HIGH-TEMPERATURE DEFORMATION OF CUBIC OXIDES

J. Routbort

To cite this version:


HAL Id: jpa-00220697
https://hal.archives-ouvertes.fr/jpa-00220697
Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
HIGH-TEMPERATURE DEFORMATION OF CUBIC OXIDES*

J.L. Routbort

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439 USA

Abstract.- The stress-strain curves for MgO and NiO have a work-hardening rate that decreases linearly with increasing stress to a steady state (θ=0) while the curve for CoO has an upper yield point and a work-hardening rate that is negative but increases to zero when steady state is achieved. These results predict that the shapes of the creep curves for NiO and MgO are similar, and different from those obtained for CoO. Finally, the steady-state stress \( \tau_s \) divided by the shear modulus is very similar for all three oxides, with NiO having the largest value. The functional dependence of \( \tau_s \) on temperature \( T \) for all three oxides is given by \( \log \tau_s = B - T/A \), where \( A \) and \( B \) are constants.

1. Introduction.- High-temperature stress versus strain measurements yield information on the mechanisms of work hardening and recovery. In addition, if the measurements are performed to sufficiently large strains, the competition between hardening and recovery balances and the work-hardening rate becomes zero. At this point the steady-state stress \( \tau_s \), which is developed under conditions of nearly constant strain rate (constant crosshead velocity), corresponds to the stress that must be applied to generate the same strain rate in a creep test. The resolved shear stress versus total shear strain (\( \tau \) vs. \( \gamma \)) measurement provides additional information on the behavior of the work-hardening rate and possibly on the mechanisms of hardening and recovery.

Extensive measurements have been performed on MgO single crystals over a wide temperature range of 0.4 \( T_M \) to 0.7 \( T_M \), using strain rates from \( 3 \times 10^{-7} \text{s}^{-1} \) to \( 3 \times 10^{-4} \text{s}^{-1} \). The results of these measure-

* Work supported by the U.S. Department of Energy
ments can be described by the same formalism that was developed to describe deformation in fcc metals, which predicted a stress-dependent, activation-free enthalpy and a temperature-dependent steady-state strain-rate sensitivity.

This note will report on the results of measurements of $\tau$ vs. $\gamma$ for two nonstoichiometric oxides, $\text{Ni}_{1-x}\text{O}$ and $\text{Co}_{1-x}\text{O}$. The objective of this work is to compare the deformation behavior of these two oxides, which like MgO exhibit plasticity at low temperatures, with that of MgO in order to determine whether the formalism established in the MgO work can be extended to this entire class of oxides. An investigation of the effect of the deviation from stoichiometry on the deformation of CoO is currently under way /2/.

Creep data from different laboratories for CoO single crystals of nominally the same purity are not in agreement. Two studies /3,4/ on CoO single crystals report sigmoidal creep, while the other /5/ reports normal creep behavior, e.g., a decelerating creep rate leading to a constant (steady-state) rate. Measurements of the $\tau$ vs. $\gamma$ behavior of CoO could resolve this discrepancy, since the shape of the creep curve (strain vs. time at constant $\sigma$) can be deduced from the stress versus strain data. It should be mentioned that Cabrera-Cano et al. /6/ have reported normal creep behavior for NiO single crystals; the creep data for MgO single crystals are also normal /7/.

2. Procedures.- Compression tests were performed using an apparatus described previously /1/. MgO single crystals of various orientations were tested in an inert atmosphere. The NiO crystals were compressed with the loading axis parallel to $<100>$ in an argon-oxygen atmosphere ($P_{O_2} \approx 10^{-3}$ atm.) The CoO was compressed along $<100>$ as well, but tested using a modified apparatus in which the oxygen partial pressure could be varied from $10^{-13}$ to 1 atm. at up to 1500°C. The compression rams for this apparatus are made from $\text{Al}_2\text{O}_3$ and Pt foils are used as a diffusion barrier. A boron nitride spray is used to reduce friction. The MgO crystals were purchased from various sources, while the NiO and CoO were grown from 99.999% powder by the Verneuil process using a carbon arc-image furnace. The MgO and CoO crystals are approximately 5 x 5 x 12 mm in size while the NiO crystals, which were used for another purpose after testing, were approximately 10 mm in diameter x 10 mm long.

