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The Creep of CoO Scales – the Influence of Stoichiometry, Stress and Temperature

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The plastic deformation of cobalt monoxide scales formed by complete thermal oxidation of high purity cobalt sheet has been assessed in the temperature range 925 to 1050° C at different oxygen pressures. By observing the creep-in-bend behaviour using a three-point-loading technique it has been demonstrated that these scales undergo considerable plastic deformation, both primary and secondary creep being exhibited. It has been shown that the creep behaviour of the oxide is strongly dependent on oxide composition, the scales becoming more plastic as the non-stoichiometry of the material as defined by the ambient oxygen pressure surrounding the specimen, is increased. In particular, the secondary creep rates increase linearly with increasing defect concentration. Measurements of the stress dependence of the secondary creep rates suggest that the deformation involves a process other than the Nabarro-Herring mechanism of stress-directed vacancy diffusion. An activation energy for creep of 46 kcal/mole was obtained.

1. Introduction

On the basis of theoretical considerations and experimental evidence it is recognised that the oxide scales formed on metals during thermal oxidation are under stress. It is therefore of importance to assess the deformation characteristics of such scales under the influence of these stresses, particularly the plastic deformation behaviour. However, few results of mechanical property measurements have been published [1].

Because of the vacancy concentration known to exist through an oxide scale in contact with a metal during oxidation, it is also a matter of some interest to know whether the plasticity of the oxide alters appreciably with the degree of non-stoichiometry. No detailed assessment of this particular problem has yet been attempted, although some preliminary results have been published [2]. Furthermore the corresponding data for bulk ceramic materials are somewhat in conflict [3]. Thus, for example, Reppich [4] observed that during the plastic deformation of FeO both the activation energy and the relationship between applied stress and creep rate (i.e. stress exponent) were independent of the stoichiometry of the oxide; similar observations were also reported for TiC and NbC [5]. However with MgO [6], TiO [7] and UO_2 [8, 9], these same parameters have been found to depend on oxide stoichiometry. Again whilst in general most authors [4-10] report an enhancement of the rate of plastic deformation with increase in defect concentration of the material, the results reported for TiO_2 [7, 11] are in conflict.

The object of the present studies was to examine the plastic deformation (creep) behaviour of polycrystalline cobalt monoxide scales, formed by thermal oxidation of cobalt metal, as a function of oxide stoichiometry, stress and temperature. Cobalt monoxide is a material well-suited to such studies, since its crystal and defect structure and range of stoichiometry are well documented; CoO has an NaCl structure and is a metal-deficient *p*-type semiconductor [12, 13]. The oxidation behaviour of cobalt leading to the formation of CoO scales is fairly well understood, and is of considerable practical and theoretical interest [14].

2. Experimental

2.1. Materials

Johnson-Matthey high purity (Grade 1) cobalt sheet 0.008 in. thick was used in all of the experiments. With this grade of material the total metallic impurity content is less than 15 ppm; the impurity levels in ppm are shown below:

Ni	Si	Al	Fe	Na	Cu	Mg	Ag
3	3	2	1	1	1	1	1

Gases used for oxidation and equilibration studies were supplied by British Oxygen (Special Gases Division). Four gases were used: pure oxygen, air and oxygen/nitrogen mixtures containing 1 and 0.01 vol % of oxygen. These gas mixtures were made up and analysed by British Oxygen. A typical analysis of the high purity nitrogen and oxygen as supplied is given below:

	N_2	O_2	CO_2	CO	Hydrocarbons	H_2	Ne	Ar	He	H_2O
N_2	99.9%	10	5	1	5	1	5	50	1	15
O_2	0.1%	99.5%	5	—	25	50	—	0.5%	—	200

The impurity contents are given in ppm unless otherwise stated.

All of the gases used in the experimental work were dried by passing them through a train consisting of two glass tubes containing silica gel followed by two tubes of magnesium perchlorate.

2.2. The Design, Construction and Operation of the Mechanical Testing Apparatus

2.2.1. Design and Construction of the Apparatus

The main practical difficulty associated with the measurement of the mechanical properties of oxide scales is the handling of the materials which are very weak and brittle at low temperatures. After considering the various methods which have been used for testing brittle ceramic bodies [15-18] it was decided to use a three-point-bending technique.

