Chemical partitioning for the Co-Pr system: First-principles, experiments and energetic calculations to investigate the hard magnetic phase

S. H. Zhou^{1,2}, M. J. Kramer^{1,2,3}, F. Q. Meng^{1,2}, R. W. McCallum^{1,2,3}, R. T. Ott^{1,2}

¹The Critical Materials Institute, Ames Laboratory, DOE, USA.

²Division of Materials Sciences and Engineering, Ames Laboratory, USDOE, USA.

³Department of Materials Science and Engineering, Iowa State University
Ames, IA 50011, USA

Abstract

Co₅Pr-D2_d is promising permanent magnet. Due to its peritectic formation feature, there is a synthetic challenge to produce single Co₅Pr-D2_d phase. The object of this study is to assess thermodynamic pathways for crystalline phases under far-from-equilibrium conditions by combining first-principles calculations and experimental measurements into a robust description of the thermodynamic behavior. With the energetic calculations, temperature and time dependent phase selections are predicted under varying degrees of chemical partitioning. Our calculation to assess the chemical partitioning-temperatures indicates that the major magnetic compounds: Co₁₇Pr₂-α, Co₅Pr-D2_d, Co₁₉Pr₅-β, and Co₇Pr₂-χ form from a congruent manner to eutectic reactions with decreasing cooling rate. The compositions of the compounds from these highly driven liquids can be far from equilibrium.

Key: first-principles calculation, energetic calculation, nonequilibrium phase transformation, chemical partitioning, hard magnetic Co₅Pr-D2_d

1. Introduction

Rare earth-cobalt (RE-Co) intermetallics such as Co₅Pr-D2_d [1] have received considerable attention since their discovery due to their interesting phenomena such as spin reorientation, spin compensation and non-collinear sublattice magnetization, but also due to their excellent applicability as high performance permanent magnets in phases with large uniaxial magnetocrystalline anisotropy. In close proximity to the hard magnetic Co₅Pr-D2_d compound are the soft magnetic compounds Co₁₇Pr₂-α, Co₁₉Pr₅-β, Co₇Pr₂-χ, and Co₃Pr-δ. According to the phase diagram, it is difficult to produce pure Co₅Pr-D2_d phase since it forms peritectically with the Co₁₇Pr₂-α as the primary solidification phase[2]. However, rapid solidification can suppress multiple phase formation resulting in a single Co₅Pr-D2_d phase, which can have excellent hard magnetic properties [3]. The investigations by Fuerst et al. [3] revealed that the magnetic field strength of melt spun Co-16 at.%Pr alloy composed of Co₅Pr-D2_d increases with wheel velocity, indicating the possible nonequilibrium phase transformation, i.e., percentage of the Co₅Pr-D2_d phase, increases (approaching 100%) with increasing wheel velocity. Recent, research efforts utilizing both experiments and theoretical calculations have examined new phases synthesis in nonequilibrium phase transformations from different angles such as using nonequilibrium reaction [4], composition effect on critical nucleation [5], critical cooling rate for amorphous formation [6], influence of rapid solidification on microstructure and thermodynamics [7], modeling dendrite growth

under the local nonequilibrium condition [8], nonequilibrium dynamical mean-field theory [9], applying maximal entropy to multi-component stoichiometric compound growth [10], ab initio calculations coupled with the modified mixed-basis cluster expansion method [11], density functional theory phonon calculations [12], high-entropy effects from nonequilibrium to equilibrium [13], the local nonequilibrium effects to the driving force for solidification [14] and structural enthalpy based on the modified Miedema's model [15]. The study of nonequilibrium phenomena has developed into one of the most active and exciting fields for material design, which can provide new insights beyond the equilibrium and theoretical understanding of the physics of phase selection. In our study, we have assessed the thermodynamic pathways for crystalline phases under far-from-equilibrium conditions by combining first-principles calculations and experimental measurements into a robust description of the thermodynamic behavior of undercooled liquids to predict temperature and time dependent phase selection and understand the wheel velocity dependent $\text{Co}_5\text{Pr-D2}_d$ phase formation.

While experimental investigations of phase transformations [16-21], differential thermal analysis (DTA) determined enthalpy of formation for the compound $\text{Co}_2\text{Pr-C15}$ [20], and thermodynamic modeling [2] have been done previously to quantify the phase transformations of the Co-Pr system, a number of inconsistencies remain unresolved. Ray [21] determined the phase diagram using metallography, X-ray diffraction (XRD), DTA, and electron-probe microanalysis (EPMA). The alloys were homogenized for 2-5 days at temperatures 25-100K below the lowest melting phase. The identified phases were $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$, $\text{Co}_5\text{Pr-D2}_d$, $\text{Co}_{19}\text{Pr}_5\text{-}\beta$, $\text{Co}_7\text{Pr}_2\text{-}\chi$, $\text{Co}_3\text{Pr-}\delta$, $\text{Co}_2\text{Pr-C15}$, $\text{Co}_{1.7}\text{Pr}_2$, Co_3Pr_7 , and $\text{CoPr}_3\text{-D0}_{11}$ in which $\text{CoPr}_3\text{-D0}_{11}$ with the Fe_3C prototype [22] melts congruently and the crystal structure of $\text{Co}_{1.7}\text{Pr}_2$ is unknown [21]. Furthermore, the structure and stability of several phases at low temperature remain unclear: (1) the $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ identified as $\text{Zn}_{17}\text{Th}_2$ prototype [17, 23] is different from the $\text{Ni}_{17}\text{Th}_2$ prototype in many Co-rare earth compounds [24]; (2) $\text{Co}_5\text{Pr-D2}_d$ with the CaCu_5 prototype was reported refs [19, 21, 25, 26], but the stability of this phase is in different temperature ranges reported in refs. [19, 21, 25, 26]; (3) $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ was identified with $\text{Co}_{19}\text{Ce}_5$ prototype in Ref. [21, 27, 28]. However, the temperature range over which the phase is stable is different in refs. [21, 27, 28]; (4) The $\text{Co}_7\text{Pr}_2\text{-}\chi$ phase in ref. [16, 27] crystallizes in the hexagonal Ni_7Ce_2 prototype at high-temperature and the rhombohedral Co_7Gd_2 prototype at low-temperature phase. In contrast, Buschow [29] reported that the $\text{Co}_7\text{Pr}_2\text{-}\chi$ compound has Co_7Gd_2 prototype at high-temperature and Ni_7Ce_2 prototype at low-temperature. (5). Wu et al. [30] renamed the $\text{Co}_{1.7}\text{Pr}_2$ as Co_3Pr_4 and proposed that its crystal structure being isostructural with Co_3Nd_4 . Moreau and Paccard [31] studied the Co_3Pr_7 phase and confirmed that the Co_3Pr_7 phase is isostructural with Co_2Sm_5 . In this work, we adopt $\text{Co}_2\text{Pr}_5\text{-}\gamma$ as Co_3Pr_7 name while the stabilities of the $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$, $\text{Co}_5\text{Pr-D2}_d$, $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ and $\text{Co}_7\text{Pr}_2\text{-}\chi$ phases have been investigated.

The most significant difference in invariant reactions between the experimental phase diagrams by Ray [21] and Wu [30] is that of the $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ phase. Ray [21] reported that the $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ phase forms via a peritectic reaction of Co and the liquid

while Wu [30] described $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ as a congruently melting compound. However, there is no clear evidence supporting this conclusion. The most recent assessment of Co-Pr phase equilibria optimized by Du et al. [2] using available thermodynamic and phase boundary data showing the $\text{Co}_{19}\text{Pr}_5\text{-}\beta$, $\text{Co}_7\text{Pr}_2\text{-}\chi$, $\text{Co}_3\text{Pr}\text{-}\delta$, $\text{Co}_2\text{Pr-C15}$, $\text{Co}_{17}\text{Pr}_{20}\text{-}\phi$, $\text{Co}_2\text{Pr}_5\text{-}\gamma$, and $\text{CoPr}_3\text{-D0}_{11}$ being the stable phases at 300K while the decomposition temperatures of the reactions $\text{Co}_{17}\text{Pr}_2\text{-}\alpha \rightarrow \text{Co-fcc} + \text{Co}_5\text{Pr-D2}_d$ and $\text{Co}_2\text{Pr}_5\text{-}\gamma \rightarrow \text{Co-fcc} + \text{Co}_{19}\text{Pr}_5\text{-}\beta$ phases are 1158.5K and 1123.6K.

In the present study, the experimental data by Ray [21] are considered while relative stabilities of the compounds will be further investigated. The enthalpy of formation of the $\text{Co}_2\text{Pr-C15}$ phase [20] was considered. More generally, by incorporating both first principles calculations and experimental results into our semi-empirical approach, we bring clarity to the overall thermodynamic description of this system and further analyze the possible phase transformation far from equilibrium.

