Probable Origin of ω-phases in Ti-Zr-Hf alloys Formed by Self-Propagating High-Temperature Synthesis

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Several alloys and deuterides made by self-propagating high-temperature synthesis (SHS) were measured by XRD and neutron powder diffraction. SHS creates alloys by a combustion wave passing through the sample, sustained by its own enthalpy. One series that was of interest was binary alloys of Ti-Zr, which showed considerable amounts of ω-phase material. At room temperature, the stable phase is the hcp α-phase of these metals. ω-phase is occasionally found retained in small proportions in some related alloys, such as CANDU pressure tube materials. It is also the lowest, high-pressure phase seen when pressurizing bcc β-Zr and Ti. This β-ω transition is displacive and non-quenchable. All bcc metals show a dip in the phonon dispersion curve at the point in k-space where this incipient soft mode exists. The α-ω transition is often described as martensitic. Therefore, the presence of ω-phase in these samples in large quantities is surprising. The ω-phase has two strongly related structures: an "ideal" hexagonal structure, and a slightly more distorted trigonal structure.

One explanation, put forward is that the unusual phases in these alloys are due to the unique processing method of SHS, with its rapid rise and fall of temperatures. The SHS cycle used to produce these alloys involves a hydriding and dehydriding step in their production. The hydriding of the metals is designed to remove oxygen from the free surfaces.

Part of the work performed was diffraction work on the alloys and deuterides made by this method. While XRD and NPD of the Ti powder revealed no oxide, although some retained hydride, measurements on the Zr powder showed a considerable number of extra peaks, many of which were described by α-ZrO_2 (baddelyite). Much of this oxide is probably on the surface of the Zr powder. Other peaks were also present that were not identified that were probably suboxides. Ignoring the suboxides, taking just the Zr (conservatively assuming no O-solution) and α-ZrO_2 the Zr:O ratio was 1:0.06.

A sample of $ZrD_{1.9}$ was also supplied. This showed no residual Zr, but in addition to the deuteride phase, ZrO_2 remained. This showed that hydriding was not efficient at removing oxygen from the surface of Zr. Refinements yielded the Zr:D:O ratio, assuming conservatively no O in the deuteride, was 1:1.9:0.1.

Samples of alloys Ti_2Zr and TiZr were also examined. Both showed considerable amounts of ω-phase (65 wt% and 78 wt% respectively). The X-ray pattern fits reasonably well to a phase assemblage of α and ω structured alloy. One general feature of the neutron pattern is that overall it is very weak (Fig. 1). This is because the scattering lengths of Ti and Zr are of opposite sign, $b_{Ti} = -3.37$ fm, $b_{Zr} = 7.16$ fm, so that for certain compositions of atomic sites ($Ti_{0.68}$, $Zr_{0.32}$), the mean scattering length is near 0, and the contribution to a Bragg peak from that site becomes zero, and for a phase like the α-phase with only one site, it becomes nearly invisible: a null-scattering alloy. However, attempts to fit the neutron powder pattern failed with systematic errors in certain peaks of the ω-phase. The ω-structure is simple, there are a limited number of adjustable parameters and these were insufficient to fit the pattern. No improvement was found by switching to the trigonal description of the ω-phase. A difference Fourier map was calculated, which found significant missing scatterers with positive scattering lengths in the octahedral interstices (Fig. 2). Typical interstitial elements include N, C, O. The likeliest interstitial is the O inherited from the ZrO_2.

