Note

Comments on the Role of Yttria in Gettering Sulfur in the “Y₂O₃ Dispersion Effect on Al₂O₃ Protective Coating Examined on the Basis of Five Models”

1. Introduction

We have followed with interest the work of Ikeda *et al.*¹⁾ published in this journal on the effect of yttria dispersions on the suppression of sulfur segregation to the oxide metal interface in a variety of commercial alloys. We feel we should take issue with some of the comments made by these authors with respect to the potential phases responsible for the gettering of sulfur, and in particular the comments made with respect to the formation of oxysulfide compounds by yttria. We would direct attention to the considerable work done by Gschneidner *et al.*²⁾ and, Kay and coworkers^{3–5)} on the effect of rare earth additions during steel making. We would also direct attention to the work of Seybolt,⁶⁾ who considered the thermodynamic feasibility of the formation of the oxysulfides. In our work⁷⁾ we have re-examined these issues and are satisfied that under the conditions where the rare earth reacts with sulfur in the presence of excess chromium, the most likely reaction product is the rare earth oxysulfide.

In order to validate our assertions we have included some experimental observations of these species under the conditions outlined below.

2. Experimental

Approximately 150 g of high purity Ni pellets, Cr flakes and Y metal were weighed in appropriate proportions and melted in the conventional arc melting furnace under argon atmosphere, to make an alloy of the nominal composition Ni–25wt%Cr–0.1wt%Y. The alloy was then homogenized at 1373 K in vacuum for a period of 48 hr. Coupons measuring approximately 5 × 5 × 1 mm were cut from the homogenized alloy and polished to 1 μm finish for further examination. Few coupons were oxidized in air at 1273 K for a period of 1–2 min. The specimen from the as-homogenized alloy was kept in a Pt cage and left in the iodine-methanol (100 g iodine in 1000 ml anhydrous methanol) solution for a period of 48 hr for the dissolution of the metal. The residue left in the Pt cage after the dissolution of the specimen was flushed

with anhydrous methanol in a dish and collected on a carbon coated copper grid. The same procedure was carried out on the oxidized specimen and the stripped oxide film was collected on a folding type copper grid. This method has been used by other researchers for identification of the oxides⁸⁾ and for stripping⁹⁾ the oxide films formed on the surface of metals during high temperature exposure. The copper grids were then subsequently observed in the scanning/transmission electron microscope (STEM/TEM) fitted with a beryllium window energy dispersive X-ray (EDX) detector, capable of detecting sodium and elements higher in atomic number than sodium. The operating voltage used was 200 kV. Diffraction patterns were taken from 3–5 poles from each particle, and the patterns were analyzed using the computer program Desktop MicroscopistTM. No attempt was made to carry out convergent beam electron diffraction (CBED) analysis.

3. Results

Table 1 gives the chemical composition of the homogenized alloy. The chemical analysis was carried out by glow discharge mass spectroscopy technique (GDMS) by Charles Evans & Associates, California. Since only Ni and Cr were melted during the preparation of the alloy, all the other elements present in the alloy were either present as impurities in the starting materials or were picked up during the melting process. **Figures 1(a)** and **1(b)** show the bright field image and the EDX spectra obtained from a yttrium-sulfur-oxygen rich particle from the unoxidized alloy. The Cu peaks in the spectra are from the Cu grid on which the yttrium-sulfur-oxygen rich particles were collected. From the diffraction patterns taken from this particle, it was identified^{10,11)} as yttrium oxysulfide (Y₂O₂S) with a trigonal crystal structure space group 164, P $\bar{3}$ m1 ($a=3.78$ Å, $c=6.57$ Å). The [1123] zero order laue zone (ZOLZ) and the higher order laue zone (HOLZ) diffraction patterns taken from this particle are shown in **Figures 1(c)** and **1(d)** respectively. Similar patterns were also taken from the yttrium-sulfur-oxygen rich particles in the oxide scale. They were also identified as Y₂O₂S.

4. Discussion

Ikeda *et al.*¹⁾ had investigated the effect of dispersion of Y₂O₃ in a variety of alloys, and reported the existence

Table 1. Chemical composition of the homogenized alloy. All the figures are in ppmw except for Ni and Cr which are in wt%.