2. Approaches

2.1 Experiments and results

Alloy test specimens of Co-x at. % Pr ($x=10.5\text{-}54.0$) were prepared by arc melting pure elements (99.9 Co and 99.99 Pr, wt. % [32]) on a copper hearth in an argon atmosphere. It should be noted that the purity of the Pr was considerably higher than that of previous studies. Each alloy specimen (~15 g) was arc-melted and flipped 5 times to ensure homogeneity, and then drop cast into a 6 mm diameter Cu mold to form rods. The weight loss of the alloy samples during arc melting was less than 0.5%. The as-cast rod was cut in five specimens for different heat treatments and analysis. The specimens for equilibrium measurements were wrapped in tantalum foil and sealed in quartz tubes in an argon atmosphere and quenched into water after heat treatment. Both as-cast and heat treated specimens were characterized using a Panalytical X'Pert XRD with Co-K α radiation operated at 40 kV and 30 mA, scanning electronic microscopy (SEM), EPMA with wavelength dispersive spectroscopy, as shown in Figs. 1-5. Transmission electron microscope (TEM) observation was performed on cross-sections of melt-spun ribbon using FEI Tecnai G²F20-XT transmission electron microscopy operated at 200 kV. Specimens for TEM were prepared by standard mechanical wedge polishing followed by dual-ion beam milling at liquid nitrogen temperature.

The microstructure of the as-cast Co-10.5 at.% Pr alloy is shown in Fig. 1(a) in which three phases were identified with the compositions (0.58, 10.8 and 14.3 at.%Pr). The $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ phase with $\text{Zn}_{17}\text{Th}_2$ prototype is clearly identified from the standard XRD pattern with the lattice parameters $a=8.415\text{\AA}$ and $c=12.170\text{\AA}$ as shown in Fig. 1(b). The Co-hcp structure is also confirmed. The formation of the three phases in as-cast Co-10.5 at.% Pr sample is consistent with a peritectic reaction for the $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ phase.

The Co-16.7 at. % Pr alloy was investigated using EPMA and XRD as shown in Fig. 2. The EPMA analysis for the as-cast specimens reveals a solidification microstructures comprised of the $\text{Co}_5\text{Pr-D2}_d$ (15.8 at.% Pr) and $\text{Co}_7\text{Pr}_2\text{-}\chi$ (21.8 at.% Pr) phases as shown in Fig. 2(a). The $\text{Co}_5\text{Pr-D2}_d$ phase was identified using XRD as shown in Fig. 2(b). After

heat treatment at 1194K for 168 hours, the microstructure (16.4 at.% Pr) in Fig. 2(c) is comprised of the $\text{Co}_5\text{Pr-D2}_d$ phase as identified with XRD in Fig. 2(d). The minor amount

Fig. 1. (a) SEM image showing observed microstructures and (b) the XRD data of the as-cast Co-10.5 at.% Pr alloy.

Fig. 2. (a) SEM images showing observed microstructures and (b) the XRD data of the as-cast Co-16.7 at.% Pr alloy and (c) SEM images showing observed microstructures and (d) the XRD data after heat treating the as-cast Co-16.7 at.% Pr alloy at 1194K for 168 hours, respectively.

of second phase seen in Fig. 2(c) is considered as an unfinished decomposition phase. The $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ is not identified in both as-cast and heat treated Co-16.7 at.% Pr specimens.

Fig. 3. (a) EPMA images showing observed microstructures and (b) the XRD data of the as-cast Co-20.8 at.% Pr alloy and (c) EPMA images showing observed microstructures and (d) the XRD data after heat treating as-cast Co-20.8 at.% Pr alloy at 773K for 336 hours, respectively.

EPMA results for the as-cast Co-20.8 at.% Pr alloy show five compositions possible corresponding to the $\text{Co}_5\text{Pr-D}_{2d}$ (16.3 at.% Pr), $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ (20.7 at.% Pr), $\text{Co}_7\text{Pr}_2\text{-}\chi$ (22 at.% Pr), $\text{Co}_3\text{Pr-}\delta$ (24.5 at.% Pr), and $\text{Co}_2\text{Pr-C15}$ (32.6 at.% Pr) phase shown in Fig. 3(a). The XRD results in Fig. 3(b) indicate the presence of $\text{Co}_5\text{Pr-D}_{2d}$, $\text{Co}_{19}\text{Pr}_5\text{-}\beta$, $\text{Co}_7\text{Pr}_2\text{-}\chi$, and $\text{Co}_3\text{Pr-}\delta$ but no peaks corresponding to the $\text{Co}_2\text{Pr-C15}$ structure were observed. This is consistent with non-equilibrium solidification through a number of cascading peritectics. After heat treatment at 773K for 336 hours, the compositions measured by EPMA did not correspond to those of the $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ and $\text{Co}_2\text{Pr-C15}$ phases. The XRD and EPMA results shown in Fig. 3(c-d) suggest that the $\text{Co}_5\text{Pr-D}_{2d}$ (16.5 at.% Pr), $\text{Co}_7\text{Pr}_2\text{-}\chi$ (22 at.% Pr), and $\text{Co}_3\text{Pr-}\delta$ (23.5 at.% Pr) phases are present in the heat-treated Co-20.8 at. % Pr alloy. As three solid phases is not an allowable equilibrium condition in a binary phase diagram at more than a single temperature, we conclude that the $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ phase is less stable with respect to $\text{Co}_5\text{Pr-D}_{2d}$, $\text{Co}_3\text{Pr-}\delta$ and $\text{Co}_7\text{Pr}_2\text{-}\chi$ at low temperatures.

Just like the as-cast Co-20.8 at.% Pr alloy, five compositions for the phases, $\text{Co}_5\text{Pr-D}_{2d}$ (15.8 at.% Pr), $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ (20.9 at.% Pr), $\text{Co}_7\text{Pr}_2\text{-}\chi$ (21.6 at.% Pr), $\text{Co}_3\text{Pr-}\delta$ (24 at.% Pr), and $\text{Co}_2\text{Pr-C15}$ (30.5 at.% Pr), were identified in the as-cast Co-22.2 at. % Pr alloy using

EPMA as shown in Fig. 4(a). From the XRD results in Fig. 4(b), $\text{Co}_5\text{Pr-D2}_d$, $\text{Co}_{19}\text{Pr}_5\text{-}\beta$, $\text{Co}_7\text{Pr}_2\text{-}\chi$ and $\text{Co}_3\text{Pr-}\delta$ are possible in the as-cast Co-22.2 at. % Pr alloy. The as-cast Co-22.2 at. % Pr alloy was heat-treated at 1000K and 1173K, respectively. SEM and XRD results in Fig. 4(c-f) indicate the existence of the $\text{Co}_7\text{Pr}_2\text{-}\chi$ with Ni_7Ce_2 prototype and

Fig. 4. (a) EPMA images showing observed microstructures and (b) the XRD data of the as-cast Co-22.2 at.% Pr alloy and (c) SEM images showing observed microstructures and (d) the XRD data after heat treating the as-cast Co-22.2 at.% Pr alloy at 1000K for 168 hours and (e) SEM images showing observed microstructures and (f) the XRD data after heat treating as-cast Co-22.2 at.% Pr alloy at 1173K for 168 hours, respectively.

$\text{Co}_3\text{Pr-}\delta$ phases at both temperatures. It should be noted here that the $\text{Co}_5\text{Pr-D2}_d$ phase identified using EMPA (considered as an unfinished decomposition phase) in Fig. 4(c) implies that the $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ phase is less stable with respect to the $\text{Co}_5\text{Pr-D2}_d$ and $\text{Co}_7\text{Pr}_2\text{-}\chi$

phases at 1000K. Considering the results in Ref. [28] i.e., observation of $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ phase in sample treated at 1173K, the decomposition temperature of the $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ phase is assumed to be around 1173 K in this work.

Fig. 5. (a) EPMA images showing observed microstructures and (b) the XRD data of the as-cast Co-54.0 at.% Pr alloy and (c) EPMA images showing observed microstructures and (d) the XRD data after heat treating the as-cast Co-54.0 at.% Pr alloy at 833K for 396 hours, respectively.

Specimens of the as-cast Co-54.0 at.% Pr alloy in Fig. 5(a) and (b) clearly reveal microstructures consisting of the $\text{Co}_2\text{Pr-C15}$ (33.2 at.% Pr) and $\text{Co}_{17}\text{Pr}_{20}\text{-}\phi$ (53.8 at.% Pr, structure with unclear prototype) phases plus eutectic-like minor phases formed from the liquid. After annealing at 834K for 396 hours and quenching in water, the eutectic microconstituent disappears as shown in Fig. 5(c). The compositions of the $\text{Co}_2\text{Pr-C15}$ and $\text{Co}_{17}\text{Pr}_{20}\text{-}\phi$ phases are 33.2 and 53.8 at.%Pr, respectively. The XRD result is plotted in Fig. 5(d) to be compared with expected structures determined by first-principles results in next section.

The experimental data shown in Figs. 1-5 indicate that the $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ phase is formed via a peritectic reaction. The compounds $\text{Co}_5\text{Pr-D2}_d$, $\text{Co}_7\text{Pr}_2\text{-}\chi$, and $\text{Co}_3\text{Pr-}\delta$ are stable down to 773K. The lower limit of stability of the $\text{Co}_{19}\text{Pr}_5\text{-}\beta$ phase is assumed to be around 1173K in this work. The $\text{Co}_2\text{Pr-C15}$ and $\text{Co}_{17}\text{Pr}_{20}\text{-}\phi$ phase are stable at lower limits below 834K.

