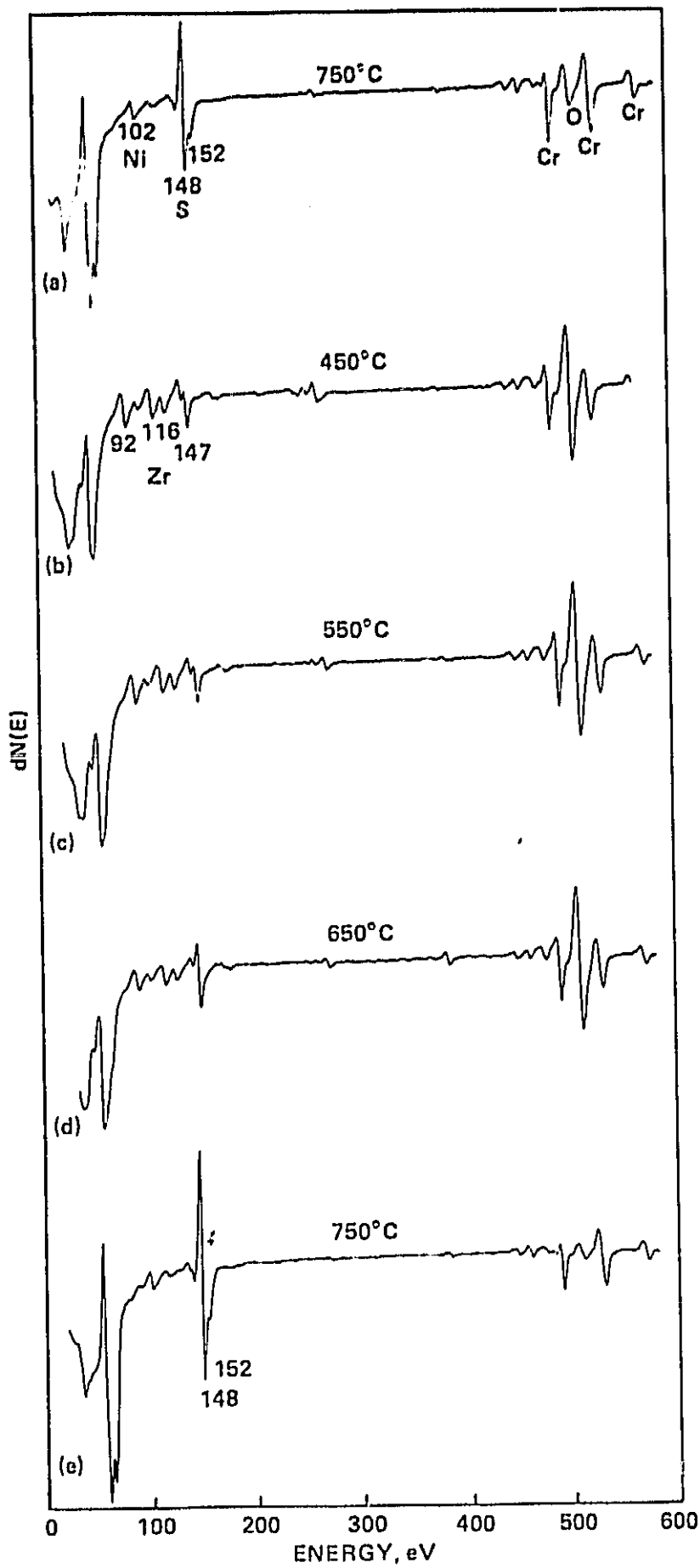


FIG 1



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FIG 2

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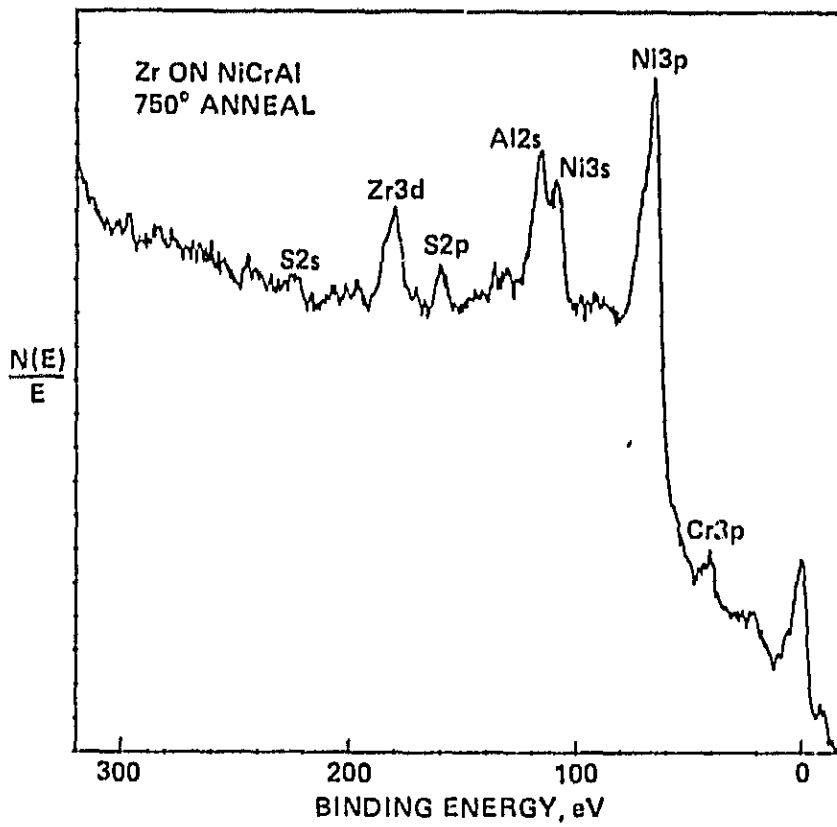


FIG 3.