The main features of the apparatus used are shown in fig. 1. The load was applied directly on to the mid-point of the specimen, which had a standard span length of 17 mm, by means of a light alumina rod (about 4 mm in diameter). To the top of this rod was attached a thin walled glass tube into which the required lead weights could be lowered by means of a winch. The oxide sample rested in a horizontal position supported near its ends on silica tubes of small diameter (about 1.5 mm). These support tubes were themselves rigidly held in position by means of fine (0.0005 in.) diameter platinum wire in slots cut into the long, thin-walled silica main support tube (see fig. 2). The deformation of the samples was small (about 0.1 cm) and a simple mechanical deflectometer was used to magnify beam deflections by a factor of about × 10. The magnified deflection was measured with a cathetometer and the overall accuracy of measurement of the central deflection of the oxide beam was ± 0.0002 cm. The furnace temperature was controlled with an "Ether" type 991 controller to ± 2° C.

2.2.2. Measurement of the Creep Behaviour of CoO Scales

At the beginning of a test, a clean degreased cobalt metal coupon (19 mm long × 4 mm wide × 0.2 mm thick) was placed in position on the silica specimen support tube and the whole unit was then lowered into the furnace. After sealing the apparatus the system was evacuated to a residual air pressure $\ngtr 10^{-4}$ torr. The furnace was switched on and the specimen was heated up to temperatures of 925, 1000 or 1050° C under vacuum. On reaching the desired temperature

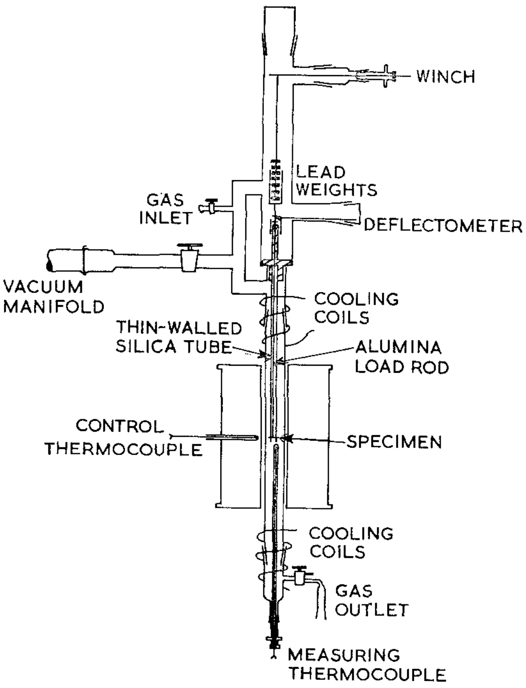

Figure 1 Apparatus for creep-in-bend experiments in controlled atmospheres.

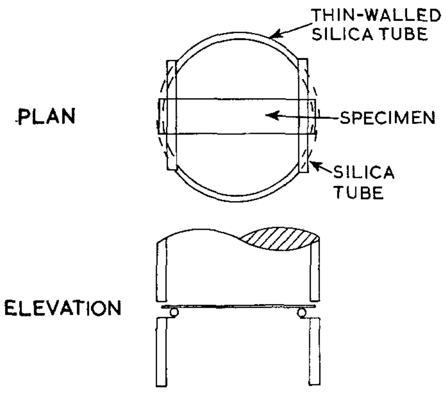

Figure 2 Details of specimen support.

the test rig was isolated from the vacuum system and the dry oxidising gas was carefully admitted and allowed to pass through the apparatus at a flow rate of about 3 l/h. The specimen was then allowed to oxidise for 20 h to ensure complete oxidation and equilibration to standard stoichiometry (even in the most dilute oxygen-containing gas) and also to ensure a standard grain structure for the $Co_{1-x}O$.

A load was then carefully lowered on to the rod assembly bringing the alumina rod into contact with the oxide beam, which was maintained at the oxidation temperature. Readings of deflection as a function of time were then taken until secondary creep was well established. On the completion of the creep test, the oxide beam was air cooled.