The enthalpy of mixing of Co-Pr liquid was measured with solution calorimeter using the isoperibolic procedure with which the temperature change resulted from the heat generated or consumed by a solid or liquid sample dissolved in liquid in crucible can be measured. Details concerning the calorimeter setup and the measurement procedure have been described previously[33]. The measurements were carried out under argon gas at atmospheric pressure and constant temperature at 1327K with continuous stirring. $\Delta H(x_{Co})$ was measured by successive additions of Co component from room temperature to a liquid Pr bath contained in a Ta crucible. The temperature change was measured by a K-type thermopile situated directly below the crucible. The enthalpy of solution corresponds to the area under the ΔT vs. time curve. For each series of measurements, the calorimeter was calibrated by dropping pure Pr samples into the bath and their heat content was taken from database by Dinsdale [34]. After measurement, the sample was easily separated from crucible indicating no obvious reaction between sample and crucible. As shown in Fig. 6, the measurements for the enthalpy of mixing of liquid were performed for composition up to 48.6 at.% Co. The standard deviation of the calibrations was of the order of $\pm 3\%$.

Fig. 6. The enthalpy of mixing for liquid Pr measured at 1327K using solution calorimeter and calculated results using the parameters in Table 3.

2.2 Computational data

To determinate the Gibbs free energy of formation for the intermediate phases, the zero K energies of the Co-hcp, Pr-dhcp and the intermetallic phases were calculated by means Vienna *ab initio* simulation package (VASP) [35, 36] employing projector augmented wave method [36, 37] and Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [38] with the high precision choice (PREC=HIGH). High precision was used to ensure that the computed absolute energies were converged to a few meV. The spin-polarized electronic-structure calculations were enabled. We relaxed the cell volumes first and then fully relaxed the cell shape and the internal atomic coordinates for all end-members (being described in Section 3) of the compounds. After

calculations, we checked all end-member structure and confirmed that the unit cells were maintained in the same crystal symmetry.

The enthalpy of formation, ΔH_f^Φ , for a given compound Φ is calculated as the difference between the energy of the compound, E_{TOT}^Φ , and linear combination of the pure element reference state energies, E_{Co}^{hcp} and E_{Pr}^{dhcp} ,

$$\Delta H_f^\Phi = E_{TOT}^\Phi - x_{Co}^\Phi E_{Co}^{hcp} - x_{Pr}^\Phi E_{Pr}^{dhcp} \quad (1)$$

where x_i^Φ is the mole fraction of component i in Φ . The calculated enthalpies of formation of the compounds, lattice parameters, and magnetic moments are listed in Tables 1 and 2, respectively.

The calculations were performed for the phases as summarized in Table 1 and plotted in Fig. 7. The enthalpies of formation for the $Co_{17}Pr_2$ composition with $Zn_{17}Th_2$ and $Ni_{17}Th_2$ prototypes indicate that $Co_{17}Pr_2$ - α has $Zn_{17}Th_2$ prototype. Taking into account the experimental results in Fig. 1(b), we conclude that $Co_{17}Pr_2$ - α with $Zn_{17}Th_2$ prototype is stable all the way to zero temperature.

The calculated results for the Co_7Pr_2 - χ phase indicate that its prototype is Ni_7Ce_2 at zero K. Considering the experimental results in Fig. 4, the prototype of the Co_7Pr_2 - χ phase is confirmed to be Ni_7Ce_2 in its stable temperature range. To determine the structure of the $Co_{17}Pr_{20}$ - ϕ phase, six prototypes, i.e., Co_3Ho_4 ($P6_3/m(176)$ and $P6_3(173)$), P_3Th_4 , Ni_3Ga_4 , Al_3Zr_4 , and $Co_{17}La_{20}$ were calculated in which Co_3Ho_4 and $Co_{17}La_{20}$ prototypes have negative enthalpies of formation at zero K. The expected XRD patterns of the $Co_{17}Pr_{20}$ - ϕ phase with the $Co_{17}La_{20}$ and Co_3Ho_4 prototypes were plotted in Fig. 5(d) to compare with the experimental XRD data. The results indicate that both $Co_{17}La_{20}$ and Co_3Ho_4 prototypes are not isostructural for the $Co_{17}Pr_{20}$ - ϕ phase, and thus, further work is needed to identify the unknown structure of the $Co_{17}Pr_{20}$ - ϕ phase.

The results shown in Figs. 1-5 and 7 indicate that the phases Co -hcp, $Co_{17}Pr_2$ - α , Co_2Pr_5 - γ , $CoPr_3$ - $D0_{11}$, and Pr -dhcp are stable all way to zero K while the Co_5Pr - $D2_d$, $Co_{19}Pr_5$ - β , Co_7Pr_2 - χ , Co_3Pr - δ , Co_2Pr - $C15$ are metastable at low temperature. The crystal structure of the $Co_{17}Pr_{20}$ - ϕ phase is unclear and its enthalpy of formation should be less than -4.91kJ/mol.

To evaluate the Gibbs free energy of the fcc, hcp and fcc solution phases, their enthalpies of mixing were calculated with first-principles approach, using 16-atom Quasirandom Structures (SQSs) [39, 40]. The concept of SQS was proposed by Zunger et al. [39] to mimic a random solution phase by reproducing the pair and multiple-body correlations using a small-sized supercell. The fcc [40], bcc [41], and hcp [42] SQS solution structures were employed in this work. The energetics of the fcc-, hcp-, and bcc-SQS at compositions of 25, 50 and 75 at.%Pr were computed using VASP [35, 36] with projector augmented wave method [36, 37] and PBE-GGA [38]. Similar to the end-members of the compounds, we relaxed the cell volumes first and then fully relaxed the cell shape and the internal atomic coordinates of the fcc-, hcp-, and bcc-SQS. After checking the structures, the cell shape and the internal atomic coordinates were found to run away from original crystal symmetry of the fcc-, hcp-, and bcc-SQS and therefore

Table 1 A summary of results from the first-principles calculations.

Phase Φ	Prototype	Space group	Formula	First-principles			
				k-points	eV/atom	ΔH_f^ϕ , kJ/mol	$\mu_m(\mu_B)$
Co	Mg (hcp)	P6 ₃ /mmc	Co	20x20x16	-6.99588	0	1.57
Co ₇₅ Pr ₂₅	hcp-SQS16		Co ₇₅ Pr ₂₅	10x8x6	-5.72534	68.52	0.92
Co ₅₀ Pr ₅₀			Co ₅₀ Pr ₅₀		-5.13409	71.49	0.49
Co ₂₅ Pr ₇₅			Co ₂₅ Pr ₂₅		-4.79544	50.10	0.00
Pr	La (dhcp)	Fm-3m	Pr	20x20x16	-4.75434	0	0.00
Co ₁₇ Pr ₂ - α	Zn ₁₇ Th ₂	R-3mh	Co ₁₇ Co ₂	6x6x4	-6.76229	22.54	1.67
			Co ₁₇ Pr ₂		-6.80277	-4.134	1.31
			Pr ₁₇ Co ₂		-4.24673	71.74	0.00
			Pr ₁₇ Pr ₂		-4.49754	24.78	0.00
	Ni ₁₇ Th ₂	P6 ₃ /mmc	Co ₁₇ Pr ₂	6x6x8	-6.79817	-3.69	1.32
Co ₅ Pr-D2 _d	CaCu ₅	P6/mmm	Co ₅ Co	24x24x26	-6.63140	35.16	1.73
			Co ₅ Pr		-6.64672	-2.36	1.14
			Pr ₅ Co		-4.18369	91.10	0.00
			Pr ₅ Pr		-4.45348	29.03	0.00
Co ₁₉ Pr ₅ - β	Co ₁₉ Ce ₅	R-3mh	Co ₁₉ Co ₅	4x4x3	-6.58463	39.68	1.74
			Co ₁₉ Pr ₅		-6.55619	-2.63	0.98
			Pr ₁₉ Co ₅		-3.93768	123.85	0.00
			Pr ₁₉ Pr ₅		-4.47387	27.06	0.00
Co ₇ Pr ₂ - χ	Ni ₇ Ce ₂	P6 ₃ /mmc	Co ₇ Co ₂	8x8x6	-6.71039	27.54	1.69
			Co ₇ Pr ₂		-6.52752	-2.87	0.92
			Pr ₇ Co ₂		-4.01864	119.044	0.04
			Pr ₇ Pr ₂		-4.49303	25.22	0.00
	Co ₇ Gd ₂	R-3mh	Co ₇ Pr ₂	6x6x4	-6.52702	-2.82	0.91
Co ₃ Pr- δ	Ni ₃ Pu	R-3mh	Co ₃ Co	6x6x4	-6.71405	27.19	1.69
			Co ₃ Pr		-6.46622	-2.97	0.80
			Pr ₃ Co		-3.77101	148.94	0.00
			Pr ₃ Pr		-4.50116	24.43	0.00
Co ₂ Pr-C15	Cu ₂ Mg	Fd-3m	Co ₂ Co	20x20x20	-6.78935	19.92	1.69
			Co ₂ Pr		---	-4.33[20]	---
			Pr ₂ Co		-4.28325	117.54	0.00
			Pr ₂ Pr		-4.52169	22.44	0.00
Co ₁₇ Pr ₂₀ - ϕ	Co ₃ Ho ₄	P6 ₃ /m(176)	Co ₃ Pr ₄	6x6x8	-5.82411	-4.91	0.00
	Co ₃ Ho ₄	P6 ₃ (173)		6x6x8	-5.82412	-4.91	0.00
	Co ₁₇ La ₂₀	C2/m	Co ₁₇ Pr ₂₀	24x24x26	-5.92090	-4.42	0.00
Co ₂ Pr ₅ - γ	B ₂ Pd ₅	C12/c1	Co ₂ Pr ₅	10x14x12	-5.46989	-7.25	0.00
CoPr ₃ -D0 ₁₁	CFe ₃	Pnma	CoPr ₃	12x10x14	-5.38308	-6.60	0.00
Co ₇₅ Pr ₂₅	fcc-SQS16	Fm-3m	Co ₇₅ Pr ₂₅	10x8x6	-5.72548	68.39	0.92
Co ₅₀ Pr ₅₀			Co ₅₀ Pr ₅₀		-5.06413	78.24	0.36
Co ₂₅ Pr ₇₅			Co ₂₅ Pr ₇₅		-4.79244	50.39	0.00
Co ₇₅ Pr ₂₅	bcc-SQS16	Im-3m	Co ₇₅ Pr ₂₅	10x8x6	-5.72657	68.40	0.92
Co ₅₀ Pr ₅₀			Co ₅₀ Pr ₅₀		-5.06502	78.16	0.00
Co ₂₅ Pr ₇₅			Co ₂₅ Pr ₇₅		-4.79705	49.95	0.00

