

Cyanogel Coordination Polymers as Precursors to Transition Metal Alloys and Intermetallics — from Traditional Heating to Microwave Processing

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Cyanogel coordination polymers are amorphous Prussian blue analogues formed in a hydrogel state by the reaction of a chlorometalate with a cyanometalate in aqueous solution. At elevated temperatures, cyanogels thermally autoreduce to form transition-metal alloys. This work demonstrates the general nature of this type of sol–gel processing chemistry to prepare binary and ternary transition-metal alloys (Pd/Co, Pt/Co, Ru/Co, Ir/Co, Pd/Ni, Pt/Ni, Pt/Ru, Pd/Fe, Pd/Fe/Co) and intermetallics (Pt₃Fe, Pt₃Co, PtCo). Tuning of the composition of the gels and alloys by a variety of methods is demonstrated. The thermal autoreduction can be induced either by convective heating or by microwave irradiation, as microwave dielectric heating of cyanogels leads to a sufficient temperature increase in the sample to cause the reduction of the metal centers.

Introduction

Transition-metal alloys are of interest in materials science particularly for their catalytic^{1,2} and magnetic properties.³ However, the interest in certain transition metal alloys, particularly those of precious metals, is much more general, as the realm of use for these materials ranges from jewelry to electronics. A variety of methods can be utilized to prepare transition-metal alloys in the bulk,^{4,5} as thin films,² or as nanoparticles.⁶ Much interest has been recently generated by low-temperature solution methods to prepare transition-metal alloy nanoparticles and nanocrystalline materials.^{7–10} The thermal processing of cyanogel coordination polymers provides an alternate, low-temperature route to metal alloy compared to traditional metallurgical procedures.⁴ Cyanogel processing is attractive mainly because it gives access to various morphologies of the alloys; additionally, reaction times can be extremely short using microwave irradiation. Pd/Co cyanogels have previously been reported to serve as precursors to Pd/Co bulk alloys,¹¹ but the sol–gel nature of the process also allowed for preparation of Pd/Co nanopar-

ticle thin films,¹² supported nanoparticles,¹³ and cellular metals with a unique morphology.^{11,14} In addition, the Pd/Co cyanogel has been shown to heat upon absorption of microwave irradiation forming alloy product in a few minutes.¹⁵ In this work, we describe the generalization of the cyanogel processing method that allows for preparation of various bulk binary and ternary transition-metal alloys with a range of compositions by conventional or microwave heating.

The elegance of cyanogels as precursors to metal alloys lies in the composition and chemistry of the cyanogel coordination polymer. The polymer network consists of transition-metal centers in positive oxidation states bridged by cyanide ligands. The metal centers have additional nonbridging ligands, some of which are also cyanide groups. At elevated temperatures, the cyanide ligands reduce the transition-metal centers to lower oxidation states, forming metal alloys and byproduct transition-metal salts, which can be easily removed from the product by washing. The temperature of this autoreduction reaction is typically relatively low (~400–650 °C) and the typical heating times short (1–2 h), making the method much less energy intensive than classical powder metallurgy⁴ or mechanical alloying and milling⁵ techniques, which are traditionally used to prepare bulk metal alloys. Moreover, the processing time can be drastically reduced by using microwave irradiation.¹⁵ Furthermore, because of the homogeneous mixing of the metal

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centers in the polymer, a cyanogel can readily serve as one bi- or even multimetal precursor, removing the challenge of alloy inhomogeneity often faced in the traditional synthesis of supported alloy catalysts by chemical reduction of transition-metal salts deposited on a substrate.^{6,16} Last, no external reducing agent is needed, as the reducing cyanide ligands are an integral part of the polymer. Although to the best of our knowledge, crystalline Prussian blue analogs have never been reported to undergo similar autoreduction chemistry, some noble metal cyanometalates have,¹⁷ and some Prussian blue analogs most likely share this feature as well. However, only cyanogels allow one to take advantage of sol–gel processing to achieve various morphologies of the alloy product.

A typical cyanogel is formed from a mixture of equimolar aqueous solutions of a chlorometalate and a cyanometalate. The nitrogen end of the cyanide ligand replaces *trans*-chloride ligands,¹⁸ forming a bridge between the metal centers that results in a 3D amorphous Prussian-blue-like polymer network. Unlike gelatinous precipitates of Prussian blue and its analogs, which form a metastable gelatinous phase, the cyanogel system undergoes a true sol–gel phase transition, forming a stable gel. The first cyanogels reported in the literature were based on the reaction of K_2PdCl_4 with $K_3Fe(CN)_6$,¹⁹ K_2PdCl_4 with $K_3Co(CN)_6$,¹¹ and $SnCl_4$ with $K_3Fe(CN)_6$,²⁰ but the possibility of using cyanogel processing as a general method to prepare a variety of metal alloys has not been discussed. Most of the work that reported the use of cyanogels as metal alloy precursors was done on the Pd/Co cyanogel with a 2:1 ratio,^{11–13,15} the ratio with the fastest kinetics of the gelation process.¹⁸

In this paper, we report a number of new cyanogels that can be thermally processed into metal alloys and intermetallics. As catalytic, magnetic, and electronic properties of alloys can vary greatly with composition, we explore tuning of the alloy composition by varying the chlorometalate to cyanometalate ratio, using cyanometalates of two different transition metals in one cyanogel, addition of a metal chloride reactant, and soaking pre-made cyanogels in metal chloride solutions. We also show that the susceptibility of cyanogels to microwave dielectric heating is a general phenomenon that allows for a rapid reduction to metal alloys. The sol–gel processing of cyanogels thus provides a new chemical tool to prepare a range of transition-metal alloys with tunable composition.

Experimental Section

Materials. Na_2PdCl_4 and $RuCl_3 \cdot 3H_2O$ were purchased from Pressure Chemicals. $K_3Co(CN)_6$, $K_2Ni(CN)_4 \cdot xH_2O$, $K_2Pd(CN)_4$, $Na_3IrCl_6 \cdot xH_2O$, and $CoCl_2 \cdot 6H_2O$ were purchased from Aldrich. K_2 -

$PtCl_4$ and Na_2PtCl_4 were purchased from Strem. $NiCl_2 \cdot 6H_2O$ and $K_3Fe(CN)_6$ were acquired from Fisher. $FeCl_3 \cdot 6H_2O$ was acquired from Allied Chemical. $K_4Ru(CN)_6$ was purchased from Alfa Aesar. All compounds were reagent grade.

Gel Preparation. Gels were typically made at room temperature from 60 mM aqueous solutions of chlorometalate and cyanometalate in various volume ratios ranging from 2:1 to 1:1. Higher concentrations of 100 mM and temperatures of 75 or 95 °C were used in systems with slower reaction kinetics. In selected gels, a third component, a metal chloride salt, was included in the initial reaction. In general, the chlorometalate solution was first mixed with the metal chloride and the mixture was then added to the cyanometalate. The mixtures were allowed to react until gels formed that were then aged for times varying between a couple hours and several days. The aging time did not affect the stoichiometry of the final alloy product. The hydrogels were then dried at room temperature to produce xerogels that were heated at 650–1000 °C for 1–32 h. Heating time was adjusted so that no cyanide stretches were present in the IR spectrum of the final product, which indicated that reduction of the polymer was complete, and to produce the desired metal product with sufficient crystal size for clear determination of composition through XRD analysis. Multiple processing runs were carried out on the Pd/Co, Pd/Ni, and Ru/Co systems to determine the reproducibility of the processing procedures. In all cases, results were invariant from run to run.

