MASTER

PROTECTIVE OXIDE FILMS

Progress Report

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Resistance Relaxation Studies

During the past year we used the resistance relaxation technique to investigate the initial oxidation of Ni. This technique has never before been used to study oxidation of metallic foils. It was found to be extremely sensitive in determining the initial oxidation rates at high temperature and high pressure where other techniques are not particularly sensitive.

The foil initially selectively oxidizes down grain boundaries and other diffusion pipelines. It is apparent that simple thin surface oxide nucleation and growth is not the dominant feature of the very early oxidation processes. These results are very exciting, since this is the only known study where the initial grain boundary oxidation kinetics has been accurately measured. Previous studies have explained the early deviation from parabolic kinetics in terms of surface reaction kinetics or different parabolic rates. Since most of these studies used conventional techniques not particularly sensitive to the initial rate kinetics, they were able to accurately assess this phenomena. Our studies brought attention to the fact that the alloy microstructure (grain size and orientation) has pronounced effect on the initial reaction kinetics and in fact the entire oxidation process. The influence of grain boundary segregation on the oxidation process can now be accurately assessed when used in combination with modern surface analytical techniques.

A second important finding in this study was the effect of interstitial impurities (particularly H and N) on the oxidation of alloys. The influence of H on the oxidation kinetics has long been suspected, but no definitive evidence has ever been presented. This study quantitatively relates to the

kinetics of oxidation to the amount of dissolved H in the foil. This can now be expanded to the study of the influence of water vapor on oxidation kinetics. One distressing anomaly has been the dramatic increase in oxidation kinetics with the introduction of water vapor. From this work it is obvious that nascent hydrogen plays an important role in the kinetics and points to an autocatalytic mechanism where H_2O is decomposed on the reactant surface.

Two referred papers on this work are to be published; copies are appended. A Master's thesis was completed on this topic over the last year: "A Study of the Oxidation of Nickel Using Resistance Measurements", by B. A. Quimby, who is now employed by Homogeneous Metals, Inc. in Herkimer, New York.

TGA

An apparatus with the adequate sensitivity to study the oxidation of Ni using the interrupted growth technique was completed during the past year. The sensitivity of the newly designed thermogravimetric system is now $\pm 1.5 \times 10^{-5}$ g for samples of approximately 1 gm. weight. This is an increase by a factor of 10 over the initially built system.

Studies to examine the chemical diffusion and point defect properties of NiO at temperatures of 800°C-1000°C were started. The results yield the deviation from stoichiometry of the NiO as a function of temperature and oxygen pressure. This is then correlated with the EPR results subsequently described.

From the thermogravimetric results it is evident that the defect population increases with oxygen pressure (see Fig. 6). This data was analyzed using the Wagner parabolic oxidation treatment, and correlates well with previous studies.

However, the defect population determined by EPR indicates a trend opposite to the Wagner model. Since EPR is particularly sensitive to the defect concentration in NiO, the Wagner approach to NiO is open to serious contention.

Characterization of Defect Structure by Physical Methods

Transport Measurements. We have continued with our methodical investigation of trapping centers in as-grown NiO by studying the electric-field and optically induced thermo-currents. The spectrum of thermo-currents in the as-grown NiO has been sufficiently studied by May 1980 or so, and more definite analysis of the spectra required the study of "different" oxide. To this end, it seemed most profitable to dope the oxide with Li by ion implantation.

Li implantation was carried out in conjunction with a group at SUNYA. Electrical, optical, Rutherford back scattering and channeling studies have been made. The result of this collaborative effort has been most successful in that it has provided a basis for the identification of one of the TSC peaks being due to Ni vacancies. This is important in relation to the thermogravimetric studies.

There were other benefits gained from this work: 1) directly related to this work was the production of a specimen containing a significant concentration of oxygen vacancies which cannot be obtained by conventional growth techniques (see section on EPR). 2) a measure of the drift mobility of small polarons in NiO was obtained, namely $10^{-4} \text{ cm}^2/\text{secV}$. We consider this to be a reliable number and an important contribution to the subject.

A refereed paper on this work is to be published, and a copy is appended. A Ph.D. and a Master's thesis were completed on this topic over the last year:

"Photoconductivity in NiO", by M. Brown, who is now employed by Bell Telephone Company at Murray Hill, New Jersey and "Thermocurrents in NiO", by J. Savi, who is now employed by Foxboro Corporation in Boston.

Electron Paramagnetic Resonance Measurements

After considerable effort in instrumentation, we have obtained some interesting EPR spectra of NiO films. Typical spectra of bulk NiO, CVD grown NiO, Li implanted CVD NiO and internally grown NiO are shown in Figs. 1, 2, 3, and 4. The vast difference between the spectra indicate that we have indeed discovered a powerful diagnostic tool for studies of oxide growth. These observations fully vindicate our initiating suggestions contained in the original proposal. The potential of EPR as a diagnostic technique becomes even more exciting when the spectrum of NiO grown under corrosion conditions is studied, see Fig. 5. Quite obviously there is a great varied and dense defect population in this material compared to the others, with corresponding impact on the understanding of corrosive growth compared to thermal growth.

We have immediately begun studying and using this new diagnostic technique in the context of the proposal subject. To this end we have measured quantitatively the relative total defect population by EPR (area integration) of films grown at various oxygen partial pressures, and compared these values with those determined by thermogravimetric methods. The results are shown in Fig. 6.

