Stable ordered structures of binary technetium alloys from first principles

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Technetium, element 43, is the only radioactive transition metal. It occurs naturally on earth in only trace amounts. Experimental investigation of its possible compounds is thus inherently difficult and limited. Half of the Tc-transition-metal systems (14 out of 28) are reported to be phase separating or lack experimental data. Using high-throughput first-principles calculations, we present a comprehensive investigation of the binary alloys of technetium with the transition metals. The calculations predict stable, ordered structures in nine of these 14 binary systems. They also predict additional compounds in all nine known compound-forming systems and in two of the five systems reported with disordered χ or σ phases. These results accentuate the incompleteness of the current knowledge of technetium alloys and should guide experimental studies to obtain accurate structural information on potential compounds, obviating some of the difficulties associated with such work.

Technetium, the only radioactive transition metal, occurs mainly in spent nuclear fuel. The practical difficulties of working with a radioactive rare material have so far hampered studies of technetium solid-state physics and chemistry. In particular, the exploration of technetium-based alloys has been very limited. The available experimental data indicate that 14 of the 28 Tc-transition-metal binary systems are non-compound-forming.[1,2] These systems are concentrated in columns IB, IIB, VIIB, and VIIIB of the periodic table. The exceptions in these columns are Zn, reported to form two compounds with Tc; Mn, reported with a disordered σ phase; and Fe, which forms one compound and a σ phase. Four additional systems, Nb and the column VIB systems, are reported with a disordered σ phase. The seven remaining binary systems of Tc with the transition metals of columns IIIB–VB are reported to be compound forming.

Recent interest in Tc alloys has been twofold. One motivation is the systematic basic research of fourth-row transition-metal alloys which might provide insight into the existence of general trends in material properties. Such an example is the recent surprising discovery that $SrTcO_3$ differs greatly from its strontium-metal-oxide neighbors, strontium molybdate and ruthenate. It turns out to be antiferromagnetic with the highest ordering temperature, roughly 1000 K, obtained in a material without a third-row transition metal whereas $SrMoO_3$ is paramagnetic with one of the highest conductivities of the metal oxides and $SrRuO_3$ is a metallic ferromagnet with a transition temperature around 160 K.[3] Another motivation for Tc-alloy investigation is the search for potential candidates for long-term nuclear-waste disposal in geological repositories by immobilization of Tc-containing residues.[4] This requires detailed knowledge of the synthesis and properties of Tc alloys. Recent studies of Tc-Zr alloys[5] and Tc deposition on gold[6] have been carried out with this purpose in mind.

First-principles calculations based on density functional theory (DFT) provide the theoretical means to complement lacking empirical data, especially in cases where experiments are difficult. Several results on technetium and technetium alloys have been published using this approach. The zero-temperature equation of state and elastic constants of pure Tc have been calculated in a study of bcc, fcc, and hcp structures of 76 elements,[7] and the stabilities of several more complex structures have been explored in a similar work.[8] These studies verify the stability of the hcp structure for elemental Tc. A few comparative studies of technetium carbides and borides, and those of other transition metals, were aimed at revealing the origin of the well-known superhardness of the corresponding tungsten structures.[9–11] It was found that the Tc compounds are also potential high-hardness materials. A similar study compared the properties of transition-metal mononitrides.[12]

In this Brief Report we present a comprehensive investigation of the binary alloys of technetium with the transition metals using high-throughput first-principles calculations. High-throughput calculations of material properties based on DFT have acquired an increasing role in recent years as an important tool for rational materials development.[13–17] They can be used to explore the phase-stability landscape of binary alloys by calculating the formation enthalpies of a large number of structures, identifying the minima at various component concentrations. These calculations can indicate the possible existence of hitherto unidentified compounds and metastable structures and their characteristics. A previous study, using this approach, reported on 12 of the Tc-transition-metal binary systems as part of a larger review of 80 binary alloys aimed at verifying the accuracy of this method.[13] The current work covers all the Tc-transition-metal alloys using projector-augmented-wave pseudopotentials[18] and the generalized gradient approximation (GGA) exchange-correlation functionals parametrized by Perdew, Burke and Ernzerhof[19] versus ultrasoft pseudopotentials and local-density-approximation exchange-correlation functionals used in Ref. 13 and a more extensive structure database. It uncovers additional ordered structures in a few of the systems discussed in Ref. 13 and in additional ones where experimental data is scarce and difficult to obtain.