Replacement of Counterions in Pd/Co Cyanogel. Na_2PdCl_4 ; $K_3Co(CN)_6$ hydrogels in a 2:1 ratio were prepared, allowed to age for 1 day at room temperature, and then placed into a deionized water bath at 70 °C. The water bath was changed daily until no precipitate was formed when a 0.12 M $AgNO_3$ solution was added to a sample of bath water indicating that the chloride salt byproduct of polymerization had been washed from the gel. The washed gels were exposed to 0.1 M solutions of $CoCl_2$ and $FeCl_3$ by either soaking the hydrogel in the metal chloride solution for 1 h or by running 50 mL of the metal chloride solution through the gel. After exposure to the metal chloride, the gels were washed with 100 mL of deionized water and dried at room temperature. Alloys were produced from the xerogels by heating in a furnace under Ar at 650 °C for 1 h.

Thermal Processing. The dried gels were heated in a three-zone programmable 2416 cm³ Carbolite furnace with a 12 °C/min ramp under flowing Ar using a flow rate of approximately 60 mL/min. Zr foil was used as an O₂ scavenger when heating more O₂ sensitive metals, such as Fe. **Warning!** During heating, hazardous gases, (CN)₂ and HCN, evolve. A series of two bubblers was used to trap the evolved gases. The first one contained an aqueous solution of bleach and the second one contained a 1 M aqueous solution of NaOH.

Microwave Processing. The microwave experiments were done in an 1100 W SHARP R-305HW domestic microwave oven. In some experiments, the dehydrated gel was placed under an argon atmosphere in a 40 cm long Pyrex tube (1.1 cm inner diameter) connected to an oil bubbler. The sample tube was placed vertically through a hole drilled in the center of the top of the microwave oven such that the sample was held 2.5 cm from the floor of the oven. Microwave detector was used to ensure no microwave radiation leaked out of the oven. **Warning!** Care should be taken to ensure that the domestic microwave is altered in a way that does not allow radiation leakage. The microwave energy distribution in the oven was mapped and the sample was placed near a maximum in the center of the oven. Alternatively, the reaction was done in an open Biotage vial with conical bottom made from metal-free glass or in a custom-made quartz crucible (1 cm in inner diameter) held 2.5–4 cm from the floor of the microwave. The

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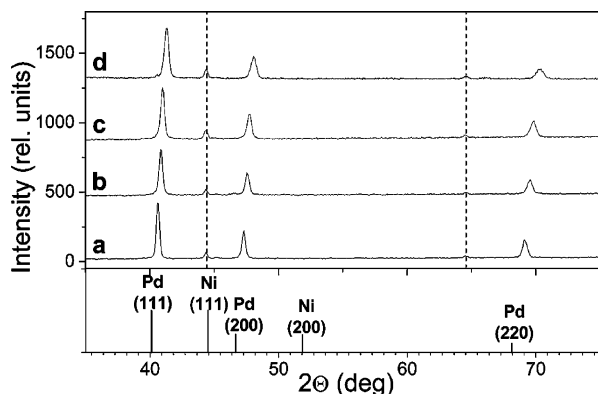


Figure 1. X-ray powder patterns of Pd/Ni alloys in Table 1 prepared from Pd/Ni cyanogels by heating under Ar at 650 °C for (a–c) 2 and (d) 1 h. The vertical lines mark the positions of the peaks of the Cr internal standard. The bottom panel shows the positions of (111), (200), and (220) peaks in the powder patterns of Pd and Ni. No peaks were present below 35°.

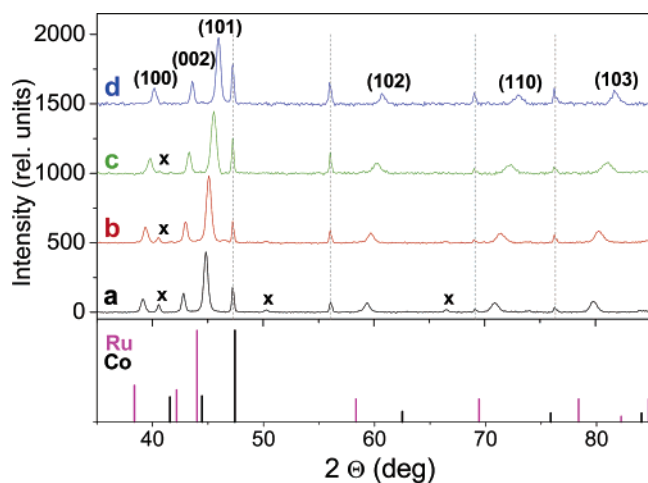


Figure 2. X-ray powder patterns of Ru/Co alloys in Table 1 prepared from Ru/Co cyanogels by heating under Ar at 650 °C for 5 h. The bottom panel shows the positions of peaks in powder patterns of Ru and Co. The vertical dashed lines show positions of the Si internal standard peaks. The marks (x) show the peaks of a reaction byproduct KCl. No peaks other than those of KCl were present below 35°.

sample was irradiated with the full output of the oven for several minutes. It was found that sample sizes larger than 0.6 g were required for the reaction to proceed. **Warning!** During heating, hazardous gases, $(\text{CN})_2$ and HCN , evolve. The experiment has to be performed in a well-ventilated hood and a series of two bubblers (a solution of bleach followed by a 1 M solution of NaOH) should be used to trap the evolved gases.

Characterization. FTIR measurements were done on a Nicolet 730 FTIR spectrometer using KBr pellets. X-ray powder diffraction (XRD) was measured using $\text{Cu K}\alpha$ radiation (1.5406 Å) on a Rigaku Miniflex instrument or a Bruker D-8 Focus XRD instrument. Some alloys were washed with water before XRD analysis to remove peaks of residual KCl and NaCl salts that are byproducts of cyanogel polymerization and decomposition. The composition of the alloys was estimated by comparison of the lattice parameter to published data or by linear interpolation between the lattice parameters of pure metals. The uncertainty in the composition was estimated from the 0.1° uncertainty in estimating the position of the peaks. EDX analysis was done on a FEI XL30 FEG-SEM equipped with a PGT-IMIX PTS EDX system using a 15 keV electron beam. The quantitative analysis was done in the IMIX software. The statistical analysis was based on 10–15 data points. Xerogels from counterion replacement experiments were coated with a 10 Å layer of carbon using a VCR IBS/TM 200S ion beam

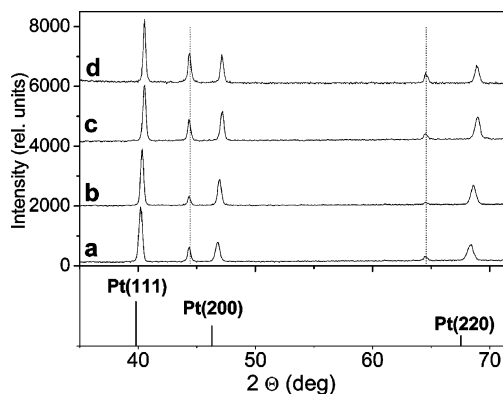


Figure 3. X-ray powder patterns of Pt/Ru alloys in Table 1 prepared from Pt/Ru cyanogels by heating under Ar at 1000 °C for 32 h. The bottom panel shows the positions of peaks in powder patterns of Pt and Ru. The vertical dashed lines show positions of the Cr internal standard peaks. No peaks were present below 35°.

sputterer to allow for EDX analysis. UV–VIS spectra were recorded on an HP 8453 diode array spectrophotometer using quartz cuvettes. Inductively coupled plasma atomic emission spectroscopy (ICP) was performed on a Perkin-Elmer optical emission spectrometer optima 4300 DV using 229 and 231 nm for detection of Co and 324, 340, and 363 nm for detection of Pd.