Table 2 A summary of results from the first-principles calculations.

Phase Φ	Prototype	First-principles				Experiment			
		a(Å)	b(Å)	c(Å)	$\mu_m(\mu_B)$	a(Å)	b(Å)	c(Å)	$\mu_m(\mu_B)$
Co	Mg (hcp)	2.492	2.492	4.023	1.57	2.507[43]	2.507	4.069	1.35[34]
Pr	La (dhcp)	3.728	3.728	12.005	0.00	3.6725[44]	3.6725	11.835	---
Co ₁₇ Pr ₂ - α	Zn ₁₇ Th ₂	8.388	8.388	12.187	1.33	8.427 [24]	8.427	12.265	1.68[25]
	Ni ₁₇ Th ₂	8.384	8.384	8.149	1.31	---	---	---	---
Co ₅ Pr-D2 _d	CaCu ₅	5.014	5.014	3.948	1.14	5.01 [21]	5.01	3.99	1.66[25]
Co ₁₉ Pr ₅ - β	Co ₁₉ Ce ₅	5.045	5.045	48.463	0.98	5.053 [21]	5.053	48.71	0.124[25]
Co ₇ Pr ₂ - χ	Ni ₇ Ce ₂	5.052	5.052	24.431	0.92	5.06 [29]	5.06	24.43	1.167[25]
	Co ₇ Gd ₂	5.053	5.053	36.671	0.91	5.06 [29]	5.06	36.52	---
Co ₃ Pr- δ	Ni ₃ Pu	5.058	5.058	24.854	0.80	5.068 [16]	5.068	24.79	0.95[25]
Co ₁₇ Pr ₂₀ - ϕ	Co ₃ Ho ₄₍₁₇₆₎	11.643	11.643	4.302	0.00	---	---	---	---
	Co ₃ Ho ₄₍₁₇₃₎	11.653	11.653	4.303	0.00	---	---	---	---
	Co ₁₇ La ₂₀	8.159	8.159	4.644	0.00	---	---	---	---
Co ₂ Pr ₅ - γ	B ₂ Pd ₅	16.763	6.461	7.053	0.00	16.54 [31]	6.48	7.1	---
CoPr ₃ -D0 ₁₁	CFe ₃	7.151	10.032	6.475	0.00	7.143 [22]	9.78	6.41	---

the enthalpy of mixing for the SQS structure was calculated with the relaxed cell volume as listed in Table 1.

Fig. 7. Enthalpy of formation at 80K, calculated using the parameters in Table 3 in comparison with the first-principles data ($\triangle$), experimental data ($\blacksquare$)[20], and modeling results (dash-line) by Du et al. [2].

3. Thermodynamic descriptions

Thermodynamic models in the present work are based on the sublattice models developed by Sundman and Agren [45]. As defined in Table 3, the total Gibbs free energy for any phase, ϕ , is generally given by the sum of three contributions,

$$G_m^\phi = {}^{ref}G_m^\phi + {}^{id}G_m^\phi + {}^{xs}G_m^\phi \quad (2)$$

where the subscript, m , indicates that all terms are molar quantities. The first term in Eq. 2 is the sum of occupancy-weighted sublattice end-member contributions, while the second and third terms are the ideal and excess parts of the Gibbs free energy of mixing, respectively.

3.1 Liquid, hcp, fcc and bcc phases

Liquid, hcp, fcc, and bcc terminal solution phases are treated as substitutional solutions with the solution model as

$$G_m^\phi = \sum_{i=Co,Pr} x_i {}^\circ G_i^\phi + RT \sum_{i=Co,Pr} x_i \ln x_i + x_{Co} x_{Pr} \sum_{j=0}^n {}^j L_{Co,Pr}^\phi (x_{Co} - x_{Pr})^j + {}^{mag}G_m^\phi. \quad (3)$$

The Gibbs free energy ${}^\circ G_i^\phi$ of the pure element i with the structure ϕ are from the database by Dinsdale [34]. The magnetic contribution, ${}^{mag}G_m^\phi$, is discussed in section 3.3, while ${}^j L_{Co,Pr}^\phi$ is the j^{th} interaction parameter between component Co and Pr, expressed as ${}^j a^\phi + {}^j b^\phi T$, with ${}^j a^\phi$ and ${}^j b^\phi$ being model parameters to be evaluated in this work.

3.2 Intermetallic phase

The $Co_{17}Pr_2$ - α , Co_5Pr -D2d, $Co_{19}Pr_5$ - β , Co_7Pr_2 - χ , Co_3Pr - δ , and Co_2Pr -C15 intermetallics are described using the two-sublattice model, $(Co,Pr)_p(Co,Pr)_q$ including end-members Co_pCo_q , Co_pPr_q , Pr_pCo_q , and Pr_pPr_q as

$$\begin{aligned} G_m^\phi = & \sum_{i=Co,Pr} y_i^I \sum_{j=Co,Pr} y_j^{II} {}^\circ G_{i:j}^\phi + RT \sum_{i=Co,Pr} (p y_i^I \ln y_i^I + q y_i^{II} \ln y_i^{II}) \\ & + y_{Co}^I y_{Pr}^I \sum_{i=Co,Pr} y_i^{II} \sum_{k=0}^n {}^k L_{Co,Pr:i}^\phi (y_{Co}^I - y_{Pr}^I)^k + y_{Co}^{II} y_{Pr}^{II} \sum_{i=Co,Pr} y_i^I \sum_{k=0}^n {}^k L_{i:Co,Pr}^\phi (y_{Co}^{II} - y_{Pr}^{II})^k \\ & ({}^\circ G_{i:j}^\phi = p {}^\circ G_i^{ref} + q {}^\circ G_j^{ref} + \Delta G_{i:j}^\phi + {}^{mag}G_{i:j}^\phi = p {}^\circ G_i^{ref} + q {}^\circ G_j^{ref} + a_{i:j}^\phi + b_{i:j}^\phi T + c_{i:j}^\phi T \ln(T) + {}^{mag}G_{i:j}^\phi) \end{aligned} \quad (4)$$

The Gibbs energy ${}^\circ G_{i:j}^\phi$ is described as of the end-member $i:j$ where ${}^\circ G_i^{ref}$ and ${}^\circ G_j^{ref}$ ($i, j = Co$ and Pr) of the elements Co and Pr from the database by Dinsdale [34]. $\Delta G_{i:j}^\phi$ in Eq. 4 is the Gibbs energy of formation of the end-member $i:j$ with no magnetic contribution included. ${}^{xs}G_m^\phi$ is the excess Gibbs energy, expressed in the Redlich-Kister polynomial [46] in Table 3 in which ${}^k L^\phi$ is the k^{th} interaction parameter and assumed to be zero in this work. y^I and y^{II} are the site fractions in the first and third sublattices, respectively, and ${}^{mag}G_{i:j}^\phi$ is the magnetic contribution [47] to Gibbs free energy as described in following section.

