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Electrotransport of cobalt, iron and chromium in BCC zirconium

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Abstract. The electrotransport behaviour of Co, Fe and Cr in β -zirconium from 1557 K to 1950 K was investigated. The radioactive tracer technique was used in this study which included ^{60}Co , ^{59}Fe and ^{51}Cr . All three solutes were found to possess negative effective charge (Z^*) in the temperature range investigated. This means that all these solutes migrate towards the anode, indicating that the electron wind force dominates in the electrotransport process in BCC zirconium. The Z^* values were also found to increase with increasing temperature as expected. The diffusion coefficients of these three solutes, Co, Fe and Cr, were found to obey the simple Arrhenius behaviour with activation energies of 1.00, 1.15 and 2.27 eV, respectively. These values suggest that Co and Fe diffuse interstitially in beta zirconium. Comparison with available data in the literature, especially at lower temperatures, shows that Co and Fe diffuse with their respective single activation energy values given above at all temperatures in the beta phase. However, the diffusion of Cr exhibited the anomalous behaviour commonly observed in the self diffusion of BCC metals (curvature in the Arrhenius plot). This anomalous behaviour can be attributed to the soft-phonon contribution of the ω -phase, in which case Cr is assumed to diffuse via a vacancy mechanism. The implication of the findings in this study on electrotransport purification are also discussed.

1. Introduction

Electrotransport is a phenomenon in which solute atoms (or even host atoms) are driven in one direction under the influence of an externally applied electric field. This process was first observed in molten lead–tin alloys in 1861 by Gerardin [1] and has since been the subject of numerous studies in various materials systems [2–10]. It has also been employed successfully as a means to purify metals [11–12]. The overall effect of electrotransport, sometimes referred to as electromigration, is generally represented by the term Z^* , the effective valence or effective charge of the solute [13–17]. A positive Z^* corresponds to migration of the solute towards the cathode and vice versa. This effective valence depends on temperature and is believed to be the sum of two separate contributions. It is a function of the true valence (Z_{e1}) of the solute ions which responds directly to the applied electric field with a force of $eE Z_{e1}$, where e is the electronic charge. The second force is due to the momentum transfer of the conduction electrons or holes and is usually called the wind force. The electron wind force results in a transport of the ions towards the anode and the hole wind force towards the cathode.

In this study, the electrotransport behaviour of cobalt, iron and chromium was investigated in β -zirconium. Zirconium is selected as the matrix material because of its importance in the nuclear industry and its anomalous self diffusion behaviour in the high temperature β phase [18–20]. The three solutes studied, especially cobalt and iron, were found to diffuse very rapidly in both α - and β -zirconium [21–23]. The electrotransport properties of these three solutes from 1140 to 1910 K will be examined and their implications for the understanding of the fundamental transport behaviour of these impurities in zirconium discussed.

2. Experimental techniques

When an electric field is applied along the length of a metallic rod, the solute atoms are driven toward one end of the rod due to electrotransport. This solute flux can be written as μEn where μ is the solute mobility, E is the electric field intensity and n is the solute concentration. The mobility is related to the effective solute valence Z^* and the solute diffusion coefficient D by

$$\mu = eDZ^*/k_B T \quad (1)$$

where k_B is the Boltzmann constant, e the electron charge and T the absolute temperature. The net flux J of the solute is the sum of the normal diffusion term and the electrotransport term represented by

$$J = -D(dn/dx) + \mu En. \quad (2)$$

In our experiments, the initial solute distribution is in the form of a function at the middle of an infinitely long rod. Using the appropriate boundary and initial conditions, the solution to the continuity equation for equation (2) can be written as:

$$n(x, t) = C_0 \exp[-(x - vt)^2/4Dt] \quad (3)$$

where

$$v = \mu E \quad (4)$$

is the net velocity of the driven ions, C_0 is a normalisation constant which arises from the mass conservation criterion and t is the time.