Results and Discussion

Alloys and Intermetallics Made from Cyanogels Prepared in a 2:1 Chlorometalate to Cyanometalate Ratio.

It has been shown previously in the Pd/Co and Pd/Fe system that gels made in the 2:1 chlorometalate to cyanometalate ratio (referred to as 2:1 gels in the remainder of this paper) are kinetically favored and exhibit faster gelation than gels made in other ratios.^{19,21} Therefore, this ratio was utilized first to probe the formation of a number of binary alloys using cyanogels as precursors.

A 2:1 $\text{Na}_2\text{PdCl}_4\text{:K}_2\text{Ni}(\text{CN})_4$ mixture polymerized and gelled through the formation of CN bridges between the Pd and Ni metal centers. IR analysis showed a CN stretch at 2198 cm^{-1} with a small shoulder around 2160 cm^{-1} , which were assigned to bridging and terminal cyanides, respectively. The CN stretch at 2131 cm^{-1} characteristic for $\text{K}_2\text{Ni}(\text{CN})_4$ was not seen, indicating that none of the cyanometalate starting material was present in the xerogel. Heating at 650 °C for 2 h under flowing argon led to the formation of a face-centered cubic (FCC) Pd/Ni alloy (Figure 1a and Table 1). The composition of the alloy was estimated from the lattice parameter based on published data²² to be 81% Pd.

The 2:1 $\text{K}_2\text{PtCl}_4\text{:K}_2\text{Ni}(\text{CN})_4$ system also formed a stable gel. The corresponding xerogel showed a broad peak at 2190 cm^{-1} with a shoulder at 2145 cm^{-1} in the IR spectrum, assigned to bridging and terminal CN. An FCC Pt/Ni alloy was obtained after 2 h of heating at 650 °C. The composition of the alloy was determined from the lattice parameter²³ to be 86(±3)% Pt.

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Table 1. Lattice Parameter and Composition of Pd/Ni, Ru/Co, and Pt/Ru Alloys Made from Cyanogels (uncertainty in lattice parameters and composition from XRD is based on the uncertainty of 0.1° in assigning the position of the peaks; composition by EDX is based on 10 data points for each sample)

figure	Na ₂ PdCl ₄	K ₂ Ni(CN) ₄	NiCl ₂	lattice parameter (±0.009) (Å)	%Pd from ref 22 (±3)
1a	2	1		3.839	81
1b	5	3	1	3.819	75
1c	7	5	3	3.806	70
	4	3	2	3.786	64
1d	1	1		3.784	63
	1	1	1	3.729	47

figure	RuCl ₃	K ₃ Co(CN) ₆	CoCl ₂	lattice parameter <i>a</i> (±0.009) (Å)	lattice parameter <i>c</i> (±0.009) (Å)	%Ru by linear interpolation ²⁴ (±3)
2a	2	1		2.653	4.218	75
	1	1		2.639	4.203	67
2b	5	3	1	2.638	4.201	66
2c	4	3	2	2.612	4.171	53
2d	1	1	1	2.589	4.142	41

figure	K ₂ PtCl ₄	K ₄ Ru(CN) ₆	RuCl ₃	lattice parameter (±0.009) (Å)	%Pt by EDX (mean ± SD)
3a	2	1		3.877	74 ± 2
3b	5	3	1	3.865	60 ± 2
3c	4	3	2	3.847	53 ± 3
3d	1	1		3.850	51 ± 2

In the 2:1 RuCl₃:K₃Co(CN)₆ system, no signs of gelation were observed at room temperature after 90 min. Upon heating at 75 °C for 3 h, the mixture formed a solid black gel. IR analysis of the xerogel showed a bridging and terminal CN at 2173 and 2141 cm⁻¹, respectively, with no stretch at 2128 cm⁻¹, characteristic for the K₃Co(CN)₆ starting material. Upon heating at 650 °C, the 2:1 Ru/Co cyanogel formed a hexagonal close-packed (HCP) Ru/Co alloy (Figure 2a and Table 1) with a composition of 75(±3)% Ru that was determined by linear interpolation²⁴ between Ru and HCP Co unit-cell parameter *a* (*a*_{Co} = 2.506 Å, *a*_{Ru} = 2.7053 Å²⁵) using the positions of the (100), (002), and (101) peaks.

A 2:1 K₂PtCl₄:K₄Ru(CN)₆ mixture also required heating at 75 °C to gel. The IR spectrum of the xerogel showed a rather broad feature between 2050 and 2200 cm⁻¹, contrasting several sharp features of the K₄Ru(CN)₆ starting material that appear between 2036 and 2110 cm⁻¹, the strongest one at 2053 cm⁻¹. Thermal analysis of the 2:1 K₂PtCl₄:K₄Ru(CN)₆ gel showed that the loss of CN ligand in this system requires higher temperatures and longer heating times than in other cyanogel systems. Heating for either 32 h at 1000 °C or 15 h at 900 °C led to the formation of one FCC phase (Figure 3a and Table 1), but at temperatures below 900 °C, a number of phases were formed. When the 2:1 K₂PtCl₄:K₄Ru(CN)₆ gel was heated at 700 °C for 8 h, at least three phases formed: two Pt-rich FCC phases with slightly different lattice parameters both smaller than pure Pt and one HCP Ru-rich phase with a slightly larger lattice parameter than Ru. Further heating of this product at 950 °C for 15 h led to the formation of a single FCC phase with a lattice parameter of 3.87 Å that is attributed to the diffusion of the two metals to produce the thermodynamic

product. This lattice parameter is identical to the lattice parameter obtained in an alloy produced by longer one-step heating, indicating that we have isolated the intermediates by interrupting the heating process. The isolation of two distinct metal phases is somewhat surprising, because analogous intermediates were not observed in the other cyanogel systems. There is some evidence that, in the Pd/Co cyanogel, a small amount of pure Pd is formed first,¹¹ into which we speculate, Co gets quickly incorporated during further heating; however, a pure Co phase is never observed in the process. The initial formation of two distinct metal phases in the Pt/Ru system could be due to slower diffusion rates in Pt and Ru when compared to the other metals studied. Both Pt and Ru are refractory (melting point: 1769 °C for Pt and 2334 °C for Ru²⁶) and because there is an inverse relationship between diffusion coefficient and the melting temperature,²⁷ one expects significantly slower diffusion rates in this system compared to the others investigated here.