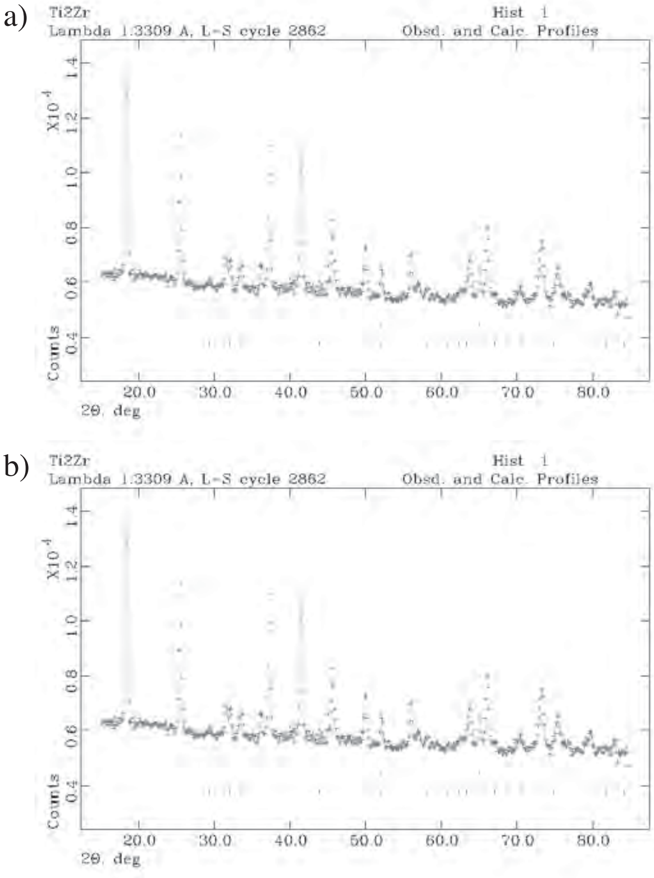

Fig 1. a) Ti_2Zr fitted assuming α and ω alloy structures. Note significant systematic differences. b) "Ti_2Zr" fitted assuming α and "ω(O)". Note significant improvement in fit.

Subsequently, it was found in the literature that there exists an oxide Ti_2ZrO that forms at the interface between Ti and ZrO_2-Zr [2-3]. The structure of this oxide is exactly the same as that of the alloy, but with an O atom sitting with 1/3 occupancy in the octahedral interstice: there are no new diffraction peaks, and in a X-ray powder diffraction pattern, the modification to the structure factors from the O atom is negligible, so that the X-ray pattern from the "ω(O)" Ti_2ZrO oxide and that of ω-Ti_2Zr is almost identical. However, since the neutron scattering length of O is quite large (b_O = 5.80 fm) with respect to Zr and Ti, the presence of O in the interstitial site would be quite visible, even when it is far from nonstoichiometric. The improvements to the fit from the addition of the small amount of O to the ω-phase are quite radical (Fig. 1).

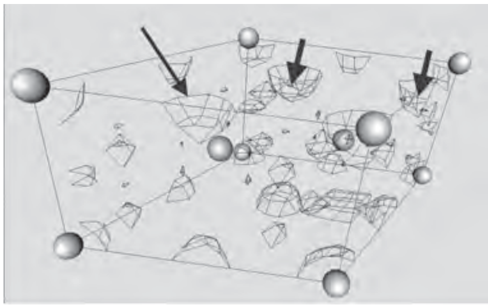

Fig 2. The difference Fourier map, generated from the fit to Fig 1a. Note the significant missing scatterers at {½, ½, 0}.

Initial refinements that are unconstrained with regard to composition yielded the results in Table 1.

Table 1: Results of preliminary, unconstrained refinements on Ti-Zr alloys

ω-phase *P6/mmm*					"Ti_2Zr" a = 4.8017(2)Å c = 3.0108(2)Å ~65 wt%			"TiZr" a = 4.8649(5)Å, c = 3.0466(4)Å ~78 wt%		
Site	*x*	*y*	*z*	*m*	Frac Zr	Frac Ti	Frac O	Frac Zr	Frac Ti	Frac O
a	0	0	0	1	0.801(10)	0.197(10)		0.859(16)	0.141(16)	
d	2/3	1/3	1/2	2	0.167(5)	0.833(5)		0.325(2)	0.675(2)	
f	1/2	1/2	0	3			0.152(4)			0.126(4)

α-phase *$P6_3/mmc$*					"Ti_2Zr" a = 3.0288(3) Å c = 4.8159(9) Å ~35 wt%		"TiZr" a = 3.088(7) Å c = 4.864(3) Å ~22 wt%	
Site	*x*	*y*	*z*	*m*	Frac Zr	Frac Ti	Frac Zr	Frac Ti
c	2/3	1/3	1/4	2	0.427(5)	0.573(5)	0.393(15)	0.607(15)

m = multiplicity; frac = fractional occupancy

There is very strong site ordering in the ω-phase refinement, with Zr preferring the A-site. This has been noted before as characteristic of ω-phase alloys [1]. This contrasts strongly to the solid solution of the α-phase. The occupancy of the octahedral site, Wyckoff site f, assuming O as the only interstitial is similar for both compositions. The composition of the "ω-phase" of "Ti_2Zr" and "TiZr" is $MO_{0.15}$ and $MO_{0.13}$, where M = Ti + Zr.

Conclusions

The interpretation from the neutron diffraction data is that the O is not removed by the hydriding/dehydriding cycle of SHS, but rather either retained as oxides or driven into solution in these alloys and their hydrides. In the case of Ti-Zr alloys, where the neutron structure factors are generally small, neutron diffraction is especially sensitive to the presence of O. In this interpretation, the retained "ω-phase" is not a pure alloy, but a non-stoichiometric suboxide of Ti-Zr. We are awaiting direct measurements from a LECO detector to test this hypothesis.

A recent study looking at the inhibition of the α→ω transition has shown that the presence of interstitials in the octahedral, *3f*-site strongly increases the activation energy for the transformation, causing the α-phase to be retained to higher pressures. The activation barrier along the reaction coordinate α-ω is basically symmetric and is the likely reason why ω(O) is retained in large quantities.

References

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