3. Results.- A $\tau$ vs. $\gamma$ curve obtained on MgO at $T = 1100^\circ$C and $\dot{\varepsilon} = 3 \times 10^{-5}\text{s}^{-1}$ shown in figure 1 (reproduced from /1/). The stress and strain have been resolved on the slip system (110) [110], which is the primary system for all three cubic oxides. The work-hardening rate
\( \theta = \theta_0 (1 - \tau/\tau_S) \), where \( \theta_0 \) is the intercept at \( \tau = 0 \) and \( \tau_S \) is the value of \( \tau \) when \( \theta = 0 \). Although the 1100°C (\( T = 0.45 \ T_M \)) results required an extrapolation to define \( \tau_S \), data obtained at higher temperatures or lower strain rates required none. The shape of the \( \tau \) vs. \( \gamma \) curve for MgO is similar to that measured in stage III for fcc metals.

Data measured for Ni\(_{1-x}\)O at temperatures from 1100 to 1400°C, \( \dot{\varepsilon} = 1.8 \times 10^{-5} \text{s}^{-1} \), and \( P_{O_2} \approx 10^{-3} \text{ atm.} \) are shown in figure 2. It should be mentioned that since the oxygen partial pressure was constant, the deviation from stoichiometry \( x \) varied with temperature. The shape of the \( \tau \) vs. \( \gamma \) curve is similar to that obtained for MgO. The work-hardening rate decreases linearly with increasing stress. Steady state is easily achieved at higher temperatures.
The deformation behavior of $\text{Co}_{1-x} \text{O}$ at $1000^\circ C$, $x = 7 \times 10^{-3}$, and $\dot{\varepsilon} = 5 \times 10^{-5} \text{s}^{-1}$ is shown in figure 3. The data show a large upper yield point followed by a negative work-hardening rate, probably the result of dislocation multiplication, which reaches zero when the steady-state stress is achieved. The value of $\tau_s$ depends on $x$ and $\dot{\varepsilon}$/$2\pi$. However, the shape of the stress vs. strain curve is independent of temperature and deviation from stoichiometry.

4. Discussion.- It is clear from a comparison of figures 1-3 that the three cubic oxides NiO, MgO, and CoO do not exhibit the same high-temperature deformation behavior. MgO and NiO behave in a similar manner, showing a positive work hardening rate which decreases linearly with increasing stress until steady state is approached. This is shown schematically in figure 4 (left) as solid lines. Creep curves ($\sigma=$constant) obtained on materials that exhibit normal creep behavior (a decreasing
creep rate with increasing strain until steady state (minimum $\dot{\varepsilon}$), which is the result of competition between hardening and recovery, is achieved) are also shown schematically as solid lines in the $\varepsilon$ vs. time ($t$) plot of figure 4. This behavior is indeed observed in single crystals of NiO /6/ and MgO /7/.

On the other hand, the $\tau$ vs. $\gamma$ behavior for CoO is quite different from that of MgO and NiO. This is shown as a dashed line in figure 4 (left). Construction of the $\varepsilon$ vs. $t$ curves (at constant $\sigma$) gives the creep curves shown as dashed lines in figure 4 (right). In this case the creep rate increases with increasing strain until a constant strain rate is achieved. This rate may not represent a steady state in the sense of a competition between processes as observed in the normal cubic oxides because a true minimum rate is never reached.

Sigmoidal creep would be manifested in the $\tau$ vs. $\gamma$ curve as additional hardening. This is not observed within experimental error up to $\varepsilon = 0.2$, a strain higher than that used by Clauser et al. /3/ but slightly lower than that ($\varepsilon \approx 0.3$) used by Nehring et al. /4/. Both groups claim that creep is sigmoidal. Close examination of the creep curves of Clauser et al. /3/ reveal that (with the exception of a slight decrease in $\dot{\varepsilon}$ for $\varepsilon \approx 0.06$) they have the inverted shape shown by the dashed lines in figure 4, which are predicted from the $\tau$ vs. $\gamma$ data. The slight decrease in $\dot{\varepsilon}$ may be due to frictional effects or to barreling, both of which are magnified as deformation increases. The interpretation given by Nehring et al. /4/ cannot be discussed because their creep data are only presented schematically. The shape of the $\varepsilon$ vs. $t$ curves reported by Krishnamachari and Jones /5/ are normal and are inconsistent with the other two creep studies and the $\tau$ vs. $\gamma$ results reported here. It is noted that the stresses they used in order to achieve the same strain rate used in the short-term tests were $\approx 2$ times larger than $\tau_s$. It is possible that if the stress-strain experiments were performed to higher strains, additional hardening would be observed. On the other hand, differences in the creep behavior of CoO could be accounted for by variations in oxygen partial pressure or actual impurity content.