In the 2:1 Na₃IrCl₆:K₃Co(CN)₆ system, the bridging reaction occurs at a much slower rate than in the other cyanogel systems. The 2:1 Na₃IrCl₆:K₃Co(CN)₆ mixture did not gel after 15 days at 95 °C, but the formation of an insoluble product after drying and the presence of bridging cyanides confirmed by IR indicated the formation of a polymer. Two CN stretches were observed: 2196 cm⁻¹, assigned to bridging CN, and 2139 cm⁻¹, assigned to terminal CN. In contrast to other cyanogel polymers, where the bridging cyanide IR absorption was more intense than observed for the terminal cyanide, the transitions for bridging and terminal CN in the Ir/Co gel were of comparable intensities, indicating a smaller ratio of bridging to terminal cyanides. This is consistent with the observation that this mixture never gelled. Heating of the Ir/Co polymer at

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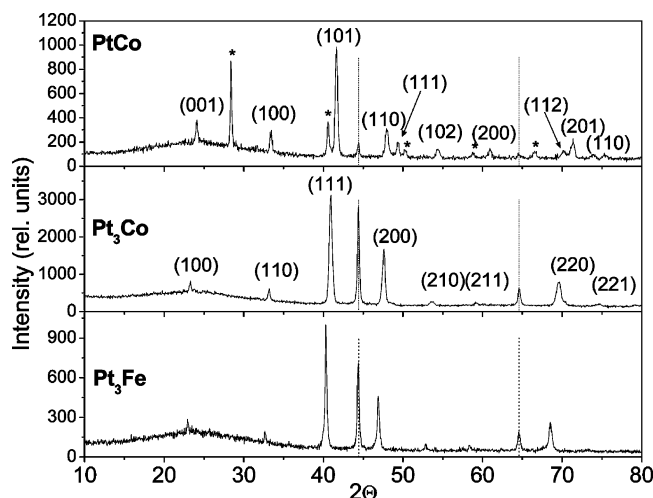


Figure 4. X-ray powder patterns of Pt_3Fe , Pt_3Co , and PtCo intermetallics prepared from Pt/Fe and Pt/Co cyanogels by heating under Ar at 650 °C for 4 h, 700 °C for 68 h, and 750 °C for 2 h, respectively. The vertical dashed lines show positions of the Cr internal standard peaks. Stars mark KCl peaks.

650 °C for 2–10 h led to a product with an FCC lattice, as shown by XRD. However, the peaks were rather broad (full width at half-maximum twice as large as for the Cr internal standard) and often not symmetrical, indicating a very small size of the crystallites and a range of compositions. A 10 h heating at 800 °C yielded an FCC Ir/Co alloy with sharp XRD peaks. Because the dependence of the lattice parameter on composition is linear,²⁴ the composition was estimated by linear interpolation between Ir ($a_{\text{Ir}} = 3.8394 \text{ \AA}$ ²⁵) and FCC Co ($a_{\text{Co}} = 3.563 \text{ \AA}$ ²⁵) to be 73(±3)% Ir.

A number of peaks between 2050 and 2220 cm^{-1} were observed in the FTIR spectrum of the 2:1 $\text{K}_2\text{PtCl}_4/\text{K}_3\text{Fe}(\text{CN})_6$ xerogel. This large number of absorptions probably results from partial decomposition of the cyanogel upon drying. The thermal reduction of this cyanogel led to the formation of a Pt_3Fe intermetallic. The Cu_3Au -type intermetallic can be distinguished from a random FCC alloy by the presence of the superlattice peaks (100), (110), (210), and (211) in the 10–80° region of the powder pattern,²⁸ Figure 4.

A Pd/Fe FCC alloy was made from a 2:1 $\text{Na}_2\text{PdCl}_4/\text{K}_3\text{Fe}(\text{CN})_6$ xerogel by heating at 650 °C for 1 h. Its composition was estimated by interpolation between the lattice parameter of Pd and FCC Fe ($a_{\text{Fe}} = 3.6544 \text{ \AA}$ ²⁵) to be 82(±3)% Pd.

Modifying the Alloy Composition by Varying the Chlorometalate to Cyanometalate Ratio. To introduce more Co into the Pd/Co alloy, we made gels with a Pd/Co ratio lower than 2:1. IR showed an increasing proportion of terminal CN ligands with an increasing amount of $\text{K}_3\text{Co}(\text{CN})_6$ in the gels. ICP and UV–VIS of filtrates obtained from the gel products confirmed that more than 99% of the precursors were incorporated into the gels made from ratios between 2:1 and 1:1. XRD indicated that heating of these gels at 650 °C for 1 h led to the formation of Pd/Co alloys with Co content increasing as the ratio of Pd/Co metal decreased (Table 2 and graphs c and d of Figure 5). It was

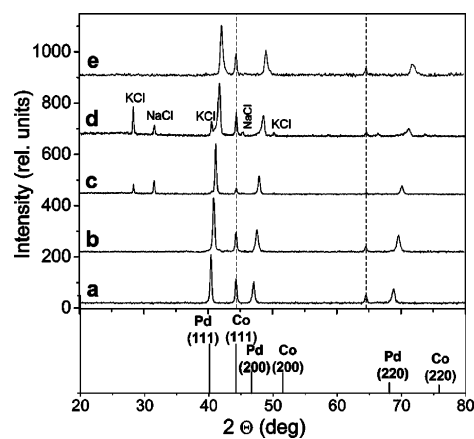


Figure 5. X-ray powder patterns of Pd/Co alloys in Table 3 prepared from Pd/Co cyanogels by heating under Ar at 650 °C for (a, c, d) 1 h or (b, e) 3 h. The vertical dashed lines mark the positions of the peaks of the Cr internal standard. Alloys a, b, and e were washed. The bottom panel shows the positions of (111), (200), and (220) peaks in the powder patterns of Pd and FCC α -Co.

also found that increasing the Pd content in the gel beyond the 2:1 ratio does not lead to a significant increase in the Pd content in the alloy. This can be explained by the insufficient amount of CN ligands to reduce all the metal centers. To enrich the alloy in Pd beyond the composition found in the alloy made from the 2:1 gel, we used a different approach. Half of the $\text{K}_3\text{Co}(\text{CN})_6$ in a 2:1 gel was replaced by $\text{K}_2\text{Pd}(\text{CN})_4$, and a Pd-enriched alloy resulted (Table 2 and Figure 5a).

The $\text{Na}_2\text{PdCl}_4/\text{K}_2\text{Ni}(\text{CN})_4$, $\text{K}_2\text{PtCl}_4/\text{K}_4\text{Ru}(\text{CN})_6$, $\text{RuCl}_3/\text{K}_3\text{Co}(\text{CN})_6$, and $\text{K}_2\text{PtCl}_4/\text{K}_3\text{Co}(\text{CN})_6$ systems also made stable gels when mixed in a 1:1 ratio. Heating of the 1:1 Pd/Ni gel at 650 °C for 1 h led to the formation of an FCC alloy enriched in Ni compared to the alloy made from the 2:1 gel (37% vs 19% Ni), Table 1 and Figure 1d. 1:1 The Pt/Ru gel heated at 950 °C for 15 h reduced to an FCC alloy enriched in Ru (49%) compared to the alloy made from the 2:1 gel (26%) (Table 1 and Figure 3d). The 1:1 Ru/Co gel when heated at 650 °C for 2 h converted to an HCP alloy with 33% Co, compared to 25% Co from 2:1 gel (Table 1). A 2 h heating of the 1:1 Pt/Co gel at 750 °C led to the formation of a PtCo intermetallic²⁹ with the tetragonal CuAu-type structure (Figure 4).