The calculations were performed with the high-throughput framework AFLOW[13,20] based on *ab initio* calculations of the energies by the VASP software.[21] The energies were

calculated at zero temperature and pressure with spin polarization and without zero-point motion or lattice vibrations. All crystal structures were fully relaxed (cell volume and shape and the basis-atom coordinates inside the cell). Numerical convergence to about 1 meV/atom was ensured by a high energy cutoff (30% higher than the highest energy cutoff for the pseudopotentials of the components) and dense 6000 **k**-point Monkhorst-Pack meshes.[22] Geometrical descriptions and calculated energies of the structures are listed in the supplemental material; see Ref. 23.

For each system, we calculated the energies of all the reported crystal structures[1,2] and approximately 230 additional structures from the AFLOW prototype database,[20] listed in Ref. 24. This protocol, involving searching many enumerated derivative structures and exhaustively exploring experimentally reported structures, is expected to give a reasonable balance between high-throughput speed and scientific accuracy to determine miscibility or the lack thereof in Tc alloys (a detailed discussion on the reliability of the method appeared in Refs. 13 and 25). In Ref. 13, it was shown that the probability of reproducing the correct ground state, if well defined and not ambiguous, is $\eta_C^\star \sim 96.7\%$ ["reliability of the method," Eq. (3)]. However, the existence of additional unexpected ground states among unexplored structures cannot be ruled out.

The calculations reveal stable structures both in systems known to order and those thought to be phase separating. We show that nine of the 14 technetium binary intermetallic systems reported as phase separating in the experimental literature[1,2] actually exhibit ordering tendencies, forming stable compounds at low temperatures (Fig. 1). Specifically, we find additional stable structures in four systems already predicted to be ordering in Ref. 13, Rh-Tc, Ru-Tc, Pt-Tc, and Pd-Tc. The discrepancies between the current predictions and those of Ref. 13, e.g., the indication of $Tc_{24}Ti_5$ and $Tc_{24}Zr_5$ compounds, arise from the larger structure database scanned in this study. We also predict stable structures in addition to those reported in all nine binary systems known from experiments to be compound forming and in one of the three systems exhibiting a disordered σ phase, Mn-Tc.[1,2]

The results are summarized in Table I. In the first column, the 28 alloying metals are ordered according to their Mendeleev numbers (or Pettifor's chemical scale).[29] The next three columns indicate whether the corresponding binary system is phase separating or compound forming, according to the experimental data and to *ab initio* calculations reported here and in a previous study.[13]

The Pettifor scale is the most successful attempt to date to enable prediction of whether a proposed system would be compound forming or not and the structure of the expected compounds, based on a single material parameter.[30] Structure maps based on this scale separate well between various reported structures and thus provide a relatively high degree of predictive insight.[29] However, the maps are purely empirical, and their predictive power is limited by the availability of reliable experimental data. (An assessment of the unsatisfactory current situation in this respect is given in Ref. 30.) It is thus important to complement the sparsity of relevant experimental data with *ab initio* total-energy assessments of the competing candidate structures as we do
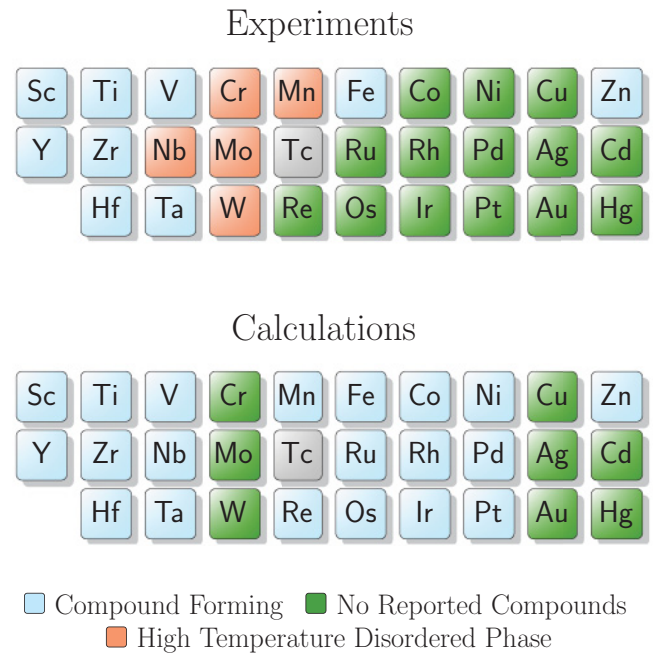

