LETTERS TO THE EDITORS

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Occurrence of the Meta-stable Omega Phase in Zirconium Alloys

TRANSFORMATION of the retained β -phase in certain titanium alloys has been shown to involve a meta-stable phase, designated, ω . A similar mode of transformation has been reported for zirconium-niobium and zirconium-molybdenum alloys (Miodownik, A. P., and Elias, W., unpublished work, 1955, and ref. 2).

An extensive survey of the occurrence of the ω -phase in zirconium alloys is being carried out in these laboratories. The results to date indicate the occurrence of the ω -phase in the following alloys: zirconium-50 at. per cent titanium, zirconium-7 at. per cent vanadium, zirconium-13 at. per cent vanadium, zirconium-4.5 at. per cent chromium, and zirconium-10 at. per cent niobium. All the samples were either water- or argon-quenched from the single-phase β -region. The intensities of the X-ray diffractions have been noted to change with ageing time, indicating progressive transformation at the two ageing temperatures studied, namely, 300° C. and 400° C.

The present results are consistent with the hexagonal crystal structure of the ω precipitate first reported by Silcock *et al.*³ for the titanium-vanadium system. However, the 'ideal' axial ratio of 0.613 has not been observed. All β quenched alloys after ageing 3-4 hr. give a value of c/a equal to 0.622 ± 0.002 . It is therefore not possible to interpret the ω lattice in zirconium alloys as cubic with three times the β -lattice parameter.

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¹ Frost, P. D., Perris, W. M., Hirsch, L. L., Doig, J. R., and Schwartz, C. M., *Trans. Amer. Soc. Metals*, **46**, 231, 255, 1056, 1073 (1954).

² Robinson, H. A., Doig, J. R., Mote, M. N., Schwartz, C. M., and Frost, P. D., *J. Metals*, **8**, 1544, 1545 (1956).

³ Silcock, J. M., Davies, M. H., and Hardy, H. K., *Inst. of Metals Monograph and Report Series No. 13*, 93, 105 (1955).

Some Properties of Chromium deposited from an Electrolyte containing Fluoride

It is well established that high-purity chromium can be produced by electrolysis of an aqueous solution of chromic acid containing a small sulphate addition, and that a significant factor governing the purity of such material is the temperature of the electrolyte¹. Oxygen and nitrogen contents of 0.02 and 0.001 weight per cent respectively or better can be attained provided the bath temperature is high, that is, in the vicinity of 80° C. Under optimum conditions the metallic impurity is extremely low.

A considerable disadvantage of this process from certain points of view is the low current efficiency

(6-12 per cent) resulting from the high operating temperature. One method of overcoming this deficiency is to replace the sulphate radical in the bath by fluoride as the active anion catalyst. Thus an aqueous solution containing 300 gm./l. chromic acid (CrO_3) and 5.25 gm./l. fluoride (F), electrolysed at 100-103° C. using a current density of 800 amp./ft.², deposited chromium at a current efficiency of 40-45 per cent for 1-hr. runs in a small-scale apparatus and at 33-35 per cent in somewhat larger equipment. The reason for these greatly improved current efficiencies is not clear.

Oxygen and nitrogen contents of 'fluoride' chromium (0.02-0.05 and 0.002-0.003 weight per cent respectively) deposited under optimum conditions were not greatly different from those of 'sulphate' material. Pick-up of tin to the extent of 0.005 per cent from the 7 per cent tin-lead anode used and of silicon to the extent of 0.036 per cent by etching of the glass container by hydrofluoric acid, occurred in a 7-hr. run. The latter result emphasizes one of the difficulties inherent in the 'fluoride' process, namely, the choice of materials to contain the reactive electrolyte. For large-scale application, and to minimize pick-up of silicon, it would probably be necessary to replace glass vessels by a suitable plastic. The other major difficulty encountered was the necessity to fit the cell with reflux condensers to minimize evaporation losses from the boiling electrolyte.

It was found that 'fluoride' chromium could be arc-cast, extruded, swaged and rolled without difficulty using a similar schedule to that already reported for 'sulphate' material^{2,3}. This being so, it was possible to compare the properties of wrought and of recrystallized samples of each material. Ductile/brittle transition temperatures obtained in slow, three-point bending are presented in Table 1.

Table 1. TRANSITION TEMPERATURES OF 'SULPHATE' AND 'FLUORIDE' CHROMIUM

Material	Composition (weight per cent)		Transition temperature (° C.)	
	Oxygen	Nitrogen	As rolled	Recrystallized
'Sulphate' chromium	—	0.002	-60	380
'Fluoride' chromium	0.012	0.001	—	195
'Fluoride' chromium	0.025	0.002	-87	121

Thus the transition temperature of 'fluoride' chromium is lower than that of 'sulphate' chromium in the wrought, and particularly in the recrystallized, condition. This applies even though the nitrogen content, which has been found previously to have a profound effect on transition temperature³, is higher for the 'fluoride' chromium than for one of the 'sulphate' samples. It is possible that this improved ductility results from an action of the silicon present in modifying the detrimental nitrogen effect, which it is believed may arise either by the formation of Cottrell atmospheres around dislocations or by precipitation in dislocation lines following atmosphere formation³. It is to be expected that such modification by 'nitride-formers' would be more pronounced in recrystallized than in wrought material since high-temperature annealing would provide opportunity for 'nitride-formers' to develop their maximum effect. Nevertheless, even in recrystallized 'fluoride' specimens strength is dependent on temperature, and yield points were detected at temperatures where the material becomes deformed plastically.