It was also shown that a ternary alloy composed of Pd/Co/Fe could be made through the use of a cyanogel precursor. $\text{Na}_2\text{PdCl}_4/\text{K}_3\text{Co}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$ gels made in ratios of 5:4:1 and 2:1:1 were synthesized and heated to 650 °C for 1 h to produce magnetic products. EDX analysis of the metal products showed 49(±6)% Pd, 40(±5)% Co, and 11(±1)% Fe for the 5:4:1 system and 45(±3)% Pd, 28(±2)% Co, and 27(±2)% Fe for the 2:1:1 system. Elemental line profiles with resolution of ~500 nm did not reveal any significant inhomogeneity in composition. XRD of the 5:4:1 and 2:1:1 products indicated the presence of FCC alloys with lattice parameters $a = 3.76 \text{ \AA}$ and $a = 3.79 \text{ \AA}$, respectively, which were calculated from the position of the (111), (200), and (220) peaks. The diffraction peaks of the alloys were rather broad compared to similarly thermally treated binary systems, suggesting smaller crystallite size.

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Table 2. Lattice Parameter and Composition of Pd/Co Alloys Made from Pd/Co Cyanogels (uncertainty is based on the uncertainty of 0.1° in assigning the position of the peaks)

figure	relative amounts				lattice parameter (± 0.009) (Å)	%Pd from ref 46 (± 3)
	K ₂ Pd(CN) ₄	Na ₂ PdCl ₄	K ₃ Co(CN) ₆	CoCl ₂		
5a	1	4	1		3.839	87
5b		2	1		3.819	72
		5	3	1	3.806	64
5c		3	2		3.792	64
		5	4		3.773	57
		4	3	2	3.786	50
5d		1	1		3.745	48
5e		1	1	1	3.784	40
		2	3	4	3.672	28

It has to be noted that gelation of the 1:1 gel takes significantly longer than that of the 2:1 gel. For example, in the Pd/Co system at 60 mM, the 1:1 gel took about 10 times longer than the 2:1 gel, which gelled in approximately 1 h. This could be advantageous in some applications, such as nanoparticle synthesis, where slow kinetics is desirable, allowing for more freedom to quench the reaction at various stages. On the other hand, long reaction times might become a disadvantage in other applications, where fast processing would be desired, such as any bulk alloy or metallic sponge preparation.

Modifying the Alloy Composition by Introducing Metal Chloride into the Cyanogel. Because decreasing the chlorometalate to cyanometalate ratio significantly prolongs gelation time, we explored the substitution of chlorometalate by metal chloride in 2:1 gels as another way to change the composition of both the gels and alloys produced. Addition of metal chloride had the opposite effect on the gelation time: mixtures with metal chloride substituted for the chlorometalate gelled faster than an analogous system in which no metal chloride was present, indicating an interaction of the metal chloride with the cyanogel polymer being formed.

In the Pd/Co system, the incorporation of CoCl₂ into the gel network was confirmed by IR. It has previously been reported that a Prussian blue analog results when K₃Co(CN)₆ is mixed with a Co²⁺ salt.³⁰ IR analysis of the product made by mixing K₃Co(CN)₆ with CoCl₂ showed the presence of a CN bridge between the two Co atoms around 2175 cm⁻¹ and a Co–C stretch around 457 cm⁻¹. In the Na₂PdCl₄/K₃Co(CN)₆/CoCl₂ gels, the frequency of the Co–C stretch in the low-frequency region confirmed the formation of the Co–NC–Co bridge. In a 2:1 Na₂PdCl₄/K₃Co(CN)₆ system, a peak in the IR spectra at 501 cm⁻¹ is observed that has previously been assigned to the Co–C stretch in a Co–CN–Pd bridge. With increasing amount of CoCl₂ in the gel, the intensity of the peak at ~501 cm⁻¹ decreased, whereas a new peak grew at 457 cm⁻¹. In the CN region of the IR spectrum broad peaks were observed in the Na₂PdCl₄/K₃Co(CN)₆/CoCl₂ system that results from overlapping of the various bridging (Pd–NC–Co and Co–NC–Co) and terminal CN stretches. Graphs c and d of Figure 5 and Table 2 show XRD data of several Pd/Co alloys prepared from Na₂PdCl₄/K₃Co(CN)₆/CoCl₂ cyanogels by heating under flowing argon for 3 h, all of which have an FCC structure. With increasing Co content, the (111), (200), and (220) peaks

shift toward higher angles with respect to a Cr internal standard (Figure 5), indicating the incorporation of more Co in the alloy. It should be noted that the 2:3:4 mixture at 60 mM formed a gel-like precipitate, rather than a gel, but still reduced to a disordered alloy.

Similar results were found for the Na₂PdCl₄/K₂Ni(CN)₄/NiCl₂ gels that converted to FCC alloys upon heating at 650 °C for 2 h under flowing Ar (Table 1, graphs b and c of Figure 1). With increasing NiCl₂ content in the gel, the Ni content of the alloys increased.

In the RuCl₃/K₃Co(CN)₆/CoCl₂ gels, the incorporation of CoCl₂ into the gel network was confirmed by IR in the same way as in the Pd/Co system. The 4:3:2 mixture of 100 mM precursors resulted in small pieces of gel suspended in liquid and the 1:1:1 mixture formed a gel-like precipitate. Heating at 650 °C for 5 h led to the formation of HCP alloys (Figure 2, Table 1). One can see that with increasing amount of CoCl₂ in the gels, all the peaks belonging to the hexagonal powder pattern (labeled (100), (002), (101), (102), (110), (103)), shift toward higher angles, which agrees with the inclusion of smaller Co atoms in the lattice. The composition of the alloys (Table 1) was estimated by linear interpolation.²⁴

Heating of the K₂PtCl₄/K₄Ru(CN)₆/RuCl₃ gels at 1000 °C for 32 h resulted in the formation of FCC alloys (graphs b and c of Figure 3 and Table 1). Their lattice parameters determined from XRD decreased with increasing Ru content in the original gel mixture and in the final alloy as determined by EDX.

An Fe-enriched Pd/Fe alloy was made by substituting FeCl₃ for Na₂PdCl₄ in the Pd/Fe gel. Heating of the Na₂PdCl₄/K₃Fe(CN)₆/FeCl₃ 6:5:4 gel at 850 °C led to the formation of an FCC alloy with 63(± 3)% Pd (by linear interpolation between a_{Pd} and a_{Fe}).

A K₂PtCl₄/K₃Co(CN)₆/CoCl₂ 15:8:1 gel upon an 8 h heating at 700 °C formed a disordered alloy containing 75(± 5)% Pt, determined from the lattice parameter using linear interpolation between pure Pt and pure Co unit-cell parameter a ($a_{\text{Pt}} = 3.9242$ Å²⁵). The same gel heated at 700 °C for 68 h converted into the Pt₃Co intermetallic (Figure 4). The lattice parameter of the ordered phase is smaller than for the disordered phase (3.82 vs 3.83 Å), which is in agreement with the literature.³¹ In traditional synthetic methods, the ordering of the Pt₃Co intermetallic requires a long annealing period (100 h³²) and its kinetics are very temperature- and composition-dependent.³¹ However, in

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Table 3. Peak Positions and Composition of Ternary Pd/Fe/Co Alloys Determined by EDX (statistics based on 15 points for each sample)

Pd:Fe:Co starting ratio	peak position in XRD ($\pm 0.1^\circ$)			at % (mean \pm SD)		
	(111)	(200)	(220)	Pd	Fe	Co
5:1:3	40.9	47.6	69.5	69 \pm 5	15 \pm 3	16 \pm 3
4:2:3	41.2	48.0	70.2	52 \pm 4	17 \pm 2	30 \pm 4
3:3:3	41.4	48.2	70.5	45 \pm 5	19 \pm 2	37 \pm 5

general, long annealing times (several days) are necessary to produce disordered Pt/Co alloys with homogeneous distribution of the two metals that then order at temperatures between 500 and 700 °C,³¹ making the reported Pt₃Co synthesis rather delicate. Although a number of papers report solution-based approaches to Pt₃Co nanoparticles,^{33,34} the data show a disordered FCC alloy rather than an intermetallic, which is probably due to the difficulty of achieving high temperatures in solution-based methods. We believe that our previously reported nanoparticle synthesis methods^{12,13} will be better suited for preparation of Pt₃Co intermetallic nanoparticles because temperatures above 500 °C are easily achievable, yet the presence of a substrate should prevent significant sintering of the particles.