An important feature of the experimental technique was that these cobalt coupons were oxidised *in situ* in the mechanical testing apparatus i.e. already positioned on the bend jig. This procedure avoided the complications of precipitation of Co_3O_4 and the imposition of cooling stresses on the CoO scale, inevitable if the samples were oxidised and then deformed in separate operations.

Creep tests were carried out:

(i) To establish the relationship between creep deflection rate and oxide stoichiometry. This series of tests was carried out at 1000°C under a constant load of 60 g on oxides of stoichiometry derived from oxygen partial pressures of 1, 2.1×10^{-1} and 1×10^{-2} atm. (The load of 60 g was chosen on the basis of some preliminary stress/strain experiments in these various oxidising gases and corresponded approximately to the yield stress of the oxide for the particular geometry of the stress system employed.)

(ii) To determine the stress dependence of secondary creep rates for oxide scales of fixed stoichiometry. These tests were carried out using loads of 50, 60, 70, and 80 g at 1000° C on oxide beams formed by oxidation and equilibration in pure oxygen.

(iii) To determine the activation energy for the rate controlling process. For this secondary creep rate, data were obtained at 925, 1000 and 1050° C for a constant load of 70 g; the oxide beams were formed by oxidation in a 1 %O_2/99 % N_2 gas mixture. The use of gas with this low oxygen partial pressure avoided the formation of Co_3O_4 which could arise at a temperature of 925° C in atmospheres with a higher oxygen content, and also minimised the undesirable change in stoichiometry of the oxide over this temperature range ($Co_{0.9986}O$ at 925° to $Co_{0.9979}O$ at 1050° C).

A minimum of three individual experiments was performed to obtain the time/deflection data either at a constant load for the various environments, or as a function of load for a given environment. The average deflection/time curves presented in the results section were drawn through points corresponding to convenient fixed time intervals; these points represent the arithmetic mean of the individual deflections after these given time intervals obtained from the original experimental curves. This method was considered to be the most convenient and satisfactory means of graphically summarising the data. The slope, i.e. creep rate of the mean curve obtained in this way, agreed well with the mean slope calculated from the individual curves; for example, the secondary creep deflection rate for a load of 60 g for an oxygen pressure of 1 atm at 1000° C was $0.43\ (3) \times 10^{-2}$ cm/h (see fig. 3), whilst the corresponding rate obtained as the mean of the individual experimental curves was $0.43 \pm 0.04 \times 10^{-2}$ cm/h.

3. Results

3.1. Creep Behaviour as a Function of Oxide Stoichiometry

Both primary and secondary (linear) creep was exhibited by the oxide in each atmosphere. The amount of plastic deformation increased as the oxygen pressure was increased, but in no case did the specimens fracture. These features are illustrated in fig. 3, where it is evident that the secondary creep rates increase as the oxygen pressure increases. This latter feature is emphasised in fig. 4, where the secondary creep rate is

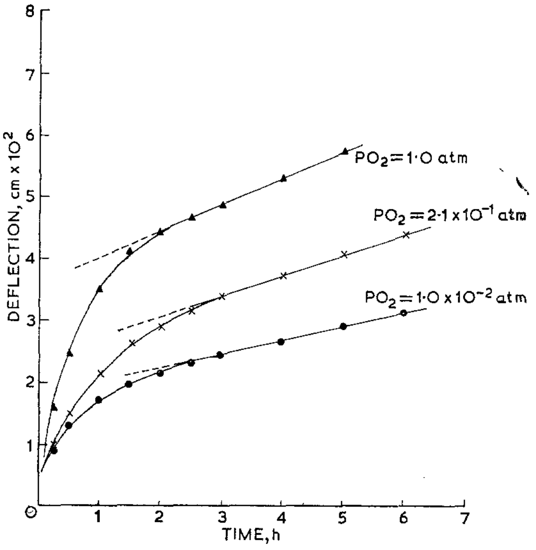

Figure 3 Average deflection of cobalt monoxide beams at 1000° C under constant load (60 g) as a function of time at various oxygen partial pressures.

plotted as a function of the departure from stoichiometry, which has been calculated from the various oxygen pressures using the results of Fisher and Tannhauser [12, 13].