The oxygen partial pressure dependence of defects determined by EPR is completely different to that determined by gravimetric methods. The sign of the power dependence is different in the two cases. On the assumption that EPR is monitoring the defects involved with the growth mechanism, we find

the astonishing result that the films are not growing in the classic manner as outlined by Wagner. The consequence of this result will be very far reaching.

In view of the importance of these results, a short paper on the first findings is in active preparation.

SUMMARY OF INITIATING WORK

The thrust of the initiating proposal was to study the growth of protective oxide films (NiO in particular) by the most significant thermodynamic approaches (resistance relaxation and interrupted thermogravimetry) and to couple these with a study of the defects involved by spectroscopic physical methods.

The advance anticipated by this approach is that the defects responsible for the growth will be studied and monitored by methods independent of the growth kinetics. In this way the theories of oxide formation can be critically tested and the role of minor impurities studied in detail as never before.

RRA

Studies have been completed on the initial oxidation of Ni. Because of the possibility of the reaction rate being controlled by transport in the gas phase at lower P_{O_2} when an Ar- O_2 gas mixture is used, an alternate system is proposed. This work will be continued.

Using a stabilized ZrO_2 tube to pump oxygen directly will allow direct oxidation to be monitored without the reaction rate being modified by the gas transport. Furthermore, the elimination of H effects can be accomplished by using this modified system.

A second proposed study involves the formation of multiple oxides. One can accurately control the formation of one or two oxides by controlling the temperature and P_{O_2} over thin Cu foils. The transition for formation of Cu_2O to Cu_2O/CuO has received little attention but is extremely important in understanding the adjustment of defect populations with valence changes. The initial oxidation studies using RRA will provide a basic study of the kinetics and provide us with the time constants for studies to be performed in the future on such complex alloys. Such studies is the first basic step into understanding the role of oxide defects in the complex multi-phase multicomponent systems.

TGA

Interrupted thermogravimetric studies will be continued on Ni with the intent of discovering some of the reasons for the anomalies in the oxidation of Ni. Of particular importance will be the determination of defect population as a function of oxide thickness. The mechanism of oxidation changes as the oxide thickens. At present, this remains one of the pressing problems in the

understanding of oxidation. Studies will be performed on different oxide thicknesses. Furthermore, the influence of dopants on the defect population will be examined. Doping with Li and Al in Ni will be performed. The defect population of oxides grown will then be examined as a function of P_{O_2} .

These studies will be carefully correlated with EPR studies on NiO. Since the defect centers contributing to the EPR spectra will change dramatically, some insight into defect characterization and densities will be examined.

Transport Measurements

A limited number of further transport measurements is required to complete our systematic investigation, which is now of considerable size and detail. These will be completed in the near future followed by a series of papers presenting our findings which will be submitted for publication.

EPR Measurements and Thermogravimetry

In view of the relatively direct interpretation of EPR with respect to defect concentration compared to the transport measurements, we propose to concentrate heavily on this technique in the future.

Our goals can be simply stated: we propose to characterize the grown oxides principally by EPR, as to the kinds and number of defects present. These results will be compared to the thermogravimetric measurements, which in principle, provide an independent measure of the principle defect present, but subject to the validity of as yet untested assumptions.

We hope to establish whether the Wagner theory is applicable or not (so

far our first results are to the contrary), what the growth defects are independent of any theory, and how they depend upon impurity concentrations, temperature, time, and so on.

We believe that even a modest success of our program will provide a very significant advance in the field.

[It is worth noting in closing that our EPR spectra are pioneering efforts, no spectra of resonances in NiO have been published as far as we are aware. The experimental difficulty in obtaining the spectra, Figs. 1-4 of the progress report COO-ER10428-02, has been sizeable. This can be appreciated by noting that our "lines" are kilo-gause wide compared to a few tens of gauss usual in non-magnetic crystals. This reduces the sensitivity of a derivative machine by a factor of 100 compared to normal systems, and in addition the mass of oxide available to us is very small. We are developing a new technique suitable for wide spectra based on modulating the power reflected from the cavity directly, rather than modulating the adsorption of this cavity with applied field modulation. The adsorption spectra are of considerable interest in their own right, and will certainly be of interest in relation to the interactions in this magnetic crystal.]

FIGURES

FOLD HERE -

Flame Fused NiO

P. .01 mW
 Amp. .01
 Sat. 5
 2 1
 Sw up to m

80

H →

FIG 1

HP1

2.5
 2.5
 2.5

FIELD OF VIEW

79

N₂O (CVD)

P. 100 W

mod. 105

Sound 100 80 100

12H

0.5 mV
100 Hz

H -

FIG 2

FOLD HERE -|

Li implanted Al₂O₃
 15 mA
 70 sec
 0.5 m.e.
 100 μ V
 3 sec
 20 min sweep time

100 μ V
 1 sec

H ->

FIG. 3

dX/dH

0.5-11
1 kg = 2.2 lb

FOLD HERE

Reel: first time
Black: second time
Red: done

0.5-11
0.5-11
100 μV

Faint Slagwell Springs

H →

FIG 4

FOLD HERE

40

MAGNETIC RESONANCE		
BY.	DATE	
SAMPLE.		
T.	K.; M.	GM.
P.	W. AT	H ₂
IMOD	A. AT	H ₂
SENT	V: ICIV	A.
T.C.	S: S.R.	M.

See page 41
g w

H --

FIG 5