The $Co_{17}Pr_{20}$ - ϕ , Co_2Pr_5 - γ , and $CoPr_3$ -D0₁₁ phases are described as stoichiometric compounds as

$$G_m^\phi = p {}^\circ G_i^{ref} + q {}^\circ G_j^{ref} + a_{i:j}^\phi + b_{i:j}^\phi T + c_{i:j}^\phi T \ln(T) + {}^{mag}G_{i:j}^\phi. \quad (5)$$

3.3 Magnetic energy

The magnetic energy contribution, ${}^{mg}G_m^\phi$ [47] of the terminal Co or a compound to Gibbs free energy is considered in this work, and expressed as:

$${}^{mg}G_m^\Phi = RT \ln(\beta^\Phi + 1) f(\tau^\Phi) = {}^{mg}H_m^\Phi - T {}^{mg}S_m^\Phi, \quad (6)$$

where β^Φ is a quantity related to the total magnetic entropy and is set equal to the Bohr magnetic moment per mole of atom. τ^Φ is defined as T/T_c^Φ and T_c^Φ is the Curie temperature. For the solution phase, T_c^Φ and β^Φ are described as:

$$T_c^\Phi = x_A {}^0T_{cA}^\Phi + x_B {}^0T_{cB}^\Phi + x_A x_B \sum_{j=0}^n {}^jL_{T(A,B)}^\Phi (x_A - x_B)^j \quad (7)$$

$$\beta^\Phi = x_A {}^0\beta_A^\Phi + x_B {}^0\beta_B^\Phi + x_A x_B \sum_{j=0}^n {}^jL_{\beta(A,B)}^\Phi (x_A - x_B)^j \quad (8)$$

where ${}^0T_{ci}^\Phi$ and ${}^0\beta_i^\Phi$ are from end-member as listed in Table 3 [25] except ${}^0\beta_{Co_{19}Pr_5}^\beta$ for the $Co_{19}Pr_5$ - β phase. Unlike other compounds, the calculated μ_m for the $Co_{19}Pr_5$ - β phase using first-principles approach in Table 1 shows significant different from the experimental data [25]. Considering $Co_{19}Pr_5$ - β being less stability with respect to Co_5Pr -D2d and Co_7Pr_2 - χ at low temperature, the first-principles calculated μ_m is employed as listed in Table 3. For the terminal fcc, hcp, and bcc phases, ${}^0T_{ci}^\Phi$ and ${}^0\beta_i^\Phi$ can be found in pure element database [34]. Lastly, ${}^jL_{T(A,B)}^\Phi$ and ${}^jL_{\beta(A,B)}^\Phi$ are the magnetic interaction parameters between the elements A and B.

4. Model parameter evaluation and phase diagram calculation

The comprehensive thermodynamic model is detailed in Table 3, for which 27 Gibbs free energy of formation parameters (ΔG) and 9 binary interaction parameters (0L) are established for the Co-Pr system (see Table 3). Parameter evaluation was performed using experimental data combined with first-principles results and was carried out in an iterative manner as described briefly below.

The parameter evaluation process was begun with the liquid phase. With the experimental data in Fig. 6 as well as the liquidus data [21] in Fig. 8, the model parameters were evaluated. The calculated enthalpy of mixing of the liquid phase is plotted in Fig. 6 showing good agreement with the experimental data. The first-principles data in Table 1 were used to evaluate the thermodynamic parameters of the fcc, hcp, and bcc phases. Since no data is available, the parameter ${}^0L_{Co,Pr}^{dhcp}$ is assumed to be same as ${}^0L_{Co,Pr}^{bcc}$.

With the absence of available data, the unstable end-members of individual compounds in Eq.4 are treated as constants and determined using first-principles from the calculated enthalpies of formation listed in Table 1. The coefficients for the stable end members ($a_{Co:Pr}^\Phi$, $\Phi = \alpha$, D2d, β , χ , δ , C15, ϕ , γ , or D011) are evaluated from the first-principles data and magnetic contributions; the details of which are given below.

The Gibbs free energy of the stable end members is rewritten as

$${}^oG_{Co:Pr}^\Phi = x_{Co}^\Phi {}^oG_{Co}^{ref} + x_{Pr}^\Phi {}^oG_{Pr}^{ref} + \Delta H_{Co:Pr}^\Phi - T \Delta S_{Co:Pr}^\Phi + {}^{mag}G_m^\Phi, \quad (9)$$

where the term ${}^oG_{Co}^{ref}$ normally refers to the GH SERCO function in SGTE database [34] in

Table 3 Thermodynamic parameters for the Gibbs free energy in Eqs.2-8.

Phase	Parameter	$a+bT+cT \ln(T)$ (J/mol)	$T_c(K)$	$\beta(\mu_B)$
Liquid	${}^0L_{Co,Pr}^{liq}$	-70135+46.144T (<2000K)	0	0
		23153(>2000K)	0	0
	${}^1L_{Co,Pr}^{liq}$	-4170	0	0
	${}^2L_{Co,Pr}^{liq}$	-3090	0	0
Fcc	${}^0L_{Co,Pr}^{fcc}$	294000	0	0
	${}^1L_{Co,Pr}^{fcc}$	90000	0	0
Hcp	${}^0L_{Co,Pr}^{hcp}$	272000	0	0
	${}^1L_{Co,Pr}^{hcp}$	121000	0	0
	${}^2L_{Co,Pr}^{hcp}$	47000	0	0
Bcc	${}^0L_{Co,Pr}^{bcc}$	294000	0	0
	${}^1L_{Co,Pr}^{bcc}$	90000	0	0
Dhcp	${}^0L_{Co,Pr}^{dhcp}$	294000	0	0
Co ₁₇ Pr ₂ - α	$\Delta G_{Co:Co}^\alpha$	22537	0	0
	$\Delta G_{Co:Pr}^\alpha$	-3494.7-6.3677T+0.85Tln(T)	1173[25]	1.6842[25]
	$\Delta G_{Pr:Co}^\alpha$	71741.4	0	0
	$\Delta G_{Pr:Pr}^\alpha$	24777.2	0	0
Co ₅ Pr-D2 _d	$\Delta G_{Co:Co}^{D2_d}$	35165.9	0	0
	$\Delta G_{Co:Pr}^{D2_d}$	-3124.3-30.07T+3.91Tln(T)	912[25]	1.658[25]
	$\Delta G_{Pr:Co}^{D2_d}$	91103	0	0
	$\Delta G_{Pr:Pr}^{D2_d}$	29028	0	0
Co ₁₉ Pr ₅ - β	$\Delta G_{Co:Co}^\beta$	39678.2	0	0
	$\Delta G_{Co:Pr}^\beta$	-6175-17.54905T+2.42Tln(T)	690[25]	0.98
	$\Delta G_{Pr:Co}^\beta$	123851.1	0	0
	$\Delta G_{Pr:Pr}^\beta$	27060.9	0	0
Co ₇ Pr ₂ - χ	$\Delta G_{Co:Co}^\chi$	27544	0	0
	$\Delta G_{Co:Pr}^\chi$	-6466-18.521T+2.566Tln(T)	574[25]	1.167[25]
	$\Delta G_{Pr:Co}^\chi$	119043.5	0	0
	$\Delta G_{Pr:Pr}^\chi$	25211.9	0	0
Co ₃ Pr- δ	$\Delta G_{Co:Co}^\delta$	27191.3	0	0
	$\Delta G_{Co:Pr}^\delta$	-8368.7-7.489T+1.2Tln(T)	339[25]	0.95[25]
	$\Delta G_{Pr:Co}^\delta$	148944	0	0
	$\Delta G_{Pr:Pr}^\delta$	24428	0	0
Co ₂ Pr-C15	$\Delta G_{Co:Co}^{C15}$	19930.6	0	0
	$\Delta G_{Co:Pr}^{C15}$	-10010+1.946T	0	0
	$\Delta G_{Pr:Co}^{C15}$	117542.9	0	0
	$\Delta G_{Pr:Pr}^{C15}$	22446.6	0	0
Co ₁₇ Pr ₂₀ - ϕ	$\Delta G_{Co:Pr}^\phi$	-8826.1-32.2783T+4.935Tln(T)	0	0
Co ₂ Pr ₅ - γ	$\Delta G_{Co:Pr}^\gamma$	-9681.2+3.958T	0	0
CoPr ₃ -D0 ₁₁	$\Delta G_{Co:Pr}^{D0_{11}}$	-8732.9+3.325T	0	0

which the magnetic energy contribution is not included. The Gibbs free energy of formation $\Delta G_{Co:Pr}^\phi$ of the stable end-member Co:Pr can be written in $\Delta H_{Co:Pr}^\phi - T\Delta S_{Co:Pr}^\phi$

in which no magnetic contribution is included in $\Delta H_{Co:Pr}^\Phi$ and $\Delta S_{Co:Pr}^\Phi$.