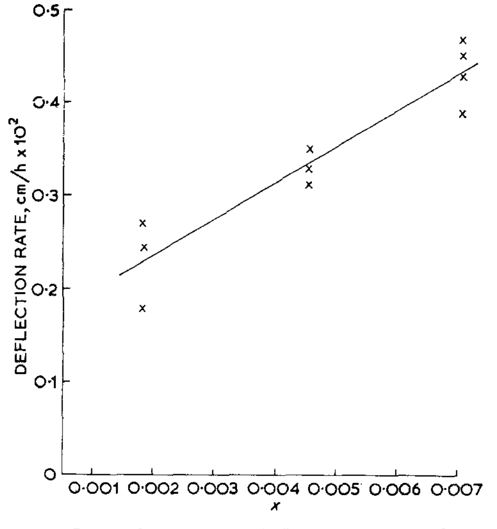

Figure 4 Secondary creep deflection rates of cobalt monoxide beams at 1000° C under constant load (60 g) as a function of x where x is given by $Co_{1-x}O$.

3.2. Creep Behaviour as a Function of Load at Constant Temperature

The oxide deformed plastically for all of the applied loads, exhibiting both primary and secondary (linear) creep (see fig. 5). It is evident that the overall deflection increases as the load increases and in particular the linear creep rate alters significantly with applied load. In fact the deflection rate ($\dot{\epsilon}$) is a function of the applied load (and therefore stress), such that:

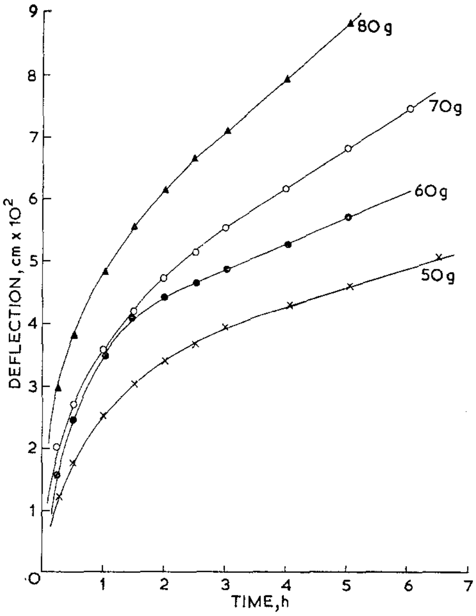

Figure 5 Average deflection of cobalt monoxide beams at 1000°C as a function of time for various loads at a constant oxygen partial pressure (1.0 atm).

$$\dot{\epsilon} \alpha \sigma^n \qquad (1)$$

where n is a constant, as illustrated in fig. 6. The best straight line through the individual points determined by the method of least squares satisfied expression 1 with $n = 2.3$. Other limited secondary creep data for beams oxidised and deformed at an oxygen pressure of 1×10^{-2} atm and 1000° C, suggested an approximate value for n of 2.4. These secondary creep rates which were measured only for loads of 60 and 70 g are given in table I. These data suggest that the same deformation mechanism is operative at these limiting oxygen pressures, i.e. in oxide of corresponding limiting compositions.

3.3. The Effect of Temperature on the Creep Behaviour

The results of these experiments are summarised in fig. 7. It can be seen that the total deformation after a given period increases markedly with increase of temperature and that both primary and secondary creep are exhibited at all temperatures. The linear creep rate increases with increasing temperature.