Incorporation of a metal chloride into the 2:1 gel was also used to prepare Pd/Co/Fe ternary gels and alloys. XRD showed the presence of a single FCC phase. The XRD peak positions and composition of the alloys determined by EDX are shown in Table 3. With decreasing amounts of Na₂PdCl₄ and increasing amount of FeCl₃ in the starting mixture, the amount of Pd in the alloys decreased, the amount of Fe increased, and the peaks for the FCC alloys shifted toward higher angles, as expected. Interestingly, the amount of Co in the final product also varied although the initial amount of Co in the mixture was kept constant. This shows that adding FeCl₃ to the Na₂PdCl₄/K₃Co(CN)₆ gel does not simply substitute Fe for Pd, but either changes the ratio of chlorometalate to cyanometalate in the gel or changes the decomposition pathway for the gel. A more detailed investigation into the mechanism of the ternary gel formation and decomposition is necessary to clarify this question. Another interesting observation was made when we tried to dissolve the alloys in aqua regia for elemental analysis. Although pure Pd metal is readily attacked by aqua regia, the Pd/Co/Fe alloys produced through this method could not be dissolved in a reasonable amount of time even when hot aqua regia was used, suggesting an unusual degree of corrosion resistance.

Replacement of Counterions in Pd/Co Cyanogel. After having shown that the composition of cyanogels and alloys produced from them can be altered by replacing a chlorometalate by a metal chloride in the reaction mixture, we explored if the composition of gels and alloys can be also changed by soaking a pre-made cyanogel in a solution of a transition-metal chloride. One can imagine that this transition-metal chloride may situate itself either in the aqueous phase or can become associated with the polymer network. The salt remaining in the aqueous phase of the hydrogel could

be removed by washing with water or metal chloride crystals would be deposited throughout the xerogel upon solvent evaporation. It was determined that at least some of the added Co²⁺ and Fe³⁺ became associated with the network, as not all CoCl₂ and FeCl₃ could be removed by washing. There are two potential interactions between the polymer and the added metal chloride salt: the metal chloride salt could replace either the alkali cations of the network or one of the transition-metal centers in the polymer. The latter case seems unlikely, as it would involve breaking of two coordination bonds for the transition metal cation in the network. The alkali cation of the polymer network can potentially be found in two positions: by analogy to Prussian blue and its analogues, the cation could be located on the C₃ axis of the octahedral cyanometalate centers³⁵ or the cation could be positioned in the vicinity of the nitrogen side of the terminal cyanide ligands, as is typically observed in the structure of mononuclear cyanometalate complexes.^{36,37} An incoming transition-metal cation which replaces the alkali cation on the C₃ axis is associated with the network through purely ionic interaction while replacement of an alkali cation associated directly with the cyanide ligand results in the formation of a new bridging cyanide species. To explore these bonding issues, we prepared 2:1 Na₂PdCl₄:K₃Co(CN)₆ hydrogels free of residual salts and soaked them in 0.1 M CoCl₂. EDX analysis of a washed 2:1 Na₂PdCl₄:K₃Co(CN)₆ hydrogel soaked in a 0.1 M CoCl₂ solution showed a Pd:Co ratio of 2.3:1.0 (SD: 0.2), which was found to be different with 95% confidence using a Student's t-test analysis ($n = 10$) from the native gel that had a Pd:Co ratio of 3.0:1.0 (SD: 0.4). Although the IR evidence was inconclusive, the covalent association of Co(II) with the network was supported by the observation that soaking the gel in successively increasing concentrations of aqueous NaCl solution (0.1–1 M) for 24 h failed to significantly affect the Pd:Co ratio of the material supporting the idea that the Co(II) had become associated covalently with the network. The most obvious place for such a covalent association are the terminal cyanides. Native and CoCl₂-soaked gels were heated at 650 °C to produce metal alloys. Their compositions were measured using EDX, which showed that the alloy from the Co-enriched gel had a lower %Pd (62 \pm 3, mean \pm SD) than the native gel (%Pd 68 \pm 2, mean \pm SD). The increased Co content in the alloy was confirmed by FCC peaks in XRD shifted to higher angles after soaking in CoCl₂ showing a smaller unit cell than that of the alloy made from the native gel. This result indicates that at least some of the Co²⁺

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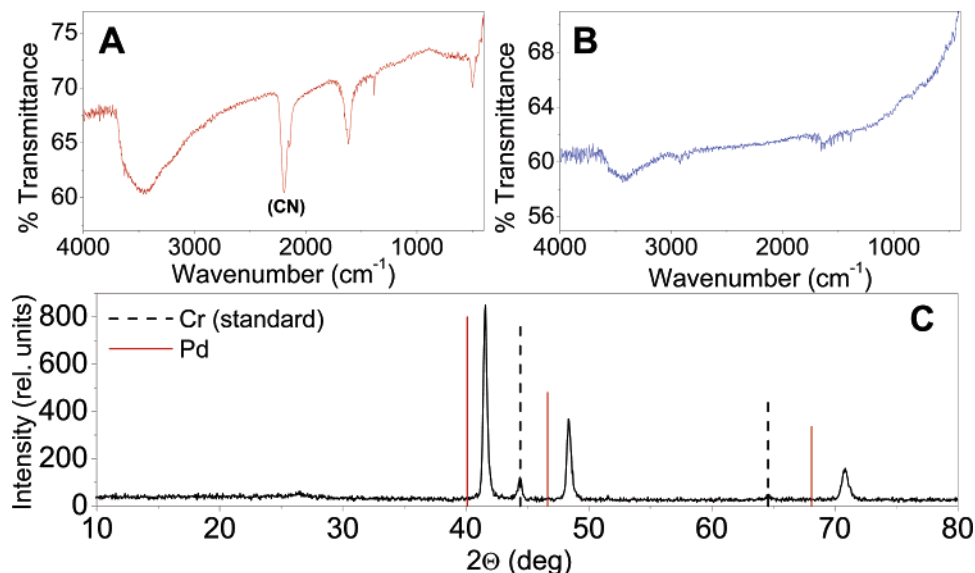


Figure 6. Infrared spectra of the 4:2:3 $\text{Na}_2\text{PdCl}_4\cdot\text{CoCl}_2\cdot\text{K}_3\text{Co}(\text{CN})_6$ cyanogel (A) before and (B) after 3 min microwave irradiation and X-ray powder pattern (C) after 3 min microwave irradiation. Solid vertical lines in the XRD show the positions of peaks in Pd. Dashed vertical lines show positions of the Cr internal standard peaks. Note that the (CN) feature disappears from the IR spectrum after microwave irradiation.

ions that become associated with the cyanogel network during soaking become incorporated into the final metal product.