The enthalpy of formation ΔH_f^Φ of the compound Φ is defined as:

$$\begin{aligned}\Delta H_f^\Phi &= H_m^\Phi - x_{Co}^\Phi H_{Co}^{hcp} - x_{Pr}^\Phi H_{Pr}^{dhcp} \\ &= ({}^{str}H_m^\Phi + {}^{mag}H_m^\Phi) - x_{Co}^\Phi ({}^{str}H_{Co}^{hcp} + {}^{mag}H_{Co}^{hcp}) - x_{Pr}^\Phi H_{Pr}^{dhcp},\end{aligned}\quad (10)$$

for which H_m^Φ is the enthalpy of the compound Φ . H_{Co}^{hcp} and H_{Pr}^{dhcp} are the enthalpies of the pure elements. The magnetic contribution is included in both H_m^Φ and H_{Co}^{hcp} expressed with terms ${}^{mag}H_m^\Phi$ and ${}^{mag}H_{Co}^{hcp}$ while ${}^{str}H_m^\Phi$ and ${}^{str}H_{Co}^{hcp}$ are the enthalpy of the structure contributions, respectively. Here we can see that ΔH_f^Φ in Eq. 10 is different from $\Delta H_{Co:Pr}^\Phi$ in Eq. 9. The discrepancy is attributed to the magnetic energy contribution. The relationship between ΔH_f^Φ and $\Delta H_{Co:Pr}^\Phi$ can be derived from Eq. 10:

$$\begin{aligned}\Delta H_f^\Phi &= {}^{str}H_m^\Phi - x_{Co}^\Phi {}^{str}H_{Co}^{hcp} - x_{Pr}^\Phi H_{Pr}^{dhcp} + {}^{mag}H_m^\Phi - x_{Co}^\Phi {}^{mag}H_{Co}^{hcp} \\ &= \Delta H_{Co:Pr}^\Phi + ({}^{mag}H_m^\Phi - x_{Co}^\Phi {}^{mag}H_{Co}^{hcp}).\end{aligned}\quad (11)$$

For each compound Φ , i.e., end-member Co:Pr, ΔH_f^Φ is enthalpy of formation calculated using first-principles approach as listed in Table 1 (here we ignore the difference of ΔH_f^Φ at 0 and 298K). The magnetic contribution, ${}^{mag}H_m^\Phi$, at 298K can be calculated using Eq. 6 with the parameters in Table 3. The term ${}^{mag}H_{Co}^{hcp}$, the magnetic

Table 4 Determination of the enthalpy of formation of the stable end-member.

Phase (Φ)	ΔH , kJ/mol of atoms			
	${}^{mag}H_m^\Phi$	$x_{Co}^\Phi {}^{mag}H_{Co}^{hcp}$	ΔH_f^Φ	$\Delta H_{Co:Pr}^\Phi$
Co-hcp	-8.520	-8.520	---	---
Pr-dhcp	---	0	---	---
Co ₁₇ Pr ₂ - α	-8.260	-7.620	-4.134	-3.495
Co ₅ Pr-D2 _d	-6.330	-7.100	-2.357	-3.124
Co ₁₉ Pr ₅ - β	-3.299	-6.746	-2.729	-6.175
Co ₇ Pr ₂ - χ	-3.030	-6.630	-2.872	-6.466
Co ₃ Pr- δ	-0.990	-6.390	-2.965	-8.369
Co ₂ Pr-C15	---	-5.680	-2.821	-8.501
			-4.33[20]	-10.01
Co ₁₇ Pr ₂₀ - ϕ	---	-3.915	-4.911	-8.826
Co ₂ Pr ₅ - γ	---	-2.434	-7.246	-9.681
CoPr ₃ -D0 ₁₁	---	-2.130	-6.602	-8.733

contribution of the pure Co-hcp phase at 298K, can be computed using Eq. 6 with the magnetic parameters in SGTE database [34]. The resulted ΔH_f^Φ , ${}^{mag}H_m^\Phi$, and $x_{Co}^\Phi {}^{mag}H_{Co}^{hcp}$

are listed in Table 4. With Eq. 11, $\Delta H_{Co:Pr}^\phi$ is calculated and listed in Table 4. By ignoring the difference between 0 and 298K, the parameter $a_{Co:Pr}^\phi$ is treated as the same as $\Delta H_{Co:Pr}^\phi$ for individual compounds and listed in Table 3. To describe the relative stable temperature ranges of individual compounds, the $b_{i:j}^\phi$ and $c_{i:j}^\phi$ parameters in Eq. 4 were computed from the upper and lower limits of the decomposition temperatures of individual compounds as well as the liquidus data [21], Table 3.

With the thermodynamic parameters in Table 3, the Co-Pr phase diagram is calculated and plotted in Fig. 8. The accuracy of this calculation arises from the utilization of both first-principles calculations and experiments to clarify the relative stability of the intermetallic phases. Our findings show several significant differences in comparison with previous reports [2]. Notably, (i) the calculated enthalpies of formation for the compounds shown in Fig. 7 and the experimental observations in Figs. 1-5 indicate that $Co_{17}Pr_2-\alpha$, $Co_2Pr_5-\gamma$, and $CoPr_3-D0_{11}$ are the stable phases all way to 0 K while Co_5Pr-D2_d , $Co_{19}Pr_5-\beta$, $Co_7Pr_2-\chi$, $Co_3Pr-\delta$, $Co_2Pr-C15$, and $Co_{17}Pr_{20}-\phi$ are metastable at low temperature. As the dash-lines in Fig. 8 calculated using parameters by Du et al.

Fig. 8. The Co-Pr phase diagram resulting from the present model using the parameters in Table 3, experimental data ∇ overall alloy composition, $\bullet$ phase composition after heat treatment.

[2], the decomposition temperatures of the reactions $Co_{17}Pr_2-\alpha \rightarrow Co-fcc + Co_5Pr-D2_d$ and $Co_2Pr_5-\gamma \rightarrow Co-fcc + Co_{19}Pr_5-\beta$ phases are 1158.5K and 1123.6K, respectively, indicating the calculated phase diagram by Du et al. [2] conflicts with our first-principles results for the phase relative stabilities in Fig. 7 and experimental observations in Figs. 1-5 and in refs. [17-19, 21, 24-27]. (ii) The model parameters of the hcp, fcc, and bcc phases were evaluated with the SQSs results in Table 1. (iii) The calculated enthalpy of mixing of liquid shows good agreement with the experimental results in Fig. 6.

5. Chemical Partitioning-Temperature-Phase Transformation (CPTPT) calculation

To understand the varying degrees of chemical partitioning, the Gibbs free energies for the liquid and δ phases at $T=900K$ are plotted in Fig. 9. The two equilibrium liquidus

compositions (${}^i x_{equ}^{liq}$ equilibrium with δ at ${}^i x_{equ}^{\delta}$) are also shown, bounding the full range of homogeneous liquid compositions for which there is a positive driving force for the formation of the δ phase. This range includes two important regimes where (i) partitionless solidification may be observed and (ii) some degree of chemical

Fig. 9. The Gibbs free energies of the liquid and $\text{Co}_3\text{Pr}-\delta$ phases at 900K computed with the parameters in Table 3.

partitioning is required in the composition range. The partitionless solidification, i.e., the compositions between x_0^1 and x_0^2 is defined by the criterion $G_m^{liq} = G_m^{\delta}$ bounding the partitionless range (PL-range) in Fig. 9, over which ${}^0 G_m^{liq} > {}^0 G_m^{\delta}$ such that the liquid phase may transform directly into the solid phase in a diffusionless manner. Thus, this range represents the "zero diffusion time" limit. Over a range of temperatures, these limiting compositions define so called T_0 (solid line) curves as plotted in Fig. 10, in which as previously suggested [48], the T_0 curves provide a practical limit for partitionless crystallization. The partitioning range labeled P-range in Fig. 9 between ${}^i x_{equ}^{liq}$ and x_0^i is the composition range that requires diffusion time for crystallization. From an energy standpoint, only the BC-range in Fig. 9 for a given liquid composition as indicated $x_{Pr}^{liq} = x_1$ is allowed to crystallize. BC-range is determined by cross points (at ${}^i x_{BC}^{\delta}$) between the tangent line of liquid at $x_{Pr}^{liq} = x_1$ and G_m^{δ} curve. The crystallization of the δ phase with a composition in the BC-Range from x_1 liquid will reduce the system energy.

Focusing now on the composition P-range between ${}^i x_{equ}^{liq}$ and x_0^i and considering the required diffusion time, we recognize that the limits, i.e., T_L (liquidus)-dashed lines and T_0 solid-lines in Fig. 10, represent only the two-terminal cases. A continuum should exist between them, as determined by the degree of chemical partitioning, which we described previously [48], using a parameter, η , being defined as the degree of chemical partitioning

$$\eta = (\mu_{Pr}^{liq} - {}^0 \mu_{Pr}^{liq}) / ({}^{eq} \mu_{Pr}^{liq} - {}^0 \mu_{Pr}^{liq}) \quad (12)$$

This parameter is inversely related to chemical supersaturation as described in Ref. [48] in the liquid phase, as shown in Fig. 9, for a liquid of composition $x_{Pr}^{liq} = x_1$. μ_{Pr}^{liq} , ${}^0\mu_{Pr}^{liq}$, and ${}^{eq}\mu_{Pr}^{liq}$ are the chemical potentials at the compositions x_1 , ${}^2x_{equ}^{liq}$ and x_0^2 of the liquid phase, respectively. For a given temperature, x_1 starts from x_0^2 and ends at ${}^2x_{Pr}^{liq}$ associating variation of μ_{Pr}^{liq} from ${}^0\mu_{Pr}^{liq}$ to ${}^{eq}\mu_{Pr}^{liq}$ so that η varies from 0 to 1 indicating the increasing minimum diffusional burden that accompanies the solidification transition for the range in liquid composition between ${}^2x_{Pr}^{liq}$ and x_0^2 . As shown in Fig.