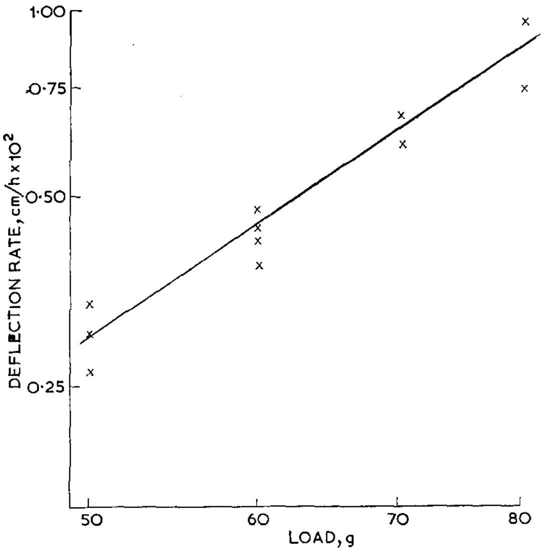

Figure 6 The log of the deflection rates of cobalt monoxide beams at 1000° C as a function of the log of the applied load at a constant oxygen partial pressure (1.0 atm).

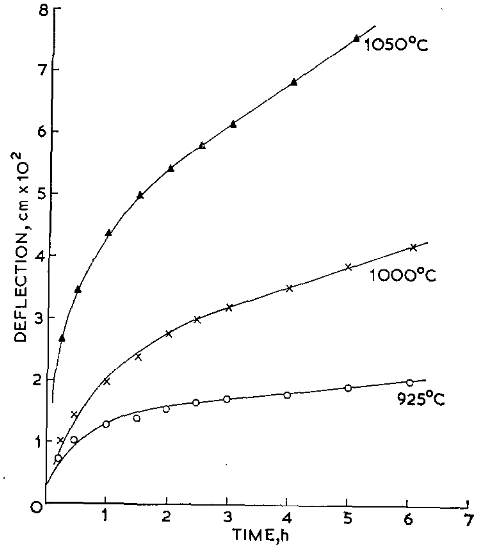

Figure 7 Average deflection of cobalt monoxide beams under constant load (70 g) as a function of time at various temperatures at a constant oxygen pressure (1.0×10^{-2} atm).

The variation of the creep rate ($\dot{\epsilon}$) with temperature (T° K) can be described by an Arrhenius type equation:

$$\dot{\epsilon} = K \exp(-Q_c/RT) \qquad (2)$$

where Q_c is the activation energy for creep, K is a constant and R is the gas constant. In fig. 8 the straight line was determined by the method of least squares from which the activation energy Q_c was calculated to be 46.9 kcal/mole.

TABLE I Secondary creep deflection rates at 1000° C

Load g	Deflection rates cm × 10^2/h	Average deflection rates cm × 10^2/h
60	0.18	0.23
	0.24	
	0.27	
70	0.31	0.33
	0.35	

Oxygen pressure = 1 × 10^{-2} atm.

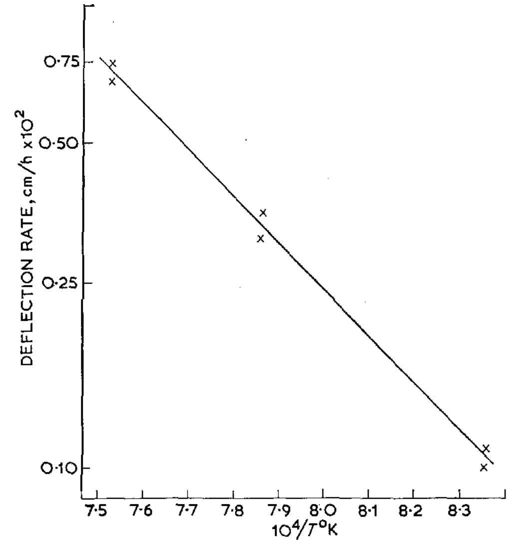

Figure 8 Secondary linear creep deflection rates of cobalt monoxide beams under constant load (70 g), as a function of the reciprocal of absolute temperature at a constant oxygen partial pressure (1.0×10^{-2} atm).