High purity iodide grade zirconium rods (produced by the van Arkel process) with a diameter of 4 mm were used in all the experiments. In each experiment, two rods each 5 cm in length were used. These rods were chemically cleaned with a 47% HNO₃:47% H₂O:6% HF solution to remove any surface contamination. A small drop, approximately 1 μ l, of the appropriate radioactive tracer (⁶⁰Co, ⁵⁹Fe or ⁵¹Cr) in the form of chloride purchased from Amersham Corporation was placed on one end of each rod and dried in air. The two rods were then held together mechanically with the ends containing the tracer facing each other. The specimen assembly was inserted into an all-metal high vacuum system and evacuated to better than 10⁻⁹ Pa using an ion pump. To prevent excessive evaporation of the diffusing tracer and to enhance heat transfer from the specimen to the chamber wall, the system was then backfilled with one-third of an atmosphere of purified argon gas. The specimen was connected to two high-vacuum, high-current feedthroughs, and was heated by passing a direct current through it. The temperature of the specimen was monitored by sighting an optical pyrometer at the sample through a Pyrex viewing port. Correction for absorption by the viewing port was

Table 1. Summary of experimental conditions and results for electrotransport of Co, Fe and Cr in BCC zirconium. Symbols are defined in § 2.

Tracer	T (K)	t (h)	E (V cm ⁻¹)	D (10 ⁻⁶ cm ² s ⁻¹)	Z^*	μ (10 ⁻⁵ cm ² V ⁻¹ s ⁻¹)	ν (10 ⁻⁶ cm s ⁻¹)
⁶⁰ Co	1600	21	0.20	3.7	-1.15	3.08	6.2
	1700	14.5	0.18	4.8	-1.76	5.76	10.4
	1820	6.3	0.20	8.4	-1.75	9.36	18.7
	1950	2	0.25	12.5	-1.74	12.9	32.3
⁵⁹ Fe	1557	24	0.17	1.2	-1.69	1.51	2.6
	1630	28.1	0.18	1.85	-2.00	2.63	4.74
	1700	14.5	0.18	2.25	-2.49	3.82	6.88
	1820	6.3	0.20	4.1	-2.41	6.29	12.6
	1893	6	0.22	5.2	-2.18	6.94	15.3
	1950	2	0.25	6.8	-2.19	8.85	22.1
⁵¹ Cr	1630	28	0.18	0.28	-1.28	0.26	0.46
	1700	44	0.21	0.62	-1.54	0.65	1.37
	1750	30	0.20	0.96	-2.11	1.34	2.68
	†1820	28	AC	1.6	—	—	—
	1910	19	0.25	3.1	-2.00	3.76	9.41

† This ⁵¹Cr specimen (at 1820 K) was heated using alternating current. Therefore, values for E , Z^* , μ and ν are not included.

made by determining the temperature difference between one sight glass and two sight glasses using the pyrometer. To avoid any uncertainties in the surface emissivity of the specimen, a hole measuring 0.38 mm in diameter and 3.5 mm deep was drilled in each specimen to simulate black body conditions. However, the surface temperature of each specimen was also recorded for comparison. The heating current density was measured by a current shunt and the electric field was determined using two zirconium wires spot-welded along the length of the specimen at a known separation (approximately 4 cm). The current-voltage readings also provided direct measurements of resistivity as a function of temperature. The α - β transformation of pure zirconium, which resulted in a discrete change in resistivity, provided a precise calibration of temperature at 1135 K. A water cooling line was welded onto the outside of the chamber to prevent excessive heating of the chamber wall during operation.

After the electrotransport run, the specimen was removed from the chamber. Because of the high temperature of the heat treatment (over 1400 K), the joints between the two sections were all diffusion bonded. The specimens were turned on a lathe into small sections. The turnings were collected and weighed accurately. All three radioactive tracers (⁶⁰Co, ⁵⁹Fe and ⁵¹Cr) were γ emitters. The radioactivity of each section was measured using a high purity Ge detector. The tracer concentration profiles were subsequently fitted to equation (3) with the best combinations of D and ν using a least-squares fitting routine.