Fig. 10. The liquidus T_L and T_0 curves computed using the parameters in Table 3.

Fig.11. (a) The δ crystallization from liquid with the degree of chemical partitioning η varying from 0 to 1 at 916K as computed and (b) the crystallization surface showing the influence of initial supersaturation indicated by the degree of chemical partitioning η on the effective liquidus with the surface varying from T_0 to T_L as computed using the parameters in Table 3.

11(a), the δ phase formation composition range from liquid with the composition represented with liq_{start}^{δ} for each η varying from 0 to 1 is calculated at 916K. The curve liq_{start}^{δ} means the composition to start crystallization with respect to a “ η ” associated with a particular degree of constraint on the level of supersaturation that can be relieved by diffusion and thus is called as "the effective liquidus".

Over a range of temperature, the full crystallizations surface i.e. "the effective liquidus" for the Co-fcc, Co-hcp, Co₁₇Pr₂- α , Co₅Pr-D2_d, Co₁₉Pr₅- β , Co₇Pr₂- χ , Co₃Pr- δ , and Co₂Pr-C15 phases comprised of these level curves are plotted in Fig. 11(b). The parameter, η , can be viewed, alternatively, as a time-scale associated with the required diffusional relaxation where $\eta=1$ corresponds to the infinite-time limit and $\eta=0$ corresponds to the zero-time limit. Thus, the effective crystallization surface that applies to any real process (i.e., one with a finite cooling rate) would be indicated by the appropriate η value. Further examination of Fig. 11(b) reveals three more important features. First, if η is on zero side, i.e., very high cooling rate, the Co₁₇Pr₂- α , Co₅Pr-D2_d, Co₁₉Pr₅- β , Co₇Pr₂- χ , Co₃Pr- δ , and Co₂Pr-C15 phases can directly form from the liquid in a congruent manner. Second, eutectic reactions are possible with the η in the middle range. Along plane A with 16.7 at.%Pr in Fig. 11(b), the solidification is in following order: single Co₅Pr-D2_d phase formation in congruent manner→eutectic reaction→peritectic reaction with increasing η . Third, the possible composition range for a compound likely becomes larger with decreasing η , i.e., composition of a compound can be far from equilibrium.

Fuerst et al. [3] revealed that the magnetic field strength of melt spun Co₈₄Pr₁₆ alloy composed of Co₅Pr-D2_d increases with increasing wheel velocity, indicating the possible nonequilibrium phase transformation. In following section, we measure the cooling rate dependent phase transformation as well as associated magnetic properties for comparison with Fig. 11.

6. Solidification rate dependent studies

The solidification rate dependence of the as-cast microstructure was studied using two rapid solidification techniques with roughly four orders of magnitude difference in cooling rates. 1.5mm rods (ROD) were prepared by injection-casting and melt spun ribbon (RIBBON) was prepared with a wheel velocity 30 m/s. Two alloys were investigated, Co-x at. % Pr (x=10.5 and 16.7). Fig. 12(a) shows the microstructure of the ROD from which we can see the phase formation changes between the surface and center of the ROD indicating a cooling rate-dependent phase transformation. At the surface, the interface between the sample and the Cu mold resulted in the highest cooling rate, and thus, a single phase Co₁₇Pr₂- α is observed. With decreasing cooling rate, indicated in the direction of the arrow from surface to center in Fig. 12(a), the second phase dendrites (Co-hcp) emerge in Fig. 12(b) which is higher magnification images in region corresponding to the square marked in Fig. 12(a). The identified compositions are A: 0.5 at.%Pr, B:9.4 at.%Pr, and C:11 at.%Pr, respectively. As the SEM and XRD results shown in Fig. 12(c-d) for the Co-10.5 at.% Pr RIBBON sample, the single

$\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ phase was obtained. We conclude that the phase transformations changes from single phase to multiple phase formations with decreasing cooling rate, i.e., cooling rate-dependent phase transformation. Likewise, the Co-16.7 at. % Pr alloy also shows the cooling rate dependent phase transformation behavior. Fig. 13(a) shows the eutectic microconstituent in the ROD. The microstructure

Fig. 12. SEM images showing the cooling rate dependent phase transformation observed (a) microstructures of the different phases from surface to center of the Co-10.5 at. % Pr ROD sample; The arrow show the direction of decreasing cooling rate. (b) Microstructures and (c) XRD of the RIBBON Co-16.7 at. % Pr sample.

of the RIBBON, which is shown in Fig. 13(b), clearly illustrates the different phases between the wheel-side and the free-side. From the wheel-side to free-side, a gradual transition from a single phase to two phases was identified indicating the cooling rate effect for the nonequilibrium phase transformation. Although the XRD results in Fig.13(c) reveal that the matrix phase in the RIBBON is $\text{Co}_5\text{Pr-D2}_d$, the second phase on free-side is too fine to identify with only EPMA(or SEM) and XRD due to the thinness of the RIBBON ($\approx 25\mu\text{m}$) sample. TEM is thus employed to identify the crystal structures around the points g (on wheel side) and s (on free side) marked in Fig. 13(b). Fig. 14(a) shows the single $\text{Co}_5\text{Pr-D2}_d$ phase on wheel side as proved by diffraction (SAED) pattern selected phase at p point. In addition to the $\text{Co}_5\text{Pr-D2}_d$ phase, the $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ phase was identified on the free side at q point as shown in Fig. 14(b). From the results in Figs. 13-14, we conclude that over the cooling rate range of unlimited high to unlimited slow, the solidification of the Co-16.7 at. % Pr alloy can form in following order: single $\text{Co}_5\text{Pr-}$

D2_d phase formation in congruent manner→eutectic reaction→ peritectic reaction, which is identical with Fig. 11(b) along plane A, i.e. cooling rate controlled phase transformation.

Fig. 13. (a) SEM images showing microstructures of the Co-16.7%Pr ROD, (b) SEM images microstructures showing the different phases from wheel-side surface to free-side of the Co-16.7%Pr RIBBON (c) XRD data of Co-16.7%Pr RIBBON.

Fig. 14. Bright field TEM micrographs and corresponding selected area diffraction patterns on (a) wheel side and (b) free side of the Co-16.7%Pr alloy RIBBON.

The hysteresis loops of the magnetization for the Co-x at. % Pr (x=10.5 and 16.7) alloy of both ROD and RIBBON were measured using a vibrating sample magnetometer (VSM) with magnetic field up to 30 kOe at 300K as shown in Fig. 15. For x=10.5, the absence of any appreciable coercivity in both ROD and RIBBON samples is consistent with the in-plane anisotropy of the Co₁₇Pr₂-α compound. The slower approach to saturation of the ROD sample versus the RIBBON together with the slightly enhanced

saturation of the ROD sample is consistent with the multiphase microstructure observed in that material. The slower approach to saturation is associated with the presence of a fraction of higher anisotropy phase while the enhanced saturation is a result of a small amount of pure Co with a much higher moment per Co than the intermetallic phases. Similarly in the 16.7 at.% Pr composition, the high saturation magnetization of the ROD sample is related to a significant amount of $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ while the lower coercivity results from the larger grain size of the uniaxial $\text{Co}_5\text{Pr-D2}_d$ compound. This is consistent with observations in Ref. [3]. Two important features are noted: (1) $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$ is a soft magnetic compound while $\text{Co}_5\text{Pr-D2}_d$ is a hard magnetic compound and (2) single $\text{Co}_5\text{Pr-D2}_d$ phase with good hard magnetic properties can be obtained by suppressing formation of the deleterious phases by increasing the solidification cooling rate.

Fig.15. The hysteresis loop showing the magnetization of the ROD and RIBBON samples for the Co-x at.% Pr (x=10.5 and 16.7) alloys.

7. Summary

The first-principles calculations and experimental results indicate that $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$, $\text{Co}_2\text{Pr}_5\text{-}\gamma$, and $\text{CoPr}_3\text{-D0}_{11}$ are the stable phases at 0 K while $\text{Co}_5\text{Pr-D2}_d$, $\text{Co}_{19}\text{Pr}_5\text{-}\beta$, $\text{Co}_7\text{Pr}_2\text{-}\chi$, $\text{Co}_3\text{Pr-}\delta$, $\text{Co}_2\text{Pr-C15}$, and $\text{Co}_{17}\text{Pr}_{20}\text{-}\phi$ are metastable phases. The enthalpies of mixing of the liquid phase and solid solution (hcp, fcc, and bcc) phases are measured using solution calorimeter and calculated from first principles approach using 16-atom SQSs, respectively. The experimental investigations support the computational findings. The thermodynamic parameters required for the phase diagram calculations were evaluated. CPTPT calculation indicates that $\text{Co}_{17}\text{Pr}_2\text{-}\alpha$, $\text{Co}_5\text{Pr-D2}_d$, $\text{Co}_{19}\text{Pr}_5\text{-}\beta$, $\text{Co}_7\text{Pr}_2\text{-}\chi$, $\text{Co}_3\text{Pr-}\delta$, and $\text{Co}_2\text{Pr-C15}$ form in congruent manner and eutectic reaction with increasing cooling rate. The compositions of the compounds from these highly driven liquids can be far from equilibrium. The single hard magnetic $\text{Co}_5\text{Pr-D2}_d$ phase is able to be obtained with high cooling rate from liquid. These results demonstrate that CPTPT calculations can be a powerful tool for guiding the alloy design.