The replacement of the counterion of the polymer network was found to be facile. For example, the counterion could be replaced with an iron species by letting a 0.1 M FeCl_3 solution run through a 5 cm column of the washed hydrogel. EDX analysis of the xerogel showed the presence of iron with a Pd:Co:Fe ratio of 8:2:1. The amount of iron gained was similar to the amount of cobalt gained in the previous experiment, indicating that a similar number of alkali cations were replaced. After exposing the hydrogel to FeCl_3 solution, washing the gel with a 0.1M CsCl solution did not change the metal ratios of the xerogel, suggesting a covalent association of the iron with the network. CsCl was used in this experiment as similar systems have been previously shown to have high affinity for Cs^+ ions³⁸ and because cesium can be easily detected by EDX. A broadening of the cyanide IR stretch of the iron-washed gel when compared to the native gel also suggested a covalent interaction. The iron became incorporated into the alloy when heated at 650 °C for 1 h, forming an alloy with a Pd:Co:Fe ratio of 5:3:1 according to EDX. The incorporation of iron into the alloy was also confirmed by a shift of the FCC peaks in XRD to higher angles after soaking in FeCl_3 compared to the alloy prepared from the native gel.

The above experiments suggest that small and controllable changes in the composition of the alloys can be achieved by soaking a pre-made gel in a solution of metal chloride, which gives the production of metals from cyanogels an additional degree of flexibility. This method proves the opportunity to introduce metal cations that are not compatible with the cyanogel precursors and would lead to premature precipitation if added to the initial reaction mixture.

Microwave Processing of Cyanogels. We have previously reported microwave-induced autoreduction of the $\text{Na}_2\text{PdCl}_4/$

$\text{K}_3\text{Co}(\text{CN})_6$ 2:1 gel with significant reduction in processing time.¹⁵ In this work, we have extended this procedure to other cyanogels. A $\text{Na}_2\text{PdCl}_4/\text{CoCl}_2/\text{K}_3\text{Co}(\text{CN})_6$ 4:2:3 gel, upon a 3 min microwave irradiation, showed results similar to those of the $\text{Na}_2\text{PdCl}_4/\text{K}_3\text{Co}(\text{CN})_6$ 2:1 gel. Before irradiation, the IR spectrum (Figure 6A) of the gel contained terminal and bridging CN stretches (between 2140 and 2200 cm^{-1}), a Pd–C stretch ($\sim 500 \text{ cm}^{-1}$), and features associated with water (3400 and 1600 cm^{-1}). After irradiation, only the water peaks remained in the IR spectrum (Figure 6B) and a Pd/Co FCC alloy with 53(± 3)% Pd formed (Figure 6C). The 1384 cm^{-1} peak in the IR belongs to an impurity. Similarly to the $\text{Na}_2\text{PdCl}_4/\text{K}_3\text{Co}(\text{CN})_6$ 2:1 gel, sparking was observed in the reaction tube and eventually the whole reaction volume glowed orange.

The $\text{RuCl}_3/\text{K}_3\text{Co}(\text{CN})_6$ 2:1 gel is also a strong absorber of microwave energy. A 4 min irradiation under both air and argon caused the sample to glow orange and led to a complete reduction marked by the loss of all CN ligands as observed by IR spectroscopy (panels A and B of Figure 7). The product of the reaction was an HCP RuCo alloy. The inclusion of the smaller atoms of Co in the Ru lattice was confirmed by XRD (Figure 7C), as the HCP peaks shifted toward higher angles, reflecting the shrinking of the lattice. The composition of the alloys was estimated by linear interpolation²⁴ from the position of the peaks to be 80(± 3)% Ru.

The $\text{Na}_2\text{PdCl}_4/\text{K}_3\text{Fe}(\text{CN})_6$ 2:1 and the $\text{Na}_2\text{PdCl}_4/\text{FeCl}_3/\text{K}_3\text{Fe}(\text{CN})_6$ 4:2:3 cyanogels completely autoreduced upon 2 min and 75 s microwave irradiation, respectively, in an open tube. The CN stretches (between 2000 and 2200 cm^{-1}) in the IR spectrum disappeared after irradiation (panels A and B of Figure 8) and the gels converted to Pd/Fe FCC alloy (Figure 8C). The composition of the alloys was estimated as 81(± 3)% Pd and 70(± 3)% Pd, respectively, by linear interpolation between the lattice parameter of Pd and FCC Fe ($a = 3.6544 \text{ \AA}$ ²⁵).

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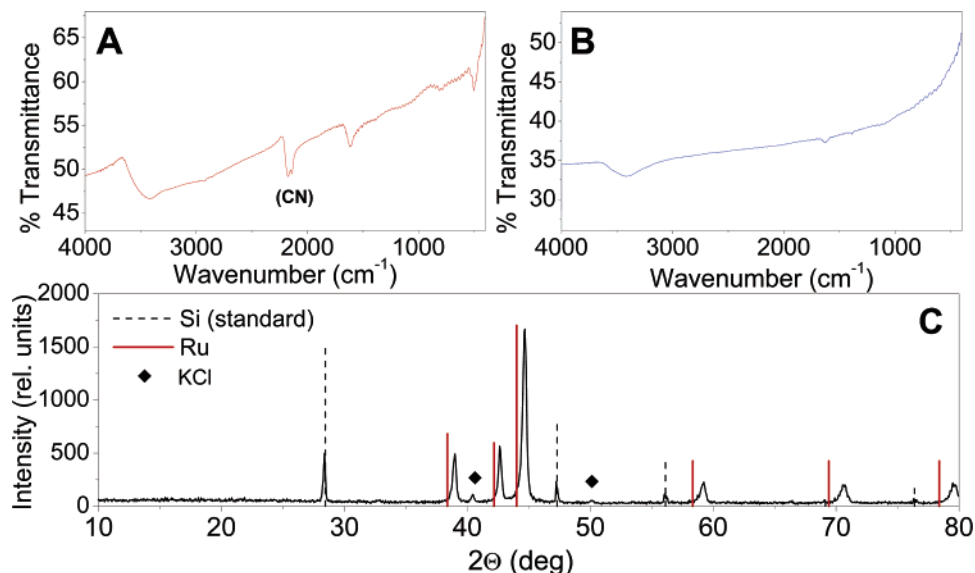


Figure 7. Infrared spectra of the 2:1 $\text{RuCl}_3/\text{K}_3\text{Co}(\text{CN})_6$ cyanogel (A) before and (B) after 4 min microwave irradiation and X-ray powder pattern (C) after 4 min microwave irradiation under air. The strong baseline in the IR spectrum of the gel is due to residual water associated with the dried gel. Note that the (CN) feature disappears from the IR spectrum after microwave irradiation. Solid vertical lines in XRD show the positions of peaks in Ru. Dashed vertical lines show positions of the Si internal standard peaks. Diamonds mark KCl peaks.