FIG. 1. (Color online) The phase-separating or compound-forming characteristics of 28 Tc-transition-metal-alloy systems as found in experiments and in *ab initio* calculations.

in this Brief Report. Ordered by this scale, Table I is divided into three parts with different experimental phase-formation characteristics. The top (systems Tc-Y to Tc-V) is occupied almost exclusively by compound-forming systems, except Nb-Tc, which is reported with a disordered χ phase. The lower part (Os-Tc and below) is almost exclusively occupied by phase-separating systems, except one compound-forming system at the bottom, Tc-Zn. The middle part is a border zone of six systems (Mo-Tc to Fe-Tc), four of which exhibit a disordered σ phase; Fe-Tc, reported with a single compound in addition to the σ phase; and Re-Tc, which is phase separating.

The picture emerging from the calculations is considerably different. Ordered structures are predicted in the three lower systems of the middle part, Re-Tc, Mn-Tc, and Fe-Tc, and in the eight upper systems of the lower part, Os-Tc to Pd-Tc, thus predicting a cluster of eleven compound-forming systems in the middle of the table. Stable structures MTc_3 of prototype $D0_{19}$ are found for eight of the nine column VIII transition metals, except Fe. For two of them, Os and Ru, the structure M_3Tc with the same prototype is also stable. Three of the compounds in this cluster, $RuTc_5$, Ir_2Tc, and Rh_2Tc, are predicted with crystal structures that have no known prototype or *Strukturbericht* designation. They were found among the symmetrically distinct fcc-, bcc- and hcp-based superstructures included in the AFLOW database.[13] These structures are described in Table II.

We also find stable, ordered structures for Nb-Tc, indicating a continuous cluster of eight compound-forming systems at the top. Within this cluster, the metals of the VB column order into structure M_2Tc of prototype $C11_b$, and those of the IIIB and IVB columns, except Ti, form a stable structure MTc_2 of prototype C14. Six of these eight systems are reported with the disordered χ phase (*Strukturbericht* A12, space group

TABLE I. Compounds observed in experiments ("Expt.") or predicted by *ab initio* calculations ("Calc.") in Tc binary alloys (structure prototypes in parentheses) and their calculated formation enthalpies ΔH. "Unkn." denotes an unknown prototype. The energy difference between a reported structure (unstable in the calculation) and a two-phase tie line is indicated in square parentheses. A ⋆ denotes unobserved prototypes described in Refs. 13 and 24. A § denotes unobserved prototypes described in Table II. "−" denotes no compounds, and "N/A" denotes no available data.