A comparison of the steady-state stress $\tau_s$ for the three cubic oxides as a function of temperature (normalized by the melting point, $T_M$) is shown in figure 5. The data were accumulated at nearly constant and equal strain rates. It should be mentioned again that whereas the MgO crystals were stoichiometric, the data for Ni$_{1-x}$O were obtained at $P_{O_2} \approx 10^{-3}$ atm., causing the deviation from stoichiometry $x$ to vary with temperature. The $\tau_s$ data for CoO are shown at $x = 10^{-4}$. Prelimina-
ry experiments indicate that the $\tau_s$ of CoO may vary by approximately a factor of 3 at 1000°C depending on $x$, and may indeed have a plateau between $T = 1000$ and 1200°C for $x \approx 10^{-3}$. The composition closest to stoichiometry is shown in figure 5 because the behavior of stoichiometric samples may be expected to be more intrinsic and thus comparable to that of MgO. For these reasons, a comparison of absolute magnitudes of $\tau_s$ should be viewed with caution. Furthermore, the $\tau_s/\mu$ ratio (where $\mu = [c'c_{44}]^{1/2}$, the shear modulus for screw dislocations) is more fundamental. The high-temperature moduli for NiO and CoO have not been measured, but if $d\mu/dT$ is assumed to be the same for all oxides, and $\mu$ values of $8.7 \times 10^4$, $6.7 \times 10^4$, and $12.3 \times 10^4$ MPa at 300 K are used for NiO, CoO, and MgO, respectively, the $\tau_s/\mu$ values for CoO and MgO are comparable while that of NiO is approximately three times larger at $T = 0.6 T_M$. The high-temperature yield stress of NiO is higher than that of CoO /8/; this is consistent with the $\tau_s$ measurements. The low-temperature ($T < 0.3 T_M$) strengths are reversed; CoO is stronger than NiO, which is stronger than MgO, but this is probably related to second-phase precipitation of $\text{Co}_3\text{O}_4$.

![Fig. 5](image.png)

Fig.5.— Comparison of the steady-state stress at nearly constant and equal strain rates for $\text{Ni}_{1-x}\text{O}$, MgO, and Co$_{0.9999}$O as a function of temperature normalized by the melting point.
The temperature dependence of the steady-state stress reported for MgO was \( \log \frac{\tau_s}{\mu} = B - \frac{T}{A} \), where the slope \( 1/A \) is proportional to the stacking-fault energy /1/, according to the cross slip theory of stage III deformation of fcc metals /11/. It can be seen from figure 5 that within experimental error, this temperature dependence is also found for nearly stoichiometric CoO and NiO. Furthermore, since the stacking fault energy of both oxides /9/ is lower than that of MgO, for which no dislocation dissociation has ever been reported, it would be expected that the \( \ln \tau_s \) vs. \( T \) plots for CoO and NiO would not be as a strong a function of \( T \) as the plots for MgO. This is apparently observed. It is interesting to note that Castaing /10/ has reported that the yield stress in \( \text{Al}_2\text{O}_3 \) exhibits the same logarithmic relation between \( \tau_s \) and \( T \) over a very wide temperature range.

5. Conclusions. The high-temperature stress-strain behavior is similar for MgO and NiO; both show a work-hardening rate that decreases with increasing stress, and steady state is achieved at \( \Theta = 0 \). This behavior can be used to predict normal creep behavior, which is observed. The \( \tau \) vs. \( \gamma \) data obtained for CoO show an upper yield point followed by a negative work-hardening rate which eventually becomes zero. This results in an inverse creep. The steady-state stress is given by \( \log \tau_s = B - \frac{T}{A} \) for all three cubic oxides, and the shear modulus-compensated steady-state stress for NiO is higher than the corresponding stresses for CoO and MgO, which are approximately equal.

6. Acknowledgments.- The author is grateful to G. Talaber and C. Wiley, who grew the CoO and NiO single crystals, and to H. Mecking and U.F. Kocks for very useful discussions.
References

/1/ Routbort, J.L., Acta Metall, 27 (1979) 649

/2/ Routbort, J.L., presented at Second Workshop on the Interactions Between Dislocations and Defects in Oxides, Lyon, France (1980)

/3/ Clauer, A.H., Seltzer, M.S. and Wilcox, B.A., J Mater. Sci. 6 (1971) 1379


/7/ See for example, Clauer, A.H. and Wilcox, B.A., J. Am. Ceram. Soc. 59 (1979) 89


/10/ Castaing, J., presented at Second Workshop on the Interactions Between Dislocations and Point Defects in Oxides, Lyon, France (1980)