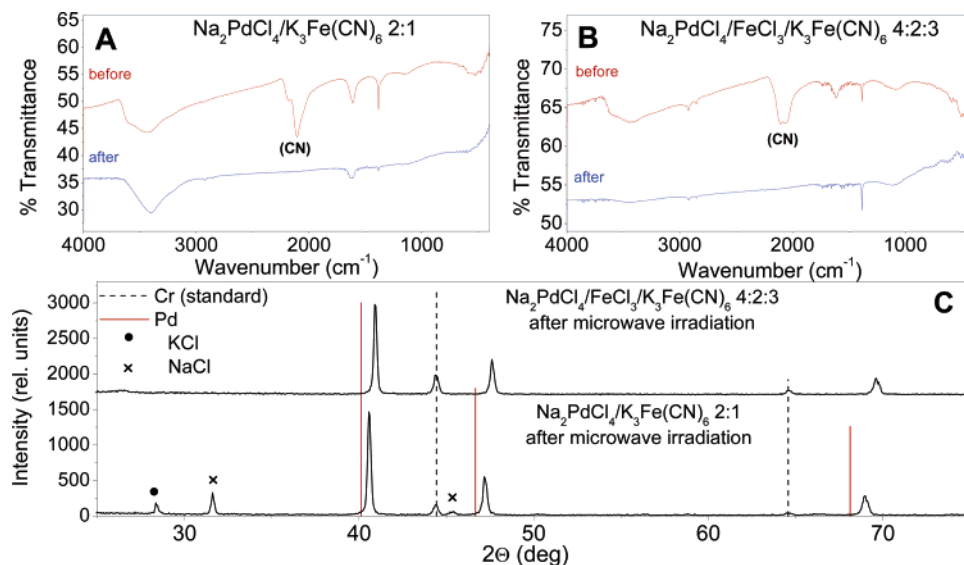


Figure 8. Infrared spectra of the (A) 2:1 $\text{Na}_2\text{PdCl}_4/\text{K}_3\text{Fe}(\text{CN})_6$ cyanogel and (B) 4:2:3 $\text{Na}_2\text{PdCl}_4/\text{FeCl}_3/\text{K}_3\text{Fe}(\text{CN})_6$ before and after microwave irradiation and (C) X-ray powder pattern after microwave irradiation. Note that the (CN) feature disappears from the IR spectrum after microwave irradiation. Solid vertical lines in the XRD show the positions of peaks in Pd. Dashed vertical lines show positions of the Cr internal standard peaks. Crosses mark NaCl peaks. The peak marked by a dot belongs to KCl.

A $\text{Na}_2\text{PtCl}_4/\text{RuCl}_3/\text{K}_4\text{Ru}(\text{CN})_6$ 4:2:3 gel was subjected to a 4 min microwave irradiation. Sparking similar to that in other cyanogels was observed in the reaction tube, but the glowing of the whole reaction volume did not occur. Before irradiation, the IR spectrum of the gel contained a broad CN peak (around 2100 cm^{-1}), which disappeared after irradiation. The product was a mixture of two phases, similar to that observed in short furnace heating: the major metallic product of the irradiation was a Pt-rich Pt/Ru FCC alloy, whereas a Ru-rich Ru/Pt HCP alloy was a minor metallic product. The peaks of the FCC alloy were significantly broader than those of similar alloys produced by furnace heating described earlier; the average crystallite size estimated from the width of the peaks by the Scherrer formula³⁹ was $\sim 140\text{ nm}$. It has been previously reported that some ceramic materials synthesized with the aid of microwave heating have finer

microstructures than materials synthesized by traditional methods.^{40,41} This observation is likely due to the limited grain growth during the short processing times in microwave synthesis.

Although the microwave irradiation of the $\text{Na}_2\text{PtCl}_4/\text{RuCl}_3/\text{K}_4\text{Ru}(\text{CN})_6$ 4:2:3 gel did not lead to the formation of a single FCC phase as observed in furnace heating at 1000°C , the results of the experiment still show great promise: the 4 min period is substantially shorter than the time required to reduce the cyanogel in traditional furnace heating. In addition, the unusually small size of the crystallites, indicated by the

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broadness of the XRD peaks (also noted during furnace heating of the Ir/Co and Pd/Co/Fe gels) suggests that cyanogels can be processed into nanocrystalline metals. This class of materials is currently subject of many experimental and theoretical works and has been shown to have improved mechanical properties, such as enhanced yield stress, limited tensile elongation, or enhanced scratch resistance and tribological properties.^{42,43}

The results described above show that many of the cyanogel coordination polymers are susceptible to microwave dielectric heating and that microwave irradiation can be used to process these gels into metals on a very short time scale. However, further studies are needed to determine the mechanism of this microwave absorption, as well as optimal conditions for the reaction. It has been reported that various factors influence the outcome of microwave solid-state synthesis.^{44,45} Some of these factors, such as microwave power and irradiation time, are apparent. Other variables, such as the weight, volume, and packing of the sample; reaction vessel dimensions; shape and orientation; and microwave source configuration are less obvious. These observations agree with ours. For example, we saw that the conversion of the gel to metal did not occur in a 600 W oven, but was successful in 1100 W ovens. However, among the 1100 W ovens, the geometric configuration of the magnetron in the SHARP R-305HW microwave oven was found to be better suited for our experiments than those in other types of ovens. We also observed in our experiments that a critical weight and volume were necessary for the reaction to proceed. Typically, samples below 0.6 g and samples in tubes thinner than 1 cm did not react. Gel grain size also played a role: a ground gel transformed into metal easily, whereas the reaction was often incomplete with larger pieces of gel. The above observations point toward the significance of the balance of energy inflow and outflow during microwave-induced reactions under our experimental conditions. We have also observed that the success of the microwave processing of cyanogels is to some degree influenced by the heat pretreatment history: gels that have been dried above room temperature for longer periods of time or dried in a microwave at lower power did not convert to metals. This could either indicate that adsorbed and/or

coordinated water plays a role in initial stages of microwave absorption or that long polymer chains (that fall apart during prolonged drying above room temperature) are necessary for microwave absorption. All these variables will be subject to further research.

Conclusions

A variety of binary and ternary transition-metal alloys (Pd/Co, Pt/Co, Ru/Co, Ir/Co, Pd/Ni, Pt/Ni, Pt/Ru, Pd/Fe, Pd/Fe/Co) and intermetallics (Pt₃Fe, Pt₃Co, PtCo) were prepared by thermal autoreduction of cyanogel coordination polymers at temperatures significantly lower than those required in metallurgical processing. The alloys available through the cyanogel processing method depend on the ability to incorporate the appropriate metal into the cyanogel network, which suggests that various other alloy systems can be accessed through this method. It has been demonstrated that the composition of the cyanogels can be modified by a variety of ways: varying the ratio of chlorometalate to cyanometalate, substituting some chlorometalate by metal chloride, using more than one type of cyanometalate in the gel, and impregnating premade cyanogel with a metal chloride. The changes in the cyanogel composition effected by all the above-mentioned methods are reflected in the composition of the alloy after reduction, which allows for ample flexibility in the control of the stoichiometry of the final metallic product. In addition to binary alloys, a number of ternary alloys have been demonstrated, suggesting that higher-order alloys are also accessible through cyanogel processing.

It was also shown that the cyanogel polymers are susceptible to microwave dielectric heating, which leads to a sufficient temperature increase in the sample to cause the reduction of the metal centers, thus allowing for the conversion of cyanogels to metal alloys in a few minutes instead of hours needed in the traditional furnace heating. The chemical and sol-gel nature of the cyanogel-based preparation of transition-metal alloys combined with the capability of ultrafast thermal processing induced by microwaves might allow for a synthesis of metallic materials with enhanced properties.

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