| Element | Compounds | | | ΔH |
	Expt.[a]	Calc. (Previous)[b]	Calc. (Present)	(meV/atom)
Y	$Tc_2Y(C14)$	$Tc_2Y(C14)$	$Tc_2Y(C14)$	−176
		$TcY_3(D0_{11})$	$TcY_3(D0_{11})$	−86
Sc		N/A	$Sc_3Tc(D0_{11})$	−182
			$Sc_2Tc(C11_b)$	−208
	$ScTc_2(C14)$		$ScTc_2(C14)$	−304
	$Sc_{0.1}Tc_{0.9}(\chi)$		$Sc_5Tc_{24}(Re_{24}Ti_5)$	−189
Zr	$Tc_{0.88}Zr_{0.12}(\chi)$		$Tc_{24}Zr_5(Re_{24}Ti_5)$	−186
	$Tc_2Zr(C14)$	$Tc_2Zr(C14)$	$Tc_2Zr(C14)$	−314
	$TcZr(Unkn.)$	$TcZr(B2)$	$TcZr(B2)$	−356
		$TcZr_2(C49)$	$TcZr_2(C49)$	−271
		$TcZr_4(D1_a)$	$TcZr_4(D1_a)$	−186
Hf		N/A	$Hf_3Tc(Mo_3Ti^\star)$	−269
			$Hf_2Tc(C49)$	−357
	$HfTc(B2)$		$HfTc(B2)$	−482
	$HfTc_2(C14)$		$HfTc_2(C14)$	−362
	$Hf_{0.1}Tc_{0.9}(\chi)$		$Hf_5Tc_{24}(Re_{24}Ti_5)$	−232
Ti	$Tc_{0.9}Ti_{0.1}(\chi)$		$Tc_{24}Ti_5(Re_{24}Ti_5)$	−190
		$Tc_2Ti(C11_b)$		[18]
			$Tc_5Ti_3(Ga_3Pt_5)$	−416
	$TcTi(B2)$	$TcTi(B2)$	$TcTi(B2)$	−492
		$TcTi_2(C49)$	$TcTi_2(C49)$	−376
		$TcTi_3(Mo_3Ti^\star)$	$TcTi_3(Mo_3Ti^\star)$	−298
Nb			$Nb_5Tc(HfPd_5^\star)$	−144
		$Nb_3Tc(Mo_3Ti^\star)$	$Nb_3Tc(Mo_3Ti^\star)$	−213
		$Nb_2Tc(C11_b)$	$Nb_2Tc(C11_b)$	−279
		$NbTc(B2)$	$NbTc(B2)$	−365
	$Nb_{0.15}Tc_{0.85}(\chi)$			[19]
Ta		N/A	$Ta_2Tc(C11_b)$	−388
	$TaTc(B2)$		$TaTc(B2)$	−501
	$Ta_{0.15}Tc_{0.85}(\chi)$			[36]
V	$TcV(B2)$	N/A	$TcV(B2)$	−377
			$TcV_2(C11_b)$	−340
			$TcV_3(Mo_3Ti^\star)$	−266
			$TcV_4(D1_a)$	−218
Mo	$Mo_{1.5}Tc_{2.4}(A15)$	N/A	−	
	$Mo_{0.3}Tc_{0.7}(\sigma)$			
W	$Tc_{0.7}W_{0.3}(\sigma)$	N/A	−	
Cr	$Cr_{0.25}Tc_{0.75}(\sigma)$	N/A	−	
Tc		(reference)		
Re	−	N/A	$ReTc_3(D0_{11})$	−5
Mn	$Mn_{0.4}Tc_{0.6}(\sigma)$	N/A	$Mn_2Tc(C14)$	−94
Fe	$FeTc(B2)$	N/A		[158]
	$Fe_{0.4}Tc_{0.6}(\sigma)$		$FeTc_2(C16)$	−4
Os	−	N/A	$Os_3Tc(D0_{19})$	−71
			$OsTc(B19)$	−83
			$OsTc_3(D0_{19})$	−57
Ru	−	$Ru_3Tc(D0_{19})$	$Ru_3Tc(D0_{19})$	−63
		$RuTc(B19)$	$RuTc(B19)$	−73
		$RuTc_3(D0_{19})$	$RuTc_3(D0_{19})$	−47
			$RuTc_5(RuTc_5^\S)$	−32
Co	−	N/A	$CoTc(B19)$	−46
			$CoTc_3(D0_{19})$	−53

TABLE I. (*Continued*)