Element	C	O	S	Al	Si	Fe	Co	Cu	Ni	Cr	Y
Ni31Cr–0.1Y	55	71	220	15	170	120	430	23	63%	31%	900

Fig. 1. (a) bright field image of a Y-S-O rich particle, (b) EDX spectra obtained from the Y-S-O rich particle, (c) $[1123]$ ZOLZ and (d) $[1123]$ HOLZ diffraction pattern taken from the Y-S-O rich particle which was identified as Y_2O_2S with a trigonal crystal structure.

of sulfur containing dispersoid particles in the alloy, but they were unable to identify the particles. In addition, they discounted the formation of an oxysulfide on the thermodynamic grounds. However, information on the thermodynamic stability of rare earth oxysulfides is available from the work of Gschneidner *et al.*²¹⁾ and Kay and co-workers.³⁻⁵⁾ Table 2 gives the standard free energy change of formation of various RE-oxides, RE-oxysulfide and RE-sulfide. It can be seen from this table that the difference in the standard free energy change of formation/mol of the RE oxide compared with RE oxysulfide at 1273 K is less than 100 kJ less negative. This difference in the case of yttria, Y_2O_3 , and Y_2O_2S is also less than 100 kJ/mol (at 1273 K, $\Delta G^\circ = -1559.93$ kJ/mol for Y_2O_3 and $\Delta G^\circ = -1465$ kJ/mol for Y_2O_2S).²⁾ This difference is very small compared with the standard free energy change of formation/mol of the oxide and the oxysulfide. Moreover, since the standard free energy change of formation of the RE-sulfide type compounds at 1273 K is much less negative than that of the RE-oxide or the RE-oxysulfide, it is quite likely that in the presence of sulfur a RE-oxide may turn into a RE-oxysulfide, but not into a RE-sulfide.

Seybolt⁶⁾ had also reported the formation of oxysulfide species in CeO_2 , La_2O_3 and Gd_2O_3 containing Ni-Cr

Table 2. Standard free energy change of formation of some reactive element compounds.^{2,4)}

Compound	ΔG° at 1273 K (cal/mol)	ΔG° at 2000 K (cal/mol)	ΔG° at 1273 K (J/mol)	ΔG° at 2000 K (J/mol)
$Ce_2O_3(s)$	-341 603	-293 621	-1 430 223	-1 229 332
$Ce_2O_2S(s)$	-327 985	-280 730	-1 373 208	-1 175 360
$La_2O_3(s)$	-342 091	-292 655	-1 432 267	-1 225 288
$La_2O_2S(s)$	-324 955	-277 700	-1 360 522	-1 162 674
$Y_2O_3(s)$	-372 582	-318 760	-1 559 926	-1 334 584
$Y_2O_2S(s)$	-349 909	-279 800	-1 465 001	-1 171 466
$CeS(s)$	-100 782	-82 680	-421 954	-346 165
$Ce_2S_3(s)$	-254 412	-199 160	-1 065 172	-833 843
$LaS(s)$	-91 043	-72 650	-381 179	-304 171
$YS(s)$	-94 840	-75 320	-397 076	-315 349

alloys. Following the analysis proposed by Seybolt⁶⁾ consider the reaction given below, which may be applicable to any RE-oxide.

Standard free energy change of formation/mol nearest 1 kJ at 1200 K are,^{2,6)}

Reactants	Products
Y_2O_3 , -1 560 kJ	Y_2O_2S , -1 457 kJ
$S_{(in\ alloy)}$, X kJ	Cr_2O_3 , -829 kJ
$Cr_{(in\ alloy)}$, -16 kJ	

For reaction (1) above to be in equilibrium, the value of X i.e. the standard free energy change associated with the solution of sulfur in the alloy at 1 200 K would have to be -162.66 kJ/mol S. This value is much more negative than $\Delta G_f^\circ = -134$ kJ/mol at 1 200 K for CrS, a very stable sulfide.⁶⁾ It is therefore likely that sulfur would not be present as free sulfur in the alloy, but as a stable sulfide. In such a situation the value of X would be more positive than -162.66 kJ/mol S, in which case the reaction (1) above would proceed spontaneously. We have also confirmed this observation in our work on lanthanum and cerium containing Ni-base chromia forming alloys. This has been reported elsewhere.⁷⁾

5. Conclusions

Based on the thermodynamic stability of the reactive element oxysulfides and our observation of this species in both the alloy and in the oxide scale formed on the alloy oxidized at 1 273 K, yttrium or yttria in the alloy would be expected to tie up sulfur in the alloy and form yttrium oxysulfide, Y_2O_2S , which has a trigonal crystal structure space group 164, $P\bar{3}m1$.

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