4. Discussion

The scales formed under the present experimental conditions of reaction temperature, specimen purity and geometry, appeared to consist of a single layer of material which was substantially compact. In particular the scales did not consist of two physically distinct layers of oxide, i.e. an inner layer with fine porosity, surmounted by an outer compact layer, as reported by some workers [14, 19-22]. A typical microstructure of a cobalt monoxide scale is illustrated in fig. 9. Although some coarse porosity in the form of voids or holes is evident, this porosity is largely the result of metallographic damage during the normal grinding and polishing operations. These

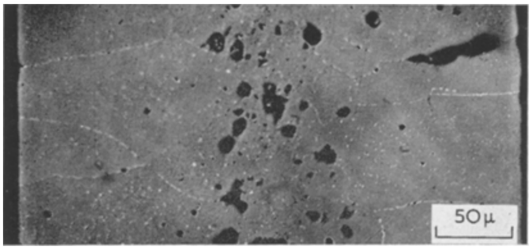

Figure 9 Cobalt monoxide scale formed by the complete thermal oxidation of cobalt sheet in oxygen (1 atm) at 1000° C after 20 h exposure.

observations are in agreement with other authors [23-25], who have also studied the morphology of scales formed from high purity cobalt.

During the cooling of the scales from the oxidation/testing temperature a small amount of precipitation of the oxide Co_3O_4 occurred, principally within the grain-boundaries of the CoO, but also to a lesser extent within the grains. This precipitation appeared as a continuous white network, which conveniently allowed an assessment of the grain size and shape of the CoO. The oxide structure (fig. 9) was made up of large columnar grains which constituted the majority of the sample ($\sim$ 80% of total thickness) and the boundaries of which were roughly normal to the length of the sample, together with an inner region made up of smaller equiaxed grains.

The absolute value of the stress-in-bend experiments is unknown, and the stress distribution throughout the specimen is complex. In addition, the stress distribution will be different at different stress levels. However, for creep behaviour in which the steady-state creep obeys the relation 1, Timoshenko [26] has derived an equation for the maximum fibre stress $\sigma_{\max}$:

$$\sigma_{\max} = 3PL/2bh^2 \left(\frac{2n+1}{3n}\right) \qquad (3)$$

where P is the load, L the distance between the specimen supports, b the width of the specimen and h is the thickness. In the present work n was found to be 2.3 and the maximum fibre stresses corresponding to the loads of 50, 60, 70 and 80 g are therefore approximately 283.5, 339.5, 395.5 and 451.5 kg/cm^2 respectively.

The creep phenomena which have been observed with oxides are very complex. A great deal of work concerning the deformation behaviour of both single and polycrystalline materials has been carried out; detailed studies have been made with Al_2O_3, BeO, MgO and UO_2 and some of the results for these materials may be used to illustrate the complexity of the situation. Thus activation energies of between 130 and 200 kcal/mole have been observed during the creep of polycrystalline and single crystals of Al_2O_3, and stress exponents varying between 1 and 5 have been reported, depending on the grain size and type of material [27-30]. Similarly, stress exponents of between 1 and 2.5 and activation energies of 96 to 145 kcal/mole have been observed during the creep of polycrystalline BeO [31-33], depending on the testing temperature and the grain size of the material. Stress exponents varying from 1 to 7 and activation energies from 36 to 175 kcal/mole have been reported for the creep of MgO [6, 34, 35]; here the stress exponents and activation energies were particularly sensitive to the testing temperature. The marked and complex effects of stoichiometry on the creep behaviour of oxides is illustrated by the results reported for UO_2 [8, 9]. For example the activation energies have been shown to vary from 65 kcal/mole for $UO_{2.16}$, to 95 kcal for $UO_{2.00}$ [8]; the stress index has likewise been shown to be sensitive to stoichiometry. Although a number of theories [18] have been put forward to attempt to explain the creep behaviour of oxides, the complexity of the results quoted above emphasise the difficulties and limitations of a unified theoretical approach even for bulk sintered materials of high density and uniform grain structure.