3. Results and discussion

Results from all the specimens in this study are summarised in table 1. Figures 1(a) and 1(b) show the data and the computer fit to the data for two of the specimens. The shape

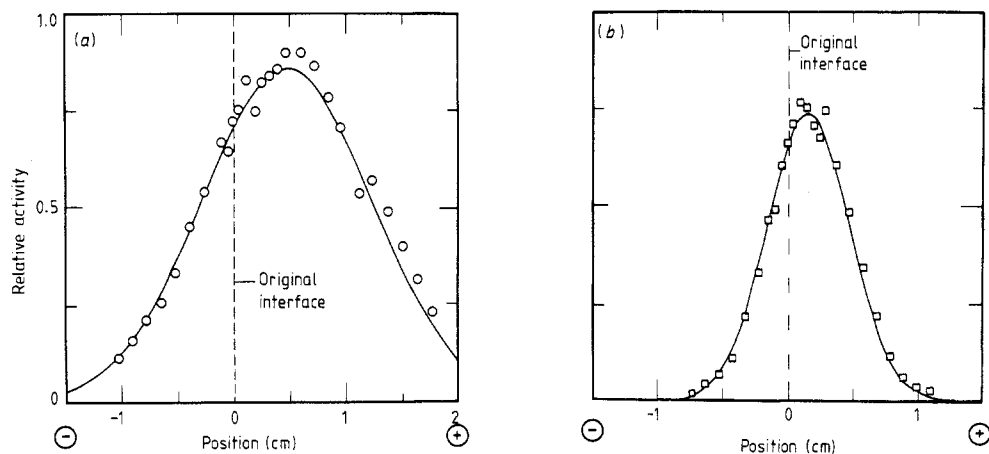


Figure 1. Solute concentration profiles for electrotransport in β -zirconium of (a) ^{60}Co heated at 1600 K for 21 h, and (b) ^{59}Fe heated at 1950 K for 2 h. The full curves represent computer fits to the data. The signs \oplus and \ominus indicate anode and cathode, respectively.

of these curves are representative of all the specimens. The computer fit was performed by iterating equation (3) with different values of D and v using a least-squares method (NL2INT) until the best fit was obtained. One ^{51}Cr specimen (operated at 1820 K) was heated using AC heating instead of DC as a calibration check to ensure that the observed movement of the profile was truly a result of the electric field applied. As expected, the peak of the chromium profile was not displaced.

The log D versus reciprocal temperature plots (Arrhenius plots) for the diffusion of the three solutes in zirconium are shown in figure 2. Within the temperature range investigated, these diffusivities can best be represented by the simple diffusion equations as follows:

$$D_{\text{Co}} = 4.7 \times 10^{-3} \exp(-1.00 \text{ eV}/k_{\text{B}} T) \quad \text{cm}^2 \text{ s}^{-1} \quad (5a)$$

$$D_{\text{Fe}} = 6.2 \times 10^{-3} \exp(-1.15 \text{ eV}/k_{\text{B}} T) \quad \text{cm}^2 \text{ s}^{-1} \quad (5b)$$

$$D_{\text{Cr}} = 3.1 \times \exp(-2.27 \text{ eV}/k_{\text{B}} T) 10^{-3} \quad \text{cm}^2 \text{ s}^{-1} \quad (5c)$$

These three equations are shown as full lines in figure 2. To obtain proper insight into the diffusion behaviour of these solutes, it is important to review the data available in the literature on diffusion in zirconium in general. The self-diffusion characteristic of β -zirconium has been extensively studied from the α - β transformation temperature of 1140 K to the melting point [18–20], whereas the diffusion of the three solutes of interest has only been examined at the lower temperatures in this range [21–23]. Comparison between present and previous data is illustrated in figure 3 by the full and broken lines, respectively. The extent of these curves indicates the range of temperature used in the studies. It is evident that the data from the studies involving Co and Fe agree remarkably well, especially in the case of the activation energies, which differ by less than 5% between the present and previous studies. Even the pre-exponential constants between the various studies are in good agreement. From these data, it is clear that both Co and Fe diffuse very rapidly in zirconium with similar activation energies of about 1 eV over the entire range of the β phase. This means that these two solutes migrate with one single

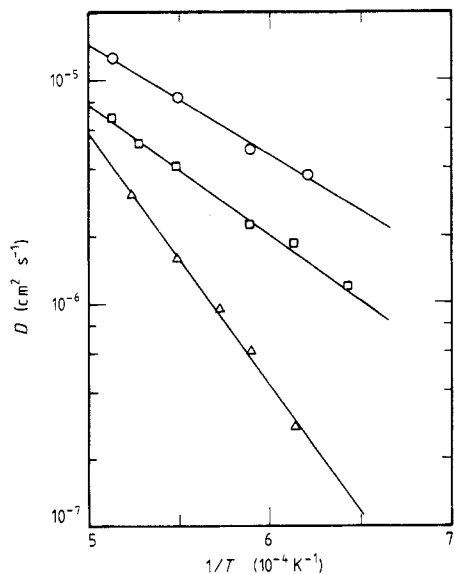


Figure 2. Diffusivity D of Co, Fe and Cr in β -zirconium against temperature. The full lines represent linear fits to the Arrhenius plots using equation (5). \circ , ^{60}Co ; \square , ^{59}Fe ; \triangle , ^{51}Cr .