Ir	–	N/A	$Ir_8Tc(Pt_8Ti)$	−89
			$Ir_2Tc(Ir_2Tc^\S)$	−224
			$IrTc(B19)$	−287
			$IrTc_3(D0_{19})$	−217
Rh	–	$Rh_2Tc(ZrSi_2)$	$Rh_2Tc(Ir_2Tc^\S)$	−157
		$RhTc(B19)$	$RhTc(B19)$	−175
		$RhTc_3(D0_{19})$	$RhTc_3(D0_{19})$	−158
Ni	–	N/A	$Ni_4Tc(D1_a)$	−30
			$NiTc_3(D0_{19})$	−106
Pt	–	$Pt_3Tc(FCC_{AB3}^{[001]})$	$Pt_3Tc(BCC_{AB3}^{[001]})$	−158
			$Pt_2Tc(CuZr_2)$	−184
		$PtTc_3(D0_{19})$	$PtTc_3(D0_{19})$	−267
Pd	–		$PdTc(RhRu^\star)$	−63
		$PdTc_3(D0_{19})$	$PdTc_3(D0_{19})$	−73
Au	–	–	–	
Ag	–	–	–	
Cu	–	–	–	
Hg	–	–	–	
Cd	–	–	–	
Zn		N/A	$Tc_2Zn(FCC_{AB2}^{[100]})$	−42
			$TcZn_3(L1_2)$	−62
		$TcZn_7(CuPt_7)$	$TcZn_7(CuPt_7)$	−55
		$TcZn_{15}(Unkn.)$		

[a] References [1] and [2].
[b] Reference [13].

$I\bar{4}3m$). In four of them, we find stable structures of prototype $Re_{24}Ti_5$, which is an ordered realization of this phase. This indicates that the χ-phase regime of stability extends to the low-temperature region of these binary-phase diagrams. In the other two systems, Nb-Tc and Ta-Tc, this structure has a higher formation enthalpy than the two-phase-region tie line, indicating decomposition of the χ phase at low temperatures. Experimental studies of the Tc-Zr system report a structure, denoted Tc_6Zr, with the crystallographic characteristics of the χ phase and a wide range of stoichiometries.[5] Our calculations thus identify the prototype and confirm the existence of a corresponding ordered structure at low temperatures. Similar behavior should be expected in the adjacent systems, Sc-Tc, Hf-Tc, and Tc-Ti.

The remaining phase-separating systems form two small groups. One is in the middle of the table with three systems reported with a σ phase and predicted to have no ordered, stable structures. The other, near the bottom, includes five systems

TABLE II. The geometry of prototypes marked by $\S$ in Table I. Atomic positions and unit-cell parameters are fully relaxed.

	$RuTc_5$	Ir_2Tc
Lattice	Monoclinic	Orthorhombic
Space Group (opt.)	Cm No. 8 (2)	$Cmcm$ No. 63
Pearson Symbol	mS12	oS12
HT Lattice	MCLC/MCLC$_1$	ORCC/ORCC
Type/Variation[a]		
Conv. Cell		
a,b,c (Å)	9.997, 2.752, 6.484	2.751, 14.374, 4.381
α,β,γ (°)	90, 75.942, 90	90, 90, 90
Wyckoff Positions[b]	Ru1 0,0, − 0.00140 (2a)	Ir1 0,0.998,1/4 (4c)
	Tc1 0.390,0, − 0.277 (2a)	Ir2 0,0.668,1/4 (4c)
	Tc2 −0.335,0, − 0.331 (2a)	Tc1 0,0.334,1/4 (4c)
	Tc3 0.055,0,0.388 (2a)	
	Tc4 0.334,0,0.334 (2a)	
	Tc5 −0.278,0,0.055 (2a)	
AFLOW Label[c]	"128"	"143"

[a] Reference [26].
[b] References [27] and [28].
[c] Reference [20].

for which both experiments and calculations indicate no compound formation. The Tc-Zn system remains an isolated compound-forming system in the last row of Table I. For this system, the calculations predict two ordered structures, Tc_2Zn and $TcZn_3$, in addition to the observed $TcZn_7$. We find no stable structures in the vicinity of $TcZn_{15}$, reported in experiments with an unidentified prototype.

The almost perfect grouping of systems into four well-defined clusters by their predicted phase-formation characteristics nicely complements the trends indicated by the Pettifor chemical scale. It reverses the ratio of phase-separating to compound-forming systems from the experimental databases.

Empirical data on technetium-alloy properties are incomplete and difficult to obtain due to the radioactivity of the element. Generating such data using *ab initio* electronic-structure calculations is thus of special interest. In this Brief Report, we present results of a computational high-throughput study on phase ordering in Tc alloys that are considerably different from those reported by current experimental data. These theoretical predictions should serve as a guide for future studies of these materials and as the starting point for designing desirable alloys for various potential applications.

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