Clearly a complete and unequivocal interpretation of the present results relating to the creep-in-bend behaviour of polycrystalline CoO scales of unusual structure is not possible, but certain observations can be made. The value of $n = 2.3$ for the stress exponent eliminates the possibility of the Nabarro-Herring stress directed vacancy diffusion mechanism being operative. It is of interest to note that Vandervoort and Barmore [32] found that the creep behaviour of polycrystalline BeO, with a grain size similar to that of the present material, showed a stress exponent of 2.5. These authors suggested that the behaviour was probably governed by a dislocation mechanism involving the overcoming of the Peierls stress. The possibility however of the creep deformation of CoO occurring by a grain-boundary sliding mechanism cannot be overlooked. Recently Hensler and Cullen [36] have discussed the interpretation of some creep results for polycrystalline MgO (involving stress exponents of 2.7 to 3.1), and in particular the possible mechanisms whereby the creep might be accounted for in terms of grain-boundary sliding, in the absence of any apparent grain shape change. They suggested that the creep deformation could be accommodated at triple points in the grain structure, in accordance with the theories put forward by Gifkins and Snowden [37].

Both the overall deformation and the secondary creep rates for cobalt monoxide have been shown to increase with increasing deviation from stoichiometry. These findings support the previously published results for other bulk ceramic materials such as TiO_2, UO_2, ZrO_2 and MgO [2], and can be interpreted broadly as reflecting the increased mobility of defects in a non-stoichiometric lattice. It is interesting to note that hot microhardness measurements on stoichiometric and non-stoichiometric ZrO_2 [38] also support the present observations for CoO scales despite the high deformation rates characteristic of such measurements.

As can be seen from fig. 4 the creep rates of cobalt monoxide increase linearly with increasing defect (cation vacancy) concentration. Similar results were obtained by Armstrong *et al* [9] for non-stoichiometric UO_2 and by Reppich [4] for FeO, although these authors were working with sintered oxides. On the basis of this linear concentration dependence of the creep rates, it can reasonably be assumed that the creep process involves cation diffusion through the oxide lattice.

The activation energy for creep was determined to be 46 ± 5 kcal/mole. Carter and Richardson [39] obtained a value of 34.8 kcal mole for cobalt ion diffusion in polycrystalline CoO which compares favourably with the recent value of 38.1 kcal/mole given by Chen [40] for single crystal CoO. The values of the activation energies given in the literature for anion diffusion in CoO are unfortunately in conflict. Thompson [41] has quoted a value of 36 kcal/mole which is however, considered by Chen [40] to be low; he obtained a value of 95 kcal/mole for oxygen self-diffusion in single crystal CoO.

Accepting that the activation energy for oxygen self-diffusion is about 95 kcal/mole, the activation energy for creep is clearly to be associated with cobalt ion diffusion [39, 40]. However, it is known that the slower moving species in CoO is the anion [42] and therefore the diffusion of the anion would be expected to be rate-controlling.

In this context the following observations are of interest. Gupta and Coble [43] have shown that the sintering behaviour of ZnO appears to involve the enhanced diffusion of oxygen down grain-boundaries so that the ion which moves the faster through the lattice is nevertheless slower overall and therefore rate-controlling. Enhanced boundary diffusion for the ionic species with the lower lattice diffusivity has similarly been reported for Ca^{2+} in CaF_2 and O^{2-} in MgO [43]. In the present studies the possibility of some enhancement of oxygen transport down the CoO is suggested by the preferential siting of Co_3O_4 precipitates at grain-boundaries (fig. 9). Tylecote [44] has discussed the observations of a number of workers who consider oxygen diffusion in grain-boundaries to be of importance in oxidation phenomena.

5. Conclusions

(i) Under certain experimental conditions, homogeneous cobalt monoxide scales of varying stoichiometry can be formed by the complete thermal oxidation of high purity cobalt sheet.

(ii) Under three-point-loading conditions, such polycrystalline cobalt monoxide scales undergo considerable plastic deformation at temperatures in the range 925 to 1050° C, exhibiting both primary and secondary creep.

(iii) It has been shown that the creep behaviour is markedly affected by oxide stoichiometry; in particular as the degree of non-stoichiometry increases, the material becomes more plastic.

(iv) The secondary deflection rates are a linear function of the departure from stoichiometry i.e. $\dot{\epsilon} \alpha x$, where x is defined by $Co_{1-x}O$.

(v) The secondary deflection rates are related to the stress by the expression $\dot{\epsilon} \alpha \sigma^{2.3}$.

(vi) The activation energy for the creep process has been determined to be 46 kcal/mole.

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