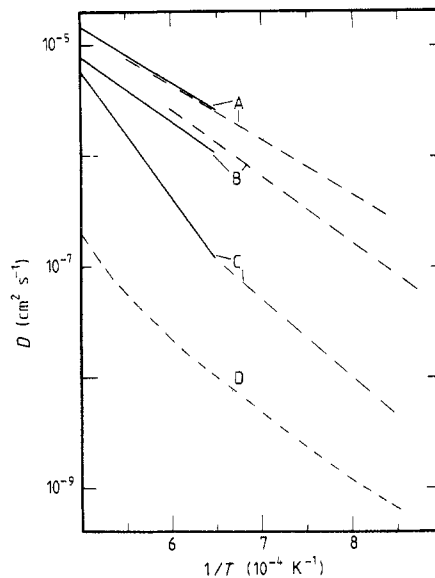


Figure 3. Comparison of the present data (full lines) with the data available in the literature (references [18–23]) (broken lines). lines A, Co; lines B, Fe; lines C, Cr; curve D, Zr self-diffusion.

activation process throughout this temperature range. Furthermore, the low activation energy of 1 eV is indicative of an interstitial mechanism.

The diffusion of Cr in zirconium is more complicated. According to the present data given in equation (5), Cr diffuses with a single activation energy of 2.27 eV at temperatures above 1400 K. However, studies at lower temperatures (less than 1400 K) yielded a significantly lower migration activation energy of 1.4 eV, as shown in figure 3. Normally, one would attribute this behaviour to two diffusion mechanisms, with the transition from one mechanism to the other at 1400 K. The enhanced diffusion at lower temperatures can be a result of short-circuit diffusion via dislocations. It is possible that the introduction of divacancies can also enhance diffusion at very high temperatures. However, when the self-diffusion behaviour of beta zirconium is examined, a more meaningful interpretation is evident. As shown in figure 3, the self-diffusion of β -zirconium exhibits an anomalous behaviour common to many BCC metals. It was found that the activation energy and the pre-exponential factor increased with increasing temperature. In addition, the self-diffusion process in zirconium has been established to occur by a vacancy mechanism. For many years, attempts have been made to explain this anomalous phenomenon by invoking divacancies, dislocations, etc. The most widely accepted explanation is that by Sanchez and de Fontaine [24] which attributes the lower apparent activation energy at lower temperatures to enhanced vacancy migration by phonon-induced displacive fluctuations (ω embryo). Later, Herzig [25] examined and confirmed this behaviour using ZrNb alloys. Federer and Lundy [18] have also examined the diffusion of ^{95}Nb in β -zirconium and they found similar anomalous behaviour in the Arrhenius plot. A comparison between the zirconium self-diffusion curve with the Cr diffusion curve suggests that the same mechanism may be operating in both cases. This would imply that Cr diffusion is also enhanced by the softer [111] phonon mode of the

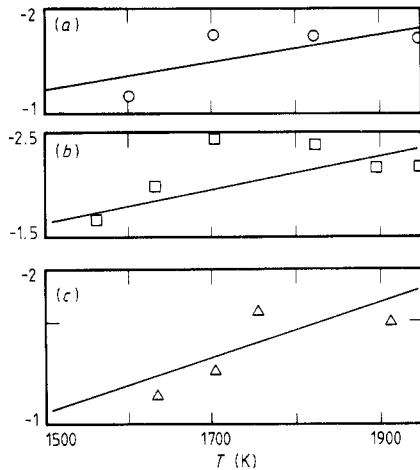


Figure 4. Effective valence Z^* of (a) Co, (b) Fe and (c) Cr in β -zirconium over the temperature range investigated.

ω embryo at low temperatures and that Cr diffuses by a vacancy mechanism and not by an interstitial one. The hypothesis that Cr diffuses by vacancy exchange is supported by its higher activation energy and lower diffusivity in β -zirconium compared with Fe and Co. In an earlier study on the diffusion of Sn and Ti in zirconium [26] over the same temperature range as that used in the present study, it was found that these two solutes diffused substitutionally with activation energies of 2.2 and 2.7 eV, respectively. These values are very similar to the 2.27 eV observed in the present Cr diffusion results.

The other parameter that can be extracted from this electrotransport study is the velocity of the solute under the applied field. This velocity, v , is related to the field intensity of the applied electric field, the effective valence and the mobility of the ions as discussed earlier in equations (1) and (4). These parameters are tabulated in table 1. To isolate the electrotransport behaviour from the kinetic contribution (mobility or diffusion), it is instructive to consider the effective valence, Z^* . The Z^* values obtained in this study are all negative. This means that the ions are all driven towards the anode (positive terminal), and is indicative of momentum transfer from the conduction electrons. This is expected, since zirconium is an electron conduction metal. Figure 4 shows the dependence of Z^* on temperature for the three solutes. It appears that the magnitude of Z^* increases with temperature due to increasing electron scattering with the solute atoms. Unfortunately, the relatively large scatter of the data prevents any quantitative analysis of the result. The scatter in the data is largely due to the fact that the Z^* values are obtained using the experimentally measured values of D and v and this process compounds the experimental error. Nevertheless, the similarity between the Z^* from the three types of solutes suggests that the electrotransport driving force which the diffusing ions experience is independent of the nature of the diffusion mechanism, that is whether the ions diffuse interstitially or by vacancy exchange. An estimate of the true valence of these three solutes can be made by extrapolating the Z^* values to low temperatures where momentum transfer from the conduction electrons (that is the wind force) is negligible. Performing such extrapolations on the data presented in figure 4 gives the true valencies of the three solute involved to be positive with magnitudes of near unity.

Schmidt *et al* [27] have studied the electrotransport response of oxygen, nitrogen and carbon in zirconium at 1898 K, 1973 K and 2073 K, using a diffusion couple method.

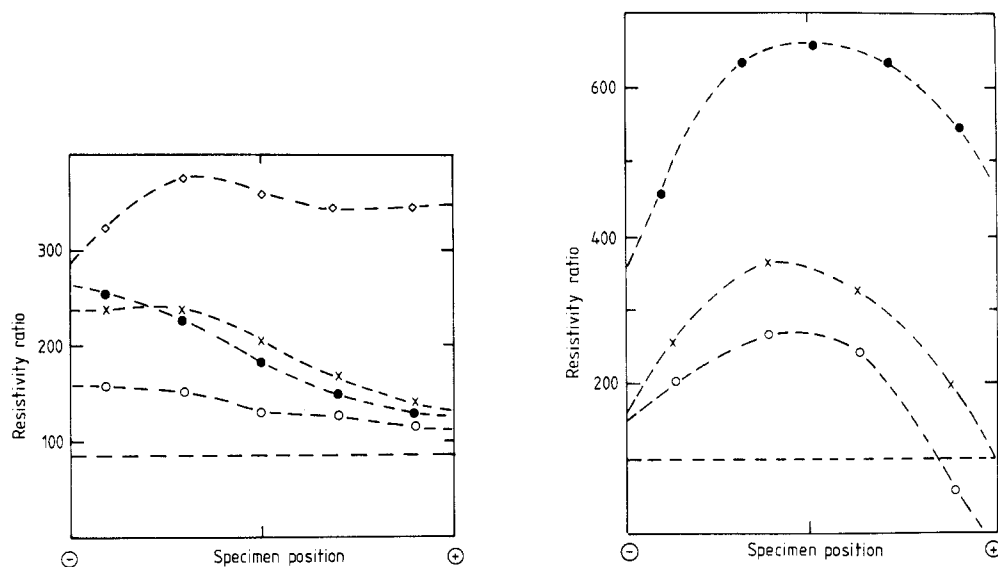


Figure 5. Electrotransport purification results of zirconium showing resistivity ratio. (a) Using zirconium adaptors \diamond , 1875 K, 720 h; \times , 1675 K, 100 h; \bullet , 1725 K, 160 h; \circ , 1825 K, 120 h. (b) Using tantalum adaptors \bullet , 1875 K, 1000 h; \times , 1850 K, 2000 h; \circ , 1900 K, 1100 h. In both parts, the broken horizontal line indicates the ratio for the starting material. The signs \oplus and \ominus indicate anode and cathode respectively.