ACKNOWLEDGMENT

This is supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy,

Advanced Manufacturing Office. The Ames Laboratory is operated by Iowa State University under DOE Contract No. DE-AC02-07CH11358.

Reference

- [1] Strnat KJ, Strnat RMW. Rare earth Co-permanent magnetics. *J Magn Magn Mater.* 1991;100:38-56.
- [2] Du ZM, Wang DH, Zhang WJ. Thermodynamic assessment of the Co-Pr, Er-Ni and Ni-Pr systems. *J Alloys Compd.* 1999;284:206-12.
- [3] Fuerst CD, Herbst JF, Murphy CB, Vanwingerden DJ. Melt-spun PrCo₅ and related Magnetic materials coercivity enhancement by carbon addition. *J Appl Phys.* 1993;74:4651-9.
- [4] Goll D, Loeffler R, Herbst J, Karimi R, Pflanz U, Stein R, et al. High-Throughput Methods for Searching New Permanent Magnet Materials. *IEEE Trans Magn.* 2014;50:2103507.
- [5] Chen ZP, Gao JE, Wu Y, Wang H, Liu XJ, Lu ZP. Designing novel bulk metallic glass composites with a high aluminum content. *Scientific Reports.* 2013;3:3353.
- [6] Liao JP, Yang BJ, Zhang Y, Lu WY, Gu XJ, Wang JQ. Evaluation of glass formation and critical casting diameter in Al-based metallic glasses. *Mater Des.* 2015;88:222-6.
- [7] Jing Y, Sheng G, Zhao G. Influence of rapid solidification on microstructure, thermodynamic characteristic and the mechanical properties of solder/Cu joints of Sn-9Zn alloy. *Mater Des.* 2013;52:92-7.
- [8] Wang K, Wang H, Liu F, Zhai H. Modeling dendrite growth in undercooled concentrated multi-component alloys. *Acta Mater.* 2013;61:4254-65.
- [9] Aoki H, Tsuji N, Eckstein M, Kollar M, Oka T, Werner P. Nonequilibrium dynamical mean-field theory and its applications. *Rev Mod Phys.* 2014;86:779-837.
- [10] Wang H, Liu F, Herlach DM. Modeling the growth kinetics of a multi-component stoichiometric compound. *J Mater Sci.* 2014;49:1537-43.
- [11] Besson R, Kwon J, Thuinet L, Avettand-Fenoel MN, Legris A. First-principles study of Al-Cu energetics and consequences on athermal formation of Cu-rich compounds. *Phys Rev B.* 2014;90:214104.
- [12] Bévillon E, Colombier JP, Dutta B, Stoian R. Ab Initio Nonequilibrium Thermodynamic and Transport Properties of Ultrafast Laser Irradiated 316L Stainless Steel. *J Phys Chem C.* 2015;119:11438-46.
- [13] Wang Z, Guo S, Liu CT. Phase Selection in High-Entropy Alloys: From Nonequilibrium to Equilibrium. *JOM.* 2014;66:1966-72.
- [14] Sobolev SL. Driving force for binary alloy solidification under far from local equilibrium conditions. *Acta Mater.* 2015;93:256-63.
- [15] Zhao S, Li J, Liu B. Thermodynamic prediction of metastable phases of Ni-Ti system formed by ion beam mixing. *Sci China-Tech Sci.* 2012;55:921-6.
- [16] Bertaut EF, Lemaire R, Schweize J. Structures Cristallines Des Composés Intermetalliques T₂Co₇ ET TCo₃ (T=Terre Rare ou Yttrium). *Bull De La Soci Francaise Miner Et De Cristal.* 1965;88:580-&.
- [17] Ostertag W, Strnat KJ. Rare Earth Co Compounds with A₂B₁₇ Structure. *Acta Crystallogr.* 1966;21:560-&.
- [18] Harris IR, Mansey RC, Raynor GV. Rare Earth Intermediate Phases. *J Less-Common Met.* 1965;9:270-&.

- [19] Velge WAJ, Buschow KHJ. Magnetic and Crystallographic Perties of some Rare Earth Co Compounds with CaZn_5 Structure. *J Appl Phys.* 1968;39:1717-&.
- [20] Deodhar SS, Ficalora PJ. Study of Reaction Kinetics for Formation of Rare Earth Transition Metal Laves Compounds. *Metall Mater Trans A.* 1975;6:1909-14.
- [21] Ray AF. Überprüfung der Zustandschaubilder der binären Systeme Cer-Kobalt, Praseodym-Kobalt und Neodym-Kobalt. *Cobalt.* 1973;4:90-3.
- [22] Buschow KHJ, Vandergo.As. Crystal Structure of Rare earth Co Compounds of Type R_3Co . *J Less-Common Met.* 1969;18:309-11.
- [23] Oesterle H. Structures and Phase Relations of Al Substituted SmCo_5 , PrCo_5 , $\text{Sm}_2\text{Co}_{17}$ and $\text{Pr}_2\text{Co}_{17}$. *J Less-Common Met.* 1973;32:385-8.
- [24] Buschow KHJ. The Crystal Structures of Rare Earth Compounds of Form R_2Ni_{17} R_2Co_{17} and R_2Fe_{17} . *J Less-Common Met.* 1966;11:204-8.
- [25] Buschow KHJ. Intermetallic Compounds of Rare Earth and 3D Transition Metals. *Rep Prog Phys.* 1977;40:1179-256.
- [26] Wang WL, Lu MW, Feng Q, Xu ZP, Zeng LM, He W. Phase relationships of the Pr-Co-Fe system at 773 K. *J Alloys Compd.* 2011;509:6787-93.
- [27] Khan Y. Crystal Structure of R_5Co_{19} . *Acta Crystallogr.* 1974;B30:1533-7.
- [28] Zhifeng H, Zhengfei G, Gang C, Qingyan H, Fuqiang Z, Ruifeng L, et al. Solid-state phase equilibria in the Co-Pt-Pr ternary system at 1173 K. *J Alloys Compd.* 2009;481:301-4.
- [29] Buschow KHJ. Rare Earth Co Intermetallic Compounds. *Philips Res Rep.* 1971;26:49-&.
- [30] Wu CH, Chuang YC, Jin XM, Guan XH. Reinvestigation of the Pr-Co binary system. *Z Metallkd.* 1992;83:32-4.
- [31] Moreau JM, Paccard D. Monoclinic Crystal Structure of R_5Co_2 ($\text{R}=\text{Pr}, \text{Nd}, \text{Sm}$) with Mn_5C_2 Structure Type. *Acta Crystallogr.* 1976;32:1654-7.
- [32] MPC. Materials Preparation Center. Ames, Iowa: US DOE.
- [33] Sommer F. Modern methods in high temperature calorimetry. *J Therm Anal.* 1988;33:15-28.
- [34] Dinsdale AT. SGTE Data for Pure Elements. *CALPHAD.* 1991; 15:317-425.
- [35] Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B.* 1996;54:11169-86.
- [36] Kresse G, Joubert D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys Rev B.* 1999;59:1758-75.
- [37] Blöchl PE. Projector augmented-wave method. *Phys Rev B.* 1994;50:17953-79.
- [38] Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett.* 1996;77:3865-8.
- [39] Zunger A, Wei SH, Ferreira LG, Bernard JE. Special quasirandom structures. *Phys Rev Lett.* 1990; 65:353-6.
- [40] Wei SH, Ferreira LG, Bernard JE, Zunger A. Electronic-Properties of Random Alloys-Special Quasirandom Structures. *Phys Rev B.* 1990;42:9622-49.
- [41] Jiang C, Wolverton C, Sofo J, Chen L-Q, Liu Z-K. First-principles study of binary bcc alloys using special quasirandom structures. *Phys Rev B.* 2004;69:214202.
- [42] Shin D, Arroyave R, Liu ZK, Van de Walle A. Thermodynamic properties of binary hcp solution phases from special quasirandom structures. *Phys Rev B.* 2006;74.

- [43] Taylor A, Floyd RW. Precision Measurements of Lattice Parameters of Non-cubic Crystals. *Acta Crystallogr.* 1950;3:285-9.
- [44] Spedding FH, Daane AH, Herrmann KW. The Crystal Structures and Lattice Parameters of High-Purity Scandium, Yttrium and the Rare Earth Metals. *Acta Crystallogr.* 1956;9:559-63.
- [45] Sundman B, Agren J. A Regular Solution Model for Phases with Several Components and Sublattices, Suitable for Computer Applications. *J Phy Chem Solids.* 1981;42:297-301.
- [46] Redlich O, Kister AT. *Ind and Eng Chem.* 1948; 40:345-8.
- [47] Hillert M, Jarl M. A model for alloying in ferromagnetic metals. *CALPHAD.* 1978;2:227–38.
- [48] Zhou SH, Napolitano RE. Energetics of nonequilibrium solidification in Al-Sm. *Phys Rev B.* 2008;78.

Graphical abstract