Their diffusion profiles were fitted by an error function. They observed that all three solutes diffused rapidly, the fastest being oxygen followed by nitrogen and then carbon. At 1973 K, the diffusion coefficients for oxygen, nitrogen and carbon were determined to be 3×10^{-5} , 5.4×10^{-6} and 5×10^{-6} $\text{cm}^2 \text{s}^{-1}$, respectively. These values are similar to the diffusivity of the three metallic impurities examined in this investigation. In the same study, it was also found [27] that the effective charge for oxygen, nitrogen and carbon in zirconium ranges from zero to -1.9 .

Electrotransport has been seriously considered to be an effective means for purifying metals. The transport data obtained here and in [27] provide the parameters necessary to calculate the effectiveness of removing the six solutes from zirconium. Data indicate that at 1973 K, the velocities of cobalt, iron, chromium, oxygen and nitrogen are 3.2×10^{-5} , 2.2×10^{-5} , 0.9×10^{-5} , 3.2×10^{-5} and 0.8×10^{-5} cm s^{-1} , respectively. These values were calculated using equation (4).

Results here imply that for a specimen of length 1 cm, it takes approximately one day to drive these three fast-diffusing solutes from the cathode to the anode. Furthermore, the high transport velocities of the three metallic impurities investigated indicate that this transport process is not limited to removing gaseous elements in zirconium, but is also capable of removing the three metallic solutes.

Figures 5(a) and 5(b) show the results of a joint study between Chalk River Nuclear Laboratories in Canada and the Ames Laboratory (Ames, Iowa) in examining electrotransport purification of zirconium [28]. The resistivity ratio is a simple method for determining the overall impurity level. This ratio is proportional to the overall purity of the materials; that is, a higher ratio value indicates a higher purity metal. Data presented in figure 5(a) were obtained from specimens with zirconium adaptors; those in figure 5(b) were from specimens using tantalum adaptors. The shape of the curves in the former

is as anticipated where resistivity values (purity) are higher in the cathode region indicating a transport of impurities towards the anode (negative Z^*). The species being removed are most likely the six 'fast' solutes (O, N, C, Co, Fe and Cr). Carbon, nitrogen and oxygen are known to migrate against the flow of electrons in tantalum [29, 30]. Therefore the use of a tantalum adaptor should have reduced the release of these impurities from the cathode end resulting in an increase in the resistivity ratio there. However, as shown in figure 5(b), the use of tantalum adaptors actually resulted in a contamination at the cathode. There is a significant difference between the two groups of specimens purified. Those presented in figure 5(a) were purified for shorter times compared with those in figure 5(b). Some slower-diffusing solutes (or impurities) may have positive effect valences. The transport movement of these slower species may not be significant at short times. However, at longer purification times, these slower solutes with positive valence values will be transported towards the cathode thus reducing the resistivity ratio there as shown in figure 5(b).

4. Conclusions

(i) The electrotransport behaviour of Co, Fe and Cr in zirconium was determined from 1557 K to 1950 K using a radioactive tracer technique. It was found that these three solutes migrate toward the anode (i.e. possess negative effective valence) as expected for electron conducting materials. The magnitude of this valence increased with the increasing temperature due to higher momentum transfer from the conduction electrons.

(ii) The diffusion coefficients of the three solutes were determined in the temperature range investigated. Results confirm that Co and Fe diffuse interstitially in the entire β -range with temperature-independent activation energies of 1.00 and 1.15 eV, respectively.

(iii) The diffusion of Cr exhibited anomalous behaviour similar to that observed in the self-diffusion behavior in β -zirconium. It was proposed that Cr diffuses by a vacancy mechanism and enhancement due to the soft-phonon contribution of the ω -phase must be considered. This is supported by the higher activation energy for diffusion observed for Cr compared with Co and Fe.

(iv) The available data on zirconium purified by electrotransport was examined in the light of the present findings. It appears that more slowly diffusing species exist, which may have